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Fundamental Studies of Hydrogen Interaction with Supported Meta
and Bimetallic Catalysts

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Fundamental studies of hydrogen interaction with supported
metal and bimetallic catalysts

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An *in situ* ^1H nuclear magnetic resonance (NMR) technique has been employed to study the interaction of hydrogen with silica supported metal and bimetallic catalysts. This technique was applied in the temperature range of 300 to 473 K and at pressures of 10^{-5} to 760 Torr. On ruthenium and rhodium catalysts two distinct adsorbed resonances were detected. We have labelled these resonances as α and β . The β resonance is associated with a more weakly adsorbed species and was observable only at pressures greater than 100 Torr. Both these resonances represent adsorbed hydrogen interacting with the metal. The delocalized nature of β hydrogen makes it difficult to associate it with any particular adsorption site. The population of β hydrogen was found to be a strong function of the concentration of surface defects. Studies of hydrogen interaction with silica supported Ru-Group Ib bimetallic catalysts revealed several interesting facts. Addition of silver to Ru was found to greatly diminish the relative amount of the β resonance. Since silver preferentially

populates edge, corner and other defect-like sites, the weakly bound species associated with the β resonance was correlated with low coordinated metal atoms. The total hydrogen population on the catalyst remained approximately the same with the addition of copper because dissociated hydrogen on ruthenium atoms can spillover to copper. We postulate that the difference in catalytic behavior of Ru, Ru-Cu and Ru-Ag is due to the surface segregation induced structure sensitivity of the weakly bound hydrogen. On silica supported platinum catalyst, no β hydrogen was detected. The availability of the β hydrogen, a weakly adsorbed species associated with the β resonance, on ruthenium and rhodium may open reaction pathways that would not be available on platinum catalysts. Several hydrocarbon reactions involving hydrogen show great sensitivity to hydrogen pressure and the catalyst metal. We postulate that some of these previously well noted hydrogen effects are the manifestation of the availability (or unavailability) of different hydrogen states with variations in pressure.

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by

Sandeep Bhatia

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DEDICATION

To my grandfather Bal Mukand Bhatia. From his visions I learnt to see
further, reach higher and go farther.

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GENERAL INTRODUCTION

Hydrogen plays an important role in heterogenous catalysis. It is a reactant or product molecule in several important reactions like ammonia synthesis and Fischer-Tropsch synthesis. Hydrogen is also involved in reactions like hydrogenation, dehydrogenation, and skeletal rearrangement reactions which are of particular importance in the catalytic reforming of petroleum feedstocks.

Hydrogen is used to reduce most metallic catalysts. The reduction conditions itself can influence the catalytic behavior and this aspect has been reviewed elsewhere (1). Hydrogen adsorption has also been extensively used to probe and to characterize the active sites on supported metal catalysts. Extent of hydrogen adsorption on previously reduced and degassed catalysts, is generally used to determine the free metal surface area of supported catalysts. The metal surface areas (or dispersion) are used to calculate turnover numbers (2). Important catalytic characteristics, such as structure sensitivity (3-6), are based on the turnover numbers and therefore indirectly on the extent of hydrogen adsorption.

The methods of determining the free metal surface area by hydrogen adsorption are not unambiguous. It is well known that the catalytically active surface sites can be influenced drastically by chance impurities, and components arising from the reactant(s). Boudart wrote as early as 1975 that the "definition of a working catalyst must include all the surface species of the

catalyst in its working state" (7). For reactions involving hydrogen, Paál suggests that working metal catalysts should always be regarded as *metal-hydrogen systems* (8). However, no satisfactory methods exist to determine the compositions of working catalysts or of metal-hydrogen systems.

The number of metal surface atoms is determined by the extent of hydrogen adsorption and an assumed (usually one) hydrogen-to-metal stoichiometry. The heterogeneity of surface sites can complicate this approach to determine the number of metal surface atoms. It is known that various metal surfaces do not behave uniformly toward hydrogen chemisorption. Surface defects (crystallographic defects or impurity atoms) can drastically influence hydrogen adsorption; both energetic and kinetic effects have been reported. For example, it has been postulated that the first hydrogen atoms adsorb preferentially on and near the steps (9). It has been shown that on the average the heat of adsorption on these sites is about 10 kJ/mol higher than on the terrace sites characteristic of the flat [111] surface.

The kinetic effect of defects or impurities on hydrogen adsorption is quite striking. On a Pt[997] surface an increase in the initial sticking probability by almost a factor of 5 was reported (10). Poelsema et al. (11, 12) investigated the H/Pt[111] system by means of He ion scattering and found the presence of steps to be crucial for the dissociation and sticking of the hydrogen molecules. The sticking probability of hydrogen on flat Pt[111] has been reported to be low (13). The catalytic activity for stepped surfaces was

elegantly demonstrated by angle dependent molecular beam measurements by Somorjai's group (14). Their results suggest that the high sticking probability on defect sites may easily cause high local concentrations of reactive hydrogen species on and near those sites. This conclusion has been offered as the explanation for the enhanced catalytic activity of highly dispersed materials. Also, as soon as the active sites become blocked by irreversible adsorption of other atoms (C, Cl, P, S) the overall reaction rate is lowered and the catalyst material then is regarded as deactivated or poisoned (15, 16). Thus, specific sites like edge and corner atoms can greatly influence the adsorption process and therefore the catalytic activity.

As noted above surface morphology can play an important role in adsorption processes. Properties such as structure insensitivity or structure sensitivity are based on variations in catalytic activity (turnover frequency) with surface morphology. There are several structure determinations of hydrogen-metal adsorption systems using LEED or ion channeling techniques. The H atoms usually "prefers" a highly coordinated sites. High resolution electron energy loss spectroscopy (HREELS) was employed to probe the local geometry of the adsorption sites. These measurements revealed the occupation of the fourfold hollow site for the systems of hydrogen on Ni[100] (17) and hydrogen on Pd[100] (18). For surfaces with hexagonal symmetry such as Ni[111] (19) and Ru[0001] (20, 21), hydrogen was located at the threefold sites. H/W[100] system seems to be the only case in which the hydrogen atoms are

located in twofold, bridge, sites (22).

Qualitatively, the generally observed decrease in the heat of adsorption of hydrogen with increasing coverage may not only indicate the operation of repulsive mutual interactions but may also point to the participation of an ensemble of metal atoms in the chemisorptive bond. More quantitative information about the ensemble size can be obtained from measurement of the uptake of strongly chemisorbed hydrogen on bimetallic surfaces, consisting of one inert and one active component for hydrogen adsorption, such as Cu-Ru or Ag-Ru. An analysis based on statistical theory following the arguments of Burton and Hyman (23) reveals at least four or five adjacent Ru atoms necessary for an unperturbed adsorption of hydrogen. This number, n , is in good agreement with reports by Yu et al. (24) who derived an ensemble size of $n = 4$ for hydrogen chemisorption on Cu-Ni alloys.

Most of the studies on the hydrogen-metal systems can be generally classified as either (i) single crystal studies under ultra high vacuum conditions or (ii) studies on dispersed metal catalysts under catalytically interesting conditions of higher pressures. The single crystal studies have helped develop an understanding of the adsorption process on an atomic scale and the reaction studies have attempted to determine the variations in catalytic activity with such factors as surface morphology (particle size), reduction conditions, etc. However, there are few bridges that link these two classes of studies. The current investigation provides such a bridge.

To study hydrogen interactions on supported metal catalysts, we have developed and used an *in situ* nuclear magnetic resonance (NMR). NMR of hydrogen was applied to identify adsorbed hydrogen species and determine the extent of hydrogen adsorption on silica supported metal and bimetallic catalysts. Since the *in situ* ^1H NMR technique can investigate hydrogen adsorption at catalytically interesting temperature and pressures, it is powerful technique for studying adsorbed hydrogen on the dispersed metal catalysts. In contrast, many of the surface science techniques are applicable to study adsorption of molecules on single crystal surfaces at vacuum conditions under which weakly bound species are not present. The "weakly" adsorbed states at elevated pressures may be the key factors in pathways for surface reactions.

Explanation of Dissertation Format

The entire dissertation contains three separate papers followed by a general summary. Each paper was written by the author in a form suitable for publication in a technical journal. Papers I and II have been submitted to Journal of Catalysis and Catalysis Today, respectively. Each paper details original work carried out by the author. Paper III will be submitted for publication with the author of this dissertation as the primary author. Appendix A gives the details of the internal standard used to calibrate NMR intensities in the present work and reported in Papers I, II and III. Appendix B compares the adsorption isotherms developed from NMR measurements to

the expected gas phase hydrogen in the sample. Appendix C discusses the possible mechanistic schemes which may be involve weakly adsorbed hydrogen. Appendix D is a study of the exchange between hydrogen associated with the two NMR peaks, α and β . Appendix D has been submitted to Physical Reviews B.

PAPER I

INTERACTION OF HYDROGEN WITH SUPPORTED RU CATALYSTS: HIGH
PRESSURE *IN SITU* NMR STUDIES

INTERACTION OF HYDROGEN WITH SUPPORTED RU CATALYSTS: HIGH
PRESSURE *IN SITU* NMR STUDIES

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ABSTRACT

An *in situ* ^1H nuclear magnetic resonance (NMR) technique has been employed to study the interaction of hydrogen with silica supported ruthenium catalysts in the temperature range of 300 to 473 K and at pressures of 10^{-5} to 760 Torr. In addition to an upfield NMR peak (called α) occurring at $\sim$ -60 ppm and observed at low pressures ($P < 100$ Torr), we have noted the emergence of a second peak (called β) occurring at $\sim$ -30 ppm at elevated pressures ($P > 100$ Torr). These two hydrogen populations represent adsorbed hydrogen interacting with Ru metal particles as indicated by the observed Knight shifts. These two hydrogen populations represent adsorbed hydrogen interacting with Ru metal particles as indicated by the observed Knight shifts. The heats of adsorption were determined by microcalorimetry to be in the range of 40 kJ/mol and 70 kJ/mol for the α hydrogen species while the heat of adsorption of the β species plateaued at approximately 10 kJ/mol. Hydrogen adsorption isotherms were obtained from the NMR peak intensities calibrated by a gadolinium doped lanthanum hydride internal reference. A higher dispersion of metal particles correlated with a larger amount of the weakly adsorbed β hydrogen species. The $\text{H/Ru}_{\text{surface}}$ ratio was observed to be in excess of 5 at elevated pressures (> 500 Torr). The high $\text{H/Ru}_{\text{surface}}$ was due to the adsorption of large amounts of β hydrogen.

INTRODUCTION

Considerable effort has been directed toward understanding the interaction of hydrogen with metals because of intense scientific interest in these systems and their practical applications in catalytic processes. Hydrogen plays a dual role in catalysis. It is a reactant or product molecule in many catalytic reactions, and it can be a powerful probe to investigate the nature of active sites. Several of the reactions involving hydrogen like hydrogenation/dehydrogenation, hydrogenolysis and skeletal rearrangement reactions are of particular importance in the catalytic reforming of petroleum feedstocks. Other important reactions include the synthesis of ammonia, of hydrocarbons or alcohols by means of the Fischer-Tropsch reaction, and solidification of unsaturated fatty acids.

In the studies of hydrogen adsorption on supported metals, a surface hydrogen-to-metal (H/M) stoichiometry of one has commonly been used and this assumption has been justified by single crystal investigations using XRD and TEM (1-3). The stoichiometry of $H/M = 1$ has been assumed because the metal particles larger than 2 nm consist largely of [111]-like faces. A maximum of one chemisorbed hydrogen atom per metal atom was observed on Pt[111] by Christmann et al. (4). However, several studies have indicated stoichiometries exceeding one. The H/Pt ratios have been found to be in the range of 1.5 to 1.65 for Pt/Al₂O₃ catalysts (5, 6) and 1.3 to 1.6 for silica supported platinum catalysts (7, 8). Wanke and Dougherty (9) have reported the adsorption of

more than one hydrogen atom per surface rhodium atom for Rh/Al₂O₃ catalysts. Kip et al. (10) have reported H/M ratios exceeding one for Pt, Rh, and Ir catalysts supported on Al₂O₃, SiO₂, and TiO₂. Sanz and Rozo (11) used NMR spectroscopy to study hydrogen adsorption on Rh/TiO₂ at room temperature. They reported the ratio of hydrogen-to-rhodium surface atoms (H/Rh_{surface}) to be 3 at a pressure of 400 Torr. In a study of unsupported transition metal clusters, Kaldor and Cox (12) have found the very high H/M ratios of 3, 5, 5, and 8 for Pd, Ni, Pt and Rh, respectively. These H/M ratios were found to increase with decreasing cluster size. All of these studies demonstrate that hydrogen can adsorb on various metals in amounts exceeding a one-to-one stoichiometry.

In order to better understand the hydrogen-metal interactions at the atomic scale, hydrogen adsorption over well defined single crystal Ru surfaces has been studied. The various methods employed include temperature programmed desorption (TPD) (13, 14), vibrational spectroscopy (15, 16) angle-resolved photoemission spectroscopy (17), low-energy electron diffraction (LEED) (13, 18-21) and measurements of the surface diffusion of hydrogen atoms (22-24). An interesting behavior was found when work function variations during adsorption were correlated with temperature programmed desorption results (13). The non-monotonic change of the work function with hydrogen dosage suggested the existence of two distinct binding states with negative (N) and positive (P) outward dipole moments, respectively. These two

states were well correlated with the two desorption peaks in the temperature programmed desorption spectra and exhibited different sticking probabilities, with the P state having a smaller sticking coefficient. Initially, the desorption involved mainly the N state which was adsorbed directly with a sticking coefficient proportional to $1-\Theta_N$ (where Θ_N is the relative coverage of the N state) and was responsible for the initial rise of the work function. With higher hydrogen exposure, the population of the P state increased and the work function asymptotically decreased to a constant value. These results were explained in two ways. One explanation was based on the assumption that lateral interactions between hydrogen atoms adsorbed on the same site gave the appearance of two binding states (16). The other explanation associated the two binding states with two different sites (13).

Several attempts have been made to identify surface sites responsible for the adsorption of hydrogen on single crystals. The two fundamental frequencies observed in high-resolution electron energy loss spectroscopy (HREELS) were assigned to the symmetric (perpendicular to the surface) and to the asymmetric (parallel to the surface) vibrational frequencies of a hydrogen atom occupying three-fold hollow sites (15, 16). LEED data (13, 20) revealed a 1×1 pattern at all coverages at a temperature above 80 K suggesting that the ordered phase experienced no surface reconstruction. Similarly, recent studies using very low energy electron diffraction (VLEED) revealed hydrogen occupied the three-fold hollow sites on the surface (21).

The occupation of subsurface sites on open surfaces such as Pd[110] (25) and Cu[110] (26) has been established and is associated with surface reconstruction. The existence of subsurface hydrogen has not been confirmed for close-packed surfaces. Yates et al. (14) have studied hydrogen adsorption on Ru[0001] by an isotope TPD method. They attributed the difference in the high temperature tail of the desorption spectra for H₂, HD, and D₂ to the desorption of subsurface hydrogen (14). Theoretical studies (22, 28) based on a pseudopotential method and local density functional approximation suggested that the Ru[0001] surface three-fold hollow sites are of lowest energy for up to one monolayer of hydrogen. The subsurface octahedral sites are also energetically favorable, but they have an energy barrier to occupation. According to these calculations, when all three-fold hollow sites are occupied this barrier is reduced and the octahedral sites become accessible.

The results from UHV studies cannot always be directly extended to high-pressure conditions such as those existing in most industrial processes. At elevated pressures, steady-state concentrations of "weakly" bonded species can exist and these species cannot be easily studied under high vacuum conditions. IR studies have attempted to identify the different hydrogen species interacting with Rh (29) and Pt (30-34) in supported catalysts at elevated pressures. On alumina supported platinum catalysts three different modes of IR absorption have been reported. A mode at 950 cm⁻¹ has been associated with strongly bound hydrogen and a mode at 2120 cm⁻¹ has been

associated with a weakly adsorbed hydrogen species. There is, however, some controversy regarding a mode observed at 2060 cm^{-1} , which appeared as a shoulder to the 2120 cm^{-1} mode at a pressure of 100 Torr. Dixon et al. (31) have assigned this shoulder to a weakly adsorbed hydrogen species while other researchers (32-34) have indicated that it is due to a CO contamination of the sample. In another IR study of alumina supported rhodium catalysts, only weakly adsorbed dissociated hydrogen was observed at 2013 cm^{-1} for pressures of 100 Torr and greater (29). It was concluded that any adsorbed hydrogen species at lower pressures were infrared inactive. It is expected that the presence of such "weakly" chemisorbed states may open new pathways for reaction mechanisms.

In this study an *in situ* NMR technique was employed to investigate the various hydrogen species interacting with the silica-supported ruthenium metal catalysts at hydrogen pressures up to 760 Torr and temperatures up to 473 K. In contrast, the standard volumetric adsorption technique commonly used to characterize active metal sites (35), *in situ* NMR allows for quantitative measurements of hydrogen adsorbed *on the metal* at elevated pressures and temperatures, independently from the silanol protons and spillover hydrogen species associated with the silica support. The technique is not limited to low pressures and/or temperatures and can be used to examine the nature of hydrogen adsorption under typical reaction conditions. In addition to the identification and quantification of the "strongly" and "weakly" adsorbed

hydrogen on the metal, we also explored the energetics of hydrogen adsorption via microcalorimetry.

EXPERIMENTAL

Catalyst Preparation and Reduction

Catalysts composed of ruthenium supported on Cab-O-sil HS5 silica were prepared by incipient wetness impregnation as described previously (35). The catalyst dispersions were determined from strongly bound hydrogen chemisorption measured via volumetric uptake measurements and found to be 29% and 19%. The catalyst samples were reduced at 450 °C for 2 h in flowing H₂ and re-reduced in the NMR probe at 225 °C for 2 h in 760 Torr of H₂ with the hydrogen evacuated and replaced every 30 min.

NMR Experiments

¹H NMR measurements were performed at 250 MHz on a home-built spectrometer. An *in situ* NMR probe was attached to a volumetric adsorption apparatus for studying the effect of adsorbate pressure (10⁻⁵ to 10³ Torr) and adsorption temperature (300 to 473 K). In the construction of the *in situ* probe we followed the design by Hadix et al. (36). The probe was placed in a CF1200 Oxford cryostat controlled by an Oxford 3120 temperature regulator. The proton background signal of the probe was found to be negligibly small. Typically 2,000 scans, with a recycle time of 0.3 s between scans, were averaged for each spectrum. For suppression of baseline artifacts in the spectra, a standard spin-temperature inversion pulse sequence was used. The

T_1 measurements were made using inversion recovery method (see Results and Table 1). Typically 2,000 scans were averaged for each spectrum, using a recycle time of 0.3s between scans to avoid saturation of the peaks corresponding to hydrogen-on-metal. This ensures that all adsorbed hydrogen is observed. The ^1H NMR shifts are referenced to tetramethylsilane (TMS) using the δ scale with negative values being upfield. The reported shifts are within an error of ± 1 ppm.

Hydrogen-on-ruthenium peak intensities were measured to quantitatively determine the amount of hydrogen adsorbed on the metal. In this work we have used lanthanum hydride ($\text{LaH}_{2.6}$) doped with 25 ppm gadolinium as an internal reference standard for the quantification of the amounts of adsorbed hydrogen. This method allowed us to avoid calibration problems associated with the Q factor of the NMR probe and Boltzmann distribution variations with temperature. $\text{LaH}_{2.6}$ is stable below 1000 K and exhibits a single motionally averaged peak at 2 ppm which could be well distinguished from the other features in a ^1H NMR spectrum of a catalyst. The reference sample was weighed and sealed in a capillary tube and placed *in situ* with the catalyst in an NMR tube. The amounts of adsorbed hydrogen were determined by comparing the integrated peak areas with that of the $\text{LaH}_{2.6}$ standard.

Microcalorimetric Experiments

The differential heats of hydrogen adsorption were measured in an isothermal Tian-Calvet type heat flow microcalorimeter (Setaram C80) connected to a standard gas volumetric system. The microcalorimeter consisted of a sample cell and a reference cell connected to a dosing volume. An MKS capacitance manometer was used to monitor gas phase adsorbate pressures. A typical experiment consisted of dosing micromolar quantities of hydrogen and monitoring the resulting differential heat flux. The integrated area under the calorimeter response curve divided by the quantity of gas adsorbed during the dose corresponded to the differential heat of adsorption. The details of the apparatus and the experimental procedure are given elsewhere (37). All calorimetric measurements were carried out isothermally at 403 K.

RESULTS

The ^1H NMR spectra of a silica supported Ru catalyst with a dispersion of 29% taken at 400 K and under various hydrogen pressures are given in Figs. 1 and 2. In spectrum A, Fig. 1, two distinct peaks were observed: a resonance at ~ 3.5 ppm due to hydrogen associated with the silica support (38), and the peak at about -60 ppm, labelled α , attributed to hydrogen dissociatively adsorbed on ruthenium particles (35, 39). Spectrum B in Fig. 1 was obtained after the same sample was dosed with 50 Torr of hydrogen and subsequently evacuated to 5×10^{-6} Torr for 2 min to remove the relatively weakly adsorbed hydrogen species. This hydrogen appears to be immobile in the evacuated samples and has been previously termed as "strongly" adsorbed hydrogen (35). The integrated intensity of this hydrogen-on-metal peak for the evacuated sample at room temperature is a measure of the dispersion of the catalyst and is in good agreement with the dispersion obtained from volumetric uptake measurements of strongly bound hydrogen as noted in a previous study (35). The change in the linewidth of the α peak for evacuated and nonevacuated samples (see Fig. 1) has been reported and discussed elsewhere (40).

At pressures greater than 100 Torr a third distinct peak, β , was noted between -30 and -50 ppm (see Fig. 2 spectra C through E). The two distinct upfield peaks, α and β , were present over the entire temperature range (300 K to 473 K) investigated in this study. The presence of separate resonance lines reveals that the hydrogen populations α and β are distinct, and not in fast

Figure 1. NMR spectra of 29% dispersed ruthenium catalyst: (A) 50 Torr, (B) dosed with H_2 and evacuated to 5×10^{-6} Torr for 2 min.

Figure 2. NMR spectra of 29% dispersed ruthenium catalyst: (A) dosed with H_2 and evacuated to 5×10^{-6} Torr for 2 min, (B) 50 Torr, (C) 100 Torr, (D) 500 Torr and (E) 760 Torr of hydrogen.

exchange with each other on the NMR time scale (i.e., on the order of $(\Delta\omega_{\alpha\beta})^{-1} \approx 0.05$ ms, where $\Delta\omega_{\alpha\beta}/2\pi$ is the difference of resonance frequencies of α and β). Clearly, the two distinct hydrogen populations must be interacting with the ruthenium metal, as is evidenced by the upfield Knight shifts (41). The variations in the spin lattice relaxation times, T_1 , of α and β with temperature are given in Table 1. The position and intensity of the α peak remains approximately constant above 100 Torr. The β hydrogen intensity increased continuously and the resonance peak moved downfield with increasing pressure (see Table 2).

The NMR spectra of hydrogen adsorbed on the silica supported ruthenium catalyst with a dispersion of 19% are given in Fig. 3. As with the 29% dispersed catalyst, two hydrogen-on-ruthenium peaks can be seen clearly at elevated pressures. The increase in the β peak intensity relative to the α intensity was less for this catalyst than for the catalyst with a dispersion of 29%, as noted in Table 3. The narrow resonance at 2 ppm results from the $\text{LaH}_{2.6}$ calibration reference.

The coverage of hydrogen on the metal surface determined from the integrated intensities was used to plot adsorption isotherms. The hydrogen adsorption isotherm at 323 K for the 29% dispersed Ru catalyst and the deconvoluted intensities of α and β are given in Fig. 4. Note that a hydrogen-to-total ruthenium ratio, $\text{H}/\text{Ru}_{\text{total}}$, of up to about 1.25 was observed. The hydrogen-to-surface ruthenium ratio, $\text{H}/\text{Ru}_{\text{surface}}$, was in excess of 5 at pressures

Table 1. Spin relaxation times, T_1 (ms), of α and β hydrogen at various temperatures.

Temperature (K)	T_1 (α)	T_1 (β)
300	17.5	13.5
400	17	13
473	16.6	12.8

Table 2. NMR shifts (± 2 ppm) of hydrogen adsorbed on 29 % dispersed supported ruthenium catalyst at 323 K.

Pressure (Torr)	NMR Shifts (ppm)	
	α	β
10	-65	
100	-62	-55
200	-60	-45
300	-58	-40
400	-57	-35
500	-55	-30
600	-51	-26
760	-44	-23

Figure 3. NMR spectra of 19% dispersed ruthenium catalyst (with internal standard) under: (A) 50 Torr, (B) 500 Torr and (C) 760 Torr of hydrogen.

Table 3. H/Ru_{surface} ratios for hydrogen adsorbed on 29% and 19 % dispersed supported ruthenium catalyst at 323 K.

Pressure (Torr)	29% Dispersed Catalyst		19% Dispersed Catalyst	
	α	β	α	β
100	1.4	0.3		
150	1.3	0.4		
200	1.3	0.7		
250	2.2	0.1		
300	1.2	1.3	2.3	0.2
350	1.1	1.6	2.3	0.2
400	1.3	2.1	2.3	0.4
500	1.3	3.3	2.1	0.6
550	1.3	3.3	2.1	0.8
600	1.3	3.7	2.1	0.9
650	1.2	4.2	2.2	1.1
760	1.2	4.4	2.1	1.2

Figure 4. Hydrogen adsorption isotherm at 323 K for 29% dispersed Ru catalyst. Total hydrogen adsorption on the metal (●), α state only (○) and β state only (■).

greater than 500 Torr. The number of surface ruthenium atoms, or dispersion, was determined from the sample that had been dosed and then evacuated for a short period of time (as noted above). This standard method assumes a one-to-one stoichiometry of strongly bound hydrogen to surface ruthenium. The α hydrogen population saturated at a pressure below 100 Torr, while the β hydrogen population became observable at 100 Torr and continued to increase for the entire pressure range studied (up to 760 Torr).

A set of isotherms for the 29% dispersed catalyst at 323 K, 400 K and 473 K is given in Fig. 5. As the temperature was increased from 323 K to 473 K, an appreciable decrease of the β population was observed. No significant desorption from the α hydrogen population was observed in this temperature range.

The hydrogen adsorption isotherm at 323 K for the catalyst with a dispersion of 19% is given in Fig. 6. Also given are the populations of the α and β state as a function of pressure. The amounts of hydrogen in each state normalized to the number of surface Ru atoms are listed in Table 3. Note that the lower dispersion catalyst had less hydrogen in the β state at a given pressure, whereas the population of hydrogen in the α state was higher.

The heats of adsorption of hydrogen on the 29% dispersed catalyst were determined by two methods: microcalorimetric measurements and by applying the Clausius-Clapeyron equation (42) to the series of adsorption isotherms derived from *in situ* NMR experiments. The differential heats of adsorption

Figure 5. Hydrogen adsorption isotherms at 323 K (●), 400 K (○) and 473 K (■) for 29% dispersed Ru catalyst.

Figure 6. Hydrogen adsorption isotherm for 19% dispersed Ru catalyst. Total hydrogen adsorption on the metal (●), α state only (○) and β state only (■), at 323 K.

determined from microcalorimetric measurements, within an error of ± 5 kJ/mol, are plotted versus pressure in Fig. 7. The initial (or zero coverage) heat of adsorption was found to be about 80 kJ/mol. In the low pressure range (10^{-2} Torr $< P < 10^{-1}$ Torr) the heat of adsorption was 60-70 kJ/mol. With increasing pressure the heat of adsorption dropped, reaching a value of approximately 40 kJ/mol at ~ 10 Torr and finally a constant value of about 10 kJ/mol at 100 Torr. The Clausius-Clapeyron equation was applied at the coverage of $H/Ru_{\text{total}} = 0.75$ (the region where the β state is partially saturated, see Fig. 5) to obtain the isosteric heat of adsorption of about 7 kJ/mol.

To investigate the catalytic properties of the α and β populations, a 1:3 mixture of ethene/hydrogen (300 Torr) was dosed on to the 29% dispersed catalyst. The hydrogen was monitored via *in situ* NMR as a function of time (Fig. 8). The two sharp peaks at -2 and 4 ppm are due to the hydrogen associated with the hydrocarbon species. At the conclusion of the reaction an upfield peak at about -40 ppm became observable. The sample was then evacuated to remove all weakly adsorbed species and hydrogen was dosed at 10 Torr. In Fig. 9. hydrogen interacting with the metal surface can be seen resonating at -48 ppm (compared to -60 ppm on a clean catalyst noted earlier). At a pressure of 300 Torr the β peak was observed at -32 ppm. The upfield resonance of -60 ppm noted for hydrogen on the clean catalyst was not observed here.

Figure 7. Heats of hydrogen adsorption isotherms at 403 K versus adsorbate pressure for 29% dispersed Ru catalyst.

Figure 8. NMR spectra of 29% dispersed catalyst dosed with 1:3 mixture of ethene/hydrogen after (A) 1 min, (B) 30 min, (C) 1 h and (D) 5 h.

Figure 9. NMR spectra of 29% dispersed catalyst dosed with 1:3 mixture of ethene/hydrogen, evacuated and dosed with (A) 10 Torr and (B) 300 Torr of hydrogen.

DISCUSSION

In this study, various hydrogen populations interacting with the ruthenium metal were observed by NMR. The population of α hydrogen saturated at a pressure below 100 Torr, while the β hydrogen population appeared at a pressure of 100 Torr and continued to increase up to 760 Torr in the temperature range of 300 to 473 K.

"Weakly" adsorbed hydrogen has been defined as that hydrogen adsorbed on the surface which can be removed via short evacuation (2 to 10 min) at room temperature (35, 43, 44). The adsorbed hydrogen that cannot be pumped out in that short interval of time has been termed the "strongly" adsorbed hydrogen. Evacuating for long time intervals (e.g. overnight) eventually removes all adsorbed hydrogen.

The heats of adsorption were measured via microcalorimetry, with the initial values at low coverage to be about 80 kJ/mol for the 29% dispersed catalyst. In comparison, the value of the initial heat of adsorption on Ru[0001] single crystals was reported to be 80 kJ/mol (13) and 120 kJ/mol (18).

The β hydrogen is a "weakly" adsorbed hydrogen species and considerably more weakly bound than the α hydrogen. The low value of the heat of adsorption of the β hydrogen raises the question of whether it is chemically or physically adsorbed. Physical adsorption is defined to be due to weak *van der Waal's* interactions or dispersion forces. The highest possible temperature at which true physical adsorption of hydrogen can occur is

regarded to be 20 K (46). The temperature and pressure of the experiments reported here suggest that physical adsorption of hydrogen is unlikely in this case. Reports in the past, in which it was claimed that physically adsorbed molecular hydrogen had been detected on single crystal metal surfaces between 100 and 300 K, have turned out mostly to suffer from water impurities, thermal gradients and spurious desorption in temperature programmed thermal desorption spectroscopy (46). The large Knight shift of the β peak shows interaction of this species with the conduction electrons of ruthenium and suggests that it does not reside primarily on the silica support. Also, the β population, as distinguished in this study, is not the hydrogen in the gas phase. The hydrogen gas by itself cannot account for all the observed hydrogen, which was in excess of 5 monolayer equivalents, and the Knight shift of the β hydrogen indicated that it is interacting with the metal. However, a fast exchange between the weakly bound hydrogen and the gas phase cannot be excluded here.

The large population of adsorbed hydrogen (H/Ru_{surface} ratios greater than five) observed in this study may play an important role in catalysis. In order to understand this phenomenon and gauge its importance to catalysis we must first address several important questions. Namely: how does the identification of a new species, β , distinct from the α species, compare with the previous studies on similar adsorption systems? Is the large amount of hydrogen observed in this study a general phenomenon? Where does all the

observed hydrogen exist in the catalyst?

Infra Red (IR) spectroscopic studies of hydrogen on alumina-supported platinum catalysts report three different IR modes. Two of the modes have been associated with a strongly adsorbed and a weakly adsorbed hydrogen species (31-34). However, the third mode has not been conclusively shown to be due to hydrogen. Dixon et al. (31) assigned the third mode observed at 100 Torr to a weakly adsorbed hydrogen species, while other researchers (32-34) have indicated it was due to CO contamination of the sample. IR studies of hydrogen on a alumina-supported rhodium catalyst revealed only a weakly adsorbed, dissociated hydrogen species at pressures above 100 Torr (29). However, in our NMR study the β hydrogen on ruthenium particles was identified and quantified distinct from the α hydrogen.

Hydrogen to metal stoichiometries of greater than one have been reported for supported metal catalysts (10, 11) and unsupported metal clusters (12). In the present work, we found the high H/Ru_{surface} stoichiometric ratios to be due to adsorption of large amounts of β hydrogen on the metal particles. While the β hydrogen population reached a H/Ru_{surface} ratio of about 4 at elevated pressures on the catalyst with a dispersion of 29%, the α hydrogen population saturated at a H/Ru_{surface} ratio of around 1.2 (Fig. 4). For the 19% dispersed catalyst, the β hydrogen population reached a H/Ru_{surface} ratio of only about 1 at elevated pressures while the α hydrogen population saturated at a H/Ru_{surface} ratio of around 2. This variation will be discussed later.

Surface science studies at submonolayer hydrogen coverages of hydrogen adsorption on Ru[0001] suggest that hydrogen is adsorbed on the threefold hollow sites (15, 16). Although small particles in supported catalysts contain different crystallographic surfaces, edges and corner atoms, it has been assumed that the immobile surface species, α_1 (which corresponds to a surface coverage of up to one monolayer), is adsorbed in the threefold hollow sites (1-3). However the location of the weakly adsorbed hydrogen species cannot be inferred from the surface science studies. Below we consider the following hypotheses regarding the nature of the large β hydrogen population: it could be associated with (i) subsurface species, (ii) multiple adsorption on some or all of the *surface* metal atoms, or (iii) adsorption on alternate sites such as bridge and atop sites or in the overlayers of a saturated layer of hydrogen atoms covering the surface.

(i) *Subsurface Hydrogen*: The existence of subsurface H on Ru[0001] is an interesting possibility discussed in the theoretical studies of Chou and Chelikowsky (27, 28). They report that the possible locations for subsurface hydrogen adsorption are the tetrahedral sites and the octahedral sites. They conclude that tetrahedral sites are energetically unfavorable for hydrogen adsorption. The octahedral sites are favorable for adsorption *if* the surface threefold hollow sites are already occupied by hydrogen and there is still hydrogen available for adsorption. The hydrogen can reach the octahedral sites by passing through the fcc site. TPD investigations by Yates et al. (14)

suggested the presence of subsurface hydrogen on Ru[0001]. They have attributed the difference in the high temperature tail of the TPD spectra for H_2 , HD and D_2 to the desorption of subsurface hydrogen (14).

However, if the β hydrogen was a subsurface species its population can be expected to increase with increasing particle size. In contrast, the β population was observed to decrease with an increase in particle size. That is, as the volume of subsurface sites increased relative to the surface, the population of the β state decreased. Furthermore, because of its closer proximity to Ru atoms, we expect the Knight shift of subsurface hydrogen to be larger than that for the hydrogen adsorbed on the surface. Again, this is in contrast to our experimental result; the Knight shift of the β peak was observed to be less than that of α . Thus, we conclude that the β hydrogen is not a subsurface species although the possibility of existence of undetected subsurface hydrogen in this system cannot be excluded. A higher ratio of defect like corner and edge atoms was correlated with a higher ratio of β hydrogen, whereas a higher ratio of atoms in the basal planes resulted in a larger α population.

(ii) *Multiple hydrogen adsorption on surface atoms:* The defect like edge and corner metal atoms have been speculated to be the sites where multiple hydrogen adsorption can occur (9, 10, 47, 48). The assumption is based on the fact that stepped sites are more active for hydrogen dissociation than the basal plane atoms (49). Specifically, a hydrogen-to-metal stoichiometry of 2 has been

assumed for hydrogen atoms coordinated to the edge and corner metal atoms (9, 47, 48). Given a particle morphology and an assumed stoichiometry, one can calculate hydrogen adsorption amounts. For example, the edge and corner atoms consist of 22% of the surface metal atoms for a perfect truncated cubo-octahedron with a dispersion of 30%. Even if a H/M stoichiometry of 2 is assumed for defect like sites (with a H/M of 1 for the basal planes) only about 25% of all the adsorbed hydrogen detected in this study can be explained. A H/M stoichiometric ratio of 18:1 and 20:1 must be assumed for the defect-like sites to account for all the hydrogen we observe on the 19% and 29% the dispersed catalysts respectively. If a H/M stoichiometry of 2 is assumed for the basal planes then the stoichiometric ratios for the defect-like sites must be 12:1 and 16:1 for the 19% and 29% dispersed catalysts, respectively, to account for all the hydrogen we observed.

(iii) *Hydrogen in the overlayer*: The large populations of hydrogen can be accounted for if, in addition to multiple adsorption on defect sites, it is assumed that the β hydrogen can be adsorbed on bridge and atop sites. Also it can be speculated that the β hydrogen exists in the overlayers or multiple layers. Mårtensson et al. (50) have studied hydrogen adsorption on stepped Ni[510] and Ni[100] surfaces at 100 K by EELS. They report molecular hydrogen chemisorbed at edge sites, over a dense layer of atomic hydrogen which covers the edge sites. No such state was observed on Ni[100] surfaces (50).

The proposal that hydrogen exists in overlayers has also been used to explain the mechanism of ethene hydrogenation reaction over metals. It has been proposed that a carbonaceous layer covers the surface and that the reaction takes place on top of the carbonaceous residues instead of on the metal surface (51). Hydrogen/deuterium exchange over the carbonaceous layer suggests that the hydrogen can interact with the metal and dissociate even when the surface is covered by carbonaceous species. It was proposed that the role of the metal is to dissociate hydrogen which can then migrate to an overlayer where the reaction takes place (51). Similarly, ^{13}C NMR studies of ethene adsorption on silica supported ruthenium catalysts, have shown that the metal can be predominantly covered by a layer consisting of strongly bound, partly dehydrogenated carbonaceous species which were not consumed during the reaction (52).

We found that the β state could be populated but the α state suppressed simply by dosing the catalyst with ethene and hydrogen. The Knight shift of the observed hydrogen population suggests that the hydrogen present was interacting with the ruthenium d electrons even in the presence of a carbonaceous layer. It can be concluded that the adsorption of β hydrogen (on surface sites or in an overlayer) is not inhibited by the presence of the carbonaceous layer on the surface. However the α hydrogen adsorption sites were blocked by the presence of the carbonaceous residue. No evidence for the α state was observed even after evacuating the sample and introducing pure

hydrogen for up to 5 hours at 400 K. Thus even when the surface sites are occupied by hydrocarbon fragments (52), β hydrogen can be adsorbed whereas the α hydrogen is suppressed.

The surface sites for β adsorption are not clearly understood and perhaps attempts to rigidly fix the location of adsorbed hydrogen to specific adsorption sites may be futile. The β hydrogen population may best be described by terms such as "hydrogen cloud" or "hydrogen fog", similar to those proposed by Mate et al. (53). They used theoretical calculations and vibrational spectroscopy to study hydrogen adsorption at submonolayer coverages on single crystals under UHV conditions and on high-surface-area metals at atmospheric pressure. They concluded that hydrogen atoms on metal surfaces are a unique form of "delocalized hydrogen". This delocalized adsorption is more pronounced for hydrogen adatoms than for other adatoms because of hydrogen's low mass. The high mobility of the β hydrogen due to its weak interaction with the surface perhaps make the binding site even harder to fix. If this view is correct the adsorbed hydrogen atoms (or molecules) should not be thought of as having a well defined bonding geometry but rather, resembling a "hydrogen cloud" or "hydrogen fog" that covers the surface.

The availability of such large amounts of "weakly" adsorbed delocalized β hydrogen can have implications for the understanding of catalytic reactions involving hydrogen. Catalytic reactions are generally thought of as occurring

between species adsorbed on different surface sites or between adsorbed species and gases. The possibility that hydrogen can populate the β state and interact with transition metals saturated with carbonaceous residues suggests that alternate routes for catalytic reactions may be operable.

CONCLUSIONS

An *in situ* NMR technique was utilized in this study to observe hydrogen adsorbed on supported ruthenium catalysts under variable temperatures and pressure conditions. Two distinct adsorbed states, α and β , were found. The β hydrogen is a much more weakly adsorbed species with a heat of adsorption of about 10 kJ/mol and was found to exist only at pressures greater than 100 Torr. The equilibrium amounts of hydrogen on the surface were found to be structure sensitive. A higher ratio of defect like corner and edge atoms correlated with a larger β population, while a larger α population was found on particles with a higher ratio of atoms in the basal planes. The availability of such large amounts of weakly adsorbed β hydrogen (greater than four monolayer equivalents) on the ruthenium particles can have implications for the understanding of catalytic reactions involving hydrogen. Also, the structure sensitivity of the β state may play a role in structure sensitive reactions.

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PAPER II

IN SITU NMR STUDIES OF HYDROGEN INTERACTION WITH
SUPPORTED RU-GROUP IB BIMETALLIC CATALYSTS

IN SITU NMR STUDIES OF HYDROGEN INTERACTION WITH
SUPPORTED RU-GROUP IB BIMETALLIC CATALYSTS

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ABSTRACT

An *in situ* NMR technique was employed to study hydrogen adsorption on silica supported Ru-Group Ib bimetallic catalysts at pressures up to one atmosphere. Two different hydrogen-on-metal resonances, α and β , were observed. Addition of silver to Ru was found to greatly diminish the relative amount of the weakly bound β hydrogen. Since silver preferentially populates edge, corner and other defect-like sites, the weakly bound β was correlated with low coordinated metal atoms. The total hydrogen population on the catalyst remains approximately the same with the addition of copper. The difference in catalytic behavior of Ru, Ru-Cu and Ru-Ag is postulated to be due to the surface segregation induced structure sensitivity of the weakly bound β hydrogen.

INTRODUCTION

The catalytic behavior exhibited by multimetallic catalysts can be quite different from that of the individual components. For example, the addition of a second metal to metallic catalysts can induce significant changes in activity and selectivity [1-5]. These changes have been attributed to "ensemble" (or geometric) and "ligand" (or electronic) effects. In addition, the observed differences in catalytic behavior may be due to the alteration (or blocking) of edges, corners and other defect-like sites, by the addition of a second metal. For example, several studies have shown that for the Ru-Cu system, Cu is effectively segregated to the surface of Ru, and for supported catalysts, the bimetallic clusters consist of a Ru core with Cu in a thin layer on the surface [6-12]. Monte Carlo simulations [13] predict that copper does not uniformly cover the surface but instead preferentially populates defect-like corner and edge lattice positions before forming a monolayer that consists of large two-dimensional islands. Kim *et al.* [14] report experimental evidence of copper preferentially populating ruthenium defect-like sites consistent with these Monte Carlo simulations.

Even though numerous studies of hydrogenolysis reactions and Fischer Tropsch synthesis have invoked ensemble effects to explain ruthenium bimetallic behavior [11, 15, 16], the lack of micromixing at the surface of these metals makes that explanation unlikely. Several studies in our laboratory correlated catalytic behavior of these systems with surface segregation induced

structure sensitivity [17-21]. Smale and King [17] have reported that the ethane hydrogenolysis activity decreased by the addition of silver to ruthenium catalysts at all temperatures between 493 and 548 K. At copper contents below about 10 to 20 atomic% the activity decreased by the addition of copper to the ruthenium catalyst at lower temperatures, but there was an increase in the turnover frequency (TOF) at elevated temperatures. At higher copper contents, the TOF did not change with surface compositions at any temperature, indicating the absence of ensemble effects. A key result of this study was the influence of Cu and Ag on the order of reaction with respect to hydrogen [17]. The addition of silver to nearly all edges, corners and other defect-like sites changed the order of reaction with respect to hydrogen to -2.4 from a value of -1.4 for pure ruthenium. In a similar set of experiments the addition of copper either did not change the order of reaction with respect to hydrogen (at 543 K) or also made it more negative (at 508 K). The variation in the effect of hydrogen on Ru-Ag and Ru-Cu relative to pure Ru was postulated to be due to an alteration in the population of a weakly bound state of hydrogen. The population of hydrogen was influenced by the availability of defect-like sites for rapid hydrogen adsorption and desorption. Kelzenberg and King [18] studied Fischer-Tropsch synthesis on Ru-Group Ib catalysts, and reported a similar structure sensitivity due to the segregation of the inactive group Ib metal to edge, corner and other defect-like sites. Once the defect-like sites were populated by the inactive copper, silver, or gold the TOF did not

change with increasing Ib content. However, the product distribution shifted to smaller molecules with increasing copper content, but remained unchanged with addition of silver. This continuous variation of product selectivity with the addition of copper was postulated to be due to surface copper acting as a source and sink of weakly bound hydrogen available for chain termination. As in the case of ethane hydrogenolysis, the state of hydrogen on these catalyst under reaction conditions appears to play a major role in determining activity and selectivity. The state of hydrogen under reaction conditions is the subject of the work presented here.

From a recent study employing an *in situ* NMR technique, we found that hydrogen adsorption on ruthenium at high pressures is structure sensitive [22]. We have observed two distinct NMR resonances, α and β , both representing hydrogen interacting with ruthenium. The population associated with the β resonance, present only at elevated pressures, was found to be a strong function of particle morphology. In the present study our objective was to investigate the variation of the hydrogen adsorption states as the surface composition was modified by the addition of copper or silver. The *in situ* NMR technique is uniquely suitable to distinguish and quantify the hydrogen species adsorbed on supported metal particles and spilled-over hydrogen on the support, and is operable up to pressures and temperatures existing under reaction conditions.

EXPERIMENTAL

Catalyst Preparation and Reduction

The Ru-Cu/SiO₂ catalysts were prepared by incipient wetness coimpregnation [23]. The impregnating solutions were prepared by dissolving Ru(NO)(NO₃)₃ (AESAR) and Cu(NO₃)₂·6H₂O (AESAR 99.999%) with dried Cab-O-Sil HS5 (300 m²/g BET area) in distilled water. The Ru-Ag/SiO₂ catalysts were prepared by incipient wetness co-impregnation of a solution of Ru(NO)(NO₃)₃ and AgNO₃ (AESAR 99.999%) with dried Cab-O-Sil HS5 silica support [24]. The ruthenium loading for all catalysts was kept at 4% by total weight of the support plus metals. The amount of copper and silver in the catalysts was determined by atomic absorption spectroscopy [23, 24]. All catalyst samples were reduced at 450 °C for 2 h in flowing H₂ and re-reduced in the NMR probe at 225 °C for 2 h in 760 Torr of hydrogen with hydrogen being evacuated and replaced every 30 min.

NMR Experiments

¹H NMR measurements were performed at 250 MHz on a home-built spectrometer. An *in situ* NMR probe was attached to a volumetric adsorption apparatus for studying the effect of adsorbate pressure (10⁻⁵ to 10³ Torr) and adsorption temperature (300 to 473 K) [22]. Typically 2,000 scans, with a recycle time of 0.3 s, were averaged for each spectrum. The ¹H NMR shifts are

referenced to tetramethylsilane (TMS) using the δ scale with negative values being upfield.

Hydrogen-on-ruthenium peak intensities were measured to quantitatively determine the amount of hydrogen adsorbed on the metal. In this work we have used lanthanum hydride ($\text{LaH}_{2.6}$) doped with 25 ppm gadolinium as an internal reference intensity standard. The details of this method and of the NMR spectrometer are given elsewhere [22]. For the Ru-Cu catalyst a standard spin-temperature inversion pulse sequence was used. However, because of low hydrogen-to-metal peak intensities for the Ru-Ag catalyst, we suppressed the slowly relaxing silanol proton magnetization. This was achieved by applying an inverting π pulse and by choosing a delay between this initial pulse and the subsequent $\pi/2$ pulse such that the recovering silanol magnetization was zero, while the hydrogen-on-metal peak intensity was completely recovered.

RESULTS AND DISCUSSION

The ruthenium dispersion (fraction of the ruthenium exposed at the surface) of the silica-supported bimetallic Ru-Ag catalyst (30 at% Ag) was determined to be 17% by volumetric uptake measurements of strongly bound hydrogen. Volumetric methods for determining the dispersion could be used for the Ru-Ag catalyst because hydrogen does not spill over from ruthenium to silver [24]. However, for the Ru-Cu catalyst volumetric measurements can lead to incorrectly high dispersion values due to hydrogen spillover from ruthenium to copper [8, 23, 25, 26]. In order to avoid errors associated with spillover, the Ru dispersion of the Ru-Cu bimetallic catalyst (18 at% Cu) was obtained from the NMR Knight shift of adsorbed hydrogen [23] and was found to be 16%. The total metal dispersion for both Ru-Cu and Ru-Ag catalysts was about 30%.

Although both Ru-Cu and Ru-Ag exhibit no miscibility in the bulk, the two bimetallics behave differently in a highly dispersed state [23, 24]. For example, Monte Carlo simulations indicate that both Cu and Ag strongly segregate to the ruthenium surface [13]. However, silver has a greater tendency to form separate particles and three-dimensional overlayers on ruthenium. In the present study, the compositions of bimetallic catalysts were chosen to obtain catalysts with surface defect-like sites (edges and corners) mostly occupied by Cu or Ag, and the basal planes retaining significant amount of exposed ruthenium [13]. Table 1 gives the calculated distribution of atoms in sites of different sites for bimetallics of compositions and dispersions

Table 1. Estimates of the population of atoms in lattice sites of different coordination for Ru-Ag and Ru-Cu particles determined via Monte Carlo simulations of cubo-octahedral structures [13]. The particles consist of 2406 total atoms yielding a total metal dispersion of about 30%.

Coordination		Ru-Ag			Ru-Cu		
		Ru	Ag	Total	Ru	Cu	Total
Edge and corner atoms	6, 7	4	164	168	0	168	168
Basal Plane atoms	8, 9	204	380	584	391	193	584
Bulk atoms	12	1476	178	1654	1654	0	1654
Total atoms		1684	722	2406	2045	361	2406

similar to the catalysts investigated in the present study. From these simulations, the predicted ruthenium dispersions were 19% for the Ru-Cu (15 at% Cu) catalyst and 14% for the Ru-Ag (30 at% Ag).

The *in situ* NMR spectra of the supported Ru-Cu catalyst taken at 400 K are given in Figure 1. Spectrum A, typical of samples with hydrogen pressures below 100 Torr, exhibits only two peaks. The resonance at ~ 3.5 ppm is due to the superposition of the $\text{LaH}_{2.6}$ calibration reference and hydrogen associated with the silica support. The second peak at about -54 ppm, labelled α , is attributed to dissociatively adsorbed hydrogen on the ruthenium particles [22, 27]. For pressures between 100 and 760 Torr a third distinct peak, β , is noted between -45 ppm and -15 ppm (spectrum B in Figure 1).

On the Ru-Ag catalyst, similar upfield NMR peaks, α and β , were observed at elevated pressures over the entire temperature range (300 K to 450 K) investigated in this study. Representative NMR spectra at 400 K are given in Figure 2. The resonance due to hydrogen associated with the silica was selectively suppressed (as described earlier), and the narrow resonance at 3 ppm resulted from the $\text{LaH}_{2.6}$ calibration reference.

We have previously reported the two separate hydrogen-on-metal resonances on the monometallic silica supported ruthenium catalyst [22]. The presence of these two separate hydrogen-on-metal resonance lines reveals that there are at least two distinct hydrogen populations. These populations represent species which are not in fast exchange with each other on the NMR

Figure 1. *In situ* NMR spectra of a supported Ru-Cu catalyst under hydrogen pressure of: (A) 50 Torr and (B) 760 Torr.

Figure 2. *In situ* NMR spectra of a supported Ru-Ag catalyst under hydrogen pressure of: (A) 50 Torr and (B) 760 Torr.

time scale (i.e., on the order of $(\Delta\omega_{\alpha\beta})^{-1} \approx 0.05$ ms, where $\Delta\omega_{\alpha\beta}/2\pi$ is the difference of resonance frequencies of α and β). The Knight shifts also suggest that both of these populations are interacting with the ruthenium metal. The interaction of α with Ru was well established previously [27]. The Knight shift of the β peak on the Ru-Cu catalyst is close to the β resonance on the monometallic ruthenium catalysts which suggests it is dominated by an interaction with the conduction electrons of ruthenium. Figure 3 is a representative spectrum of adsorbed hydrogen on a 5 wt% silica supported copper catalyst. Apart from the resonance at about 3.5 ppm due to hydrogen associated with the silica support, the only other peak observed is at 90 ppm. This resonance is due to hydrogen chemisorbed on copper particles [23]. The hydrogen adsorbed on copper saturated at about 100 Torr and no other resonances were observed on the supported monometallic copper catalyst at elevated pressures in the temperature range of 300 to 473 K.

The hydrogen population on the bimetallic clusters expressed as adsorption isotherms was determined. The intensities were obtained by integrating the deconvoluted peaks of α and β . For the Ru-Cu catalyst, the adsorption isotherms at 323 and 400 K are given in Figure 4. The adsorption isotherms for the Ru-Ag catalyst are depicted in Figure 5.

Although the ruthenium dispersions are approximately the same for the two bimetallic catalysts, the H/Ru_{surface} ratios are significantly different. At low pressures, it is well established that hydrogen can dissociatively chemisorb on

Figure 3. *In situ* NMR spectrum of a silica supported copper (5 wt%) catalyst under hydrogen pressure of 760 Torr.

Figure 4. Hydrogen adsorption isotherms of a Ru-Cu catalyst at 323 (●) and 400 K (○) determined by *in situ* NMR.

Figure 5. Hydrogen adsorption isotherms of a Ru-Ag catalyst at 323 (●), 400 (○) and 450 K (□) determined by *in situ* NMR.

ruthenium surfaces and then migrate to copper (spillover) both in the case of single-crystal surfaces [25] and supported catalysts [8, 23, 26]. In the present study we find that the spill over continues at high pressures. The total hydrogen (α and β) adsorbed on the Ru-Cu bimetallic catalyst at any given pressure is approximately the same as on the ruthenium catalyst. Consequently, the H/Ru_{surface} ratios are higher for the Ru-Cu catalyst because there are fewer ruthenium atoms exposed at the surface (Figure 6).

In contrast, at high pressures the net hydrogen adsorbed on the Ru-Ag catalyst was significantly lower than on either the monometallic Ru or the bimetallic Ru-Cu catalyst (Figure 6). It is well known that Ag does not dissociatively adsorb molecular hydrogen; it only adsorbs atomic hydrogen at temperatures below about 195 K [28]. Since hydrogen cannot adsorb on Ag, and spillover has not been observed on ruthenium-silver catalysts [24], it is not surprising that the total amount of hydrogen adsorbed on the Ru-Ag catalyst was lower. However, the ratio of the hydrogen represented by the α and β resonances is significantly altered by the presence of Ag as will be discussed later.

The isotherms determined from the deconvoluted and integrated intensities of the α and β NMR resonances, represent an upper limit to the hydrogen coverage on the surface. Part of the intensity of the β resonance may result from the gas phase hydrogen (resonating at ~ 0 ppm in the free gas phase) in fast exchange with the chemisorbed hydrogen. A lower limit of the

H/R_{surface}

Figure 6. Hydrogen adsorption isotherms of Ru($\bullet$), Ru-Cu($\circ$) and Ru-Ag($\square$) catalysts at 323 K.

hydrogen population on the metal surface was determined by subtracting the amount of gaseous hydrogen present in the sample void volume from the isotherms given in Figure 6. The reevaluated isotherms are given in Figure 7.

The isotherms of Figure 7 are further analyzed by separating the α and β populations for the silica supported Ru and Ru-Ag catalysts. The separate isotherms for α and β are given in Figure 8. Silver preferentially occupies defect-like sites and does not adsorb hydrogen [24, 28]. Thus, the change in α and β populations on the catalysts can be correlated with the corresponding change in the number of ruthenium atoms at the defect-like sites. From Figure 8A, the β population is about twice that of the α population at elevated pressures on the Ru catalyst. In contrast, on the Ru-Ag catalyst the β population was notably less than the α population (see Figure 8B). Clearly, defect like sites on the surface favor a larger β population, suggesting that this hydrogen adsorption is structure sensitive. On the other hand, the α population is saturated above 100 Torr for both Ru and Ru-Ag and does not show structure sensitivity.

What is the nature of the structure sensitive, weakly adsorbed hydrogen associated with the β resonance? The temperature and pressure of the experiments reported here suggest that physical adsorption of hydrogen is unlikely in this case. Furthermore the β population is structure sensitive and metal specific, i.e., it was observed on Ru and Ru-Group Ib bimetallics, but not on Cu or SiO₂, suggesting that it is chemisorbed. Although a higher ratio of

H/R_{surface}

Figure 7. Hydrogen adsorption isotherms of Ru(●), Ru-Cu(○) and Ru-Ag(□) catalysts at 323 K, corrected for estimated hydrogen in the gas phase.

H/R_{surface}

Figure 8A. α (●) and β (○) hydrogen adsorption isotherms of a Ru catalyst at 323 K.

H/R_{surface}

Figure 8B. α (●) and β (○) hydrogen adsorption isotherms of a Ru-Ag catalyst at 323 K.

defect-like sites favored a larger β population, its exact location (adsorption site) could not be determined from the present study. It has been shown that stepped sites are more active for hydrogen dissociation than basal plane atoms [29] and that defect-like edge and corner atoms could be the sites for multiple hydrogen adsorption [30-32]. However, it was shown that the β population is delocalized and highly mobile [33]. Therefore, it is also possible that hydrogen adsorbing at the defect-like sites rapidly diffuses over the metal surface or into an overlayer [22, 34]. Mårtensson et al. [35] have observed the existence of chemisorbed, molecular hydrogen on a hydrogen-saturated, stepped nickel surface at 100 K using EELS. No such molecular hydrogen was observed on a Ni[100] surface. This molecular hydrogen was postulated to adsorb on top of the dissociated hydrogen at the step sites. In the present study, the state of dissociation of the β hydrogen could not be determined and is the subject of further investigations. However, it can be concluded that the β peak represents a weakly chemisorbed species that interacts with the ruthenium metal.

The structure sensitivity of β hydrogen can be correlated with the structure sensitivity and the variations in the order of reaction with respect to hydrogen observed in ethane hydrogenolysis noted earlier [17]. It was earlier postulated that the variations in hydrogen effects on this reaction was due to the ability of defect-like edge and corner atoms to remove hydrogen from the surface by desorption. Therefore the presence of inactive silver on these sites

inhibits the desorption of hydrogen and increases its effective surface concentration. The order of reaction with respect to hydrogen is then more negative. Since adsorption/desorption of hydrogen on copper is an activated process [36, 37], at higher temperatures it was postulated that copper atoms occupying the corner and edge lattice positions in the Ru-Cu catalyst become active for hydrogen desorption. Hence, at low temperature copper behaves like silver and inhibits hydrogen desorption but at higher temperatures rapid desorption from copper becomes feasible. The results of Fischer-Tropsch synthesis studies [18] led to a similar postulate that copper serves as a source for hydrogen and shifts the selectivity toward smaller molecules on Ru-Cu catalysts while the selectivity remained unchanged on Ru-Ag catalysts. These postulates are consistent with the results of present study. Under reaction conditions of elevated pressures, silver merely reduces the β hydrogen population. On the other hand, copper can serve as a source/sink for β hydrogen at elevated pressures. On a per surface ruthenium basis, the α population is about the same on the Ru, Ru-Cu and Ru-Ag catalysts. On the same basis, the Ru-Cu catalyst has significantly more β hydrogen but the Ru-Ag catalysts has markedly less β hydrogen. Thus the availability of β hydrogen on Ru-Cu distinguishes it from Ru-Ag catalysts and can lead to the variations in chain growth probability observed in the Fischer-Tropsch synthesis.

CONCLUSIONS

We have observed two distinct hydrogen-on-metal resonances, α and β , on Ru and Ru-Group Ib bimetallic catalysts. The β resonance is associated with a more weakly bound species. On pure copper catalysts only one hydrogen-on-metal peak was observed, the intensity of which saturated at about 100 Torr. While the amount of hydrogen associated with the α population is not structure sensitive, the amount of hydrogen in the β state depends strongly on the surface composition. Silver is inactive for hydrogen adsorption and its presence at the defect-like corner and edge lattice positions strongly inhibits the amount of the β population on the Ru-Ag catalyst but the α population remains unaffected. Hydrogen (α and β) can spillover from Ru to Cu even at elevated pressures and saturate the entire metal surface with both states. Copper in a Ru-Cu catalyst can therefore be a sink or a source for the β population independent of ruthenium. These differences in hydrogen adsorption behavior on Ru, Ru-Cu and Ru-Ag catalysts are correlated with the differences in their observed catalytic behavior.

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PAPER III

IN SITU NMR STUDIES OF HYDROGEN EFFECTS ON SILICA
SUPPORTED PLATINUM, RHODIUM AND RUTHENIUM CATALYSTS

IN SITU NMR STUDIES OF HYDROGEN EFFECTS ON SILICA
SUPPORTED PLATINUM, RHODIUM AND RUTHENIUM CATALYSTS

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ABSTRACT

Hydrogen adsorption on supported platinum, rhodium and ruthenium catalysts was studied by *in situ* NMR techniques. At pressures greater than 100 Torr, two distinct adsorbed species α and β were observed on ruthenium and rhodium catalysts. The β hydrogen was weakly adsorbed and was observable only at pressures greater than 100 Torr. On platinum catalyst no β hydrogen was observed. Several hydrocarbon reactions involving hydrogen show great sensitivity to hydrogen pressure and to the catalyst metal. We postulate that some of these previously well noted hydrogen effects could be due to the availability (or unavailability) of β hydrogen state. The availability of the β hydrogen on ruthenium and rhodium can open reaction pathways that would not be available on platinum catalysts.

INTRODUCTION

All group VIII metal catalysts exhibit some activity for skeletal reactions of hydrocarbons, i.e., those involving the rearrangement of the original carbon skeleton. Two such reactions, hydrogenolysis and isomerization, have been postulated to be related processes with different hydrogen exponents. While Ru, Rh and Ir show higher activity for hydrogenolysis reactions, Pt is known to be more selective toward isomerization reaction (1). Ethane hydrogenolysis reaction has been studied in detail over a number of metals. A trend can be seen from these studies in which, the activity for hydrogenolysis decreases in the sequence $\text{Ru} > \text{Rh} > \text{Pt}$ (1).

It is generally accepted that hydrogenolysis involves multibonded surface species which are rather deeply dehydrogenated (2-6). Therefore it can be expected that isomerization/hydrogenolysis ratio (or, the ratio of non-degradative saturated products to hydrogenolysis) should increase at higher hydrogen pressures. Several metal catalysts do exhibit this behavior. Paál has reviewed the hydrogen pressure effects on different skeletal reactions (7).

In the present study, we have identified different adsorbed hydrogen species resulting from variations in hydrogen pressures by using *in situ* NMR techniques. We postulate that some of the hydrogen pressure effects result due to the availability (or the unavailability) of certain surface species because these different adsorbed hydrogen species may provide alternate routes for reactions.

Hydrogen adsorption on metal catalysts has been extensively studied. Sanz and Roza (8) used NMR spectroscopy to study hydrogen adsorption on Rh/TiO₂ at room temperature. They have reported the ratio of hydrogen-to-rhodium surface atoms to be as high as 3 at a pressure of 400 Torr. This suggests the presence of a large population of weakly adsorbed hydrogen species.

There have also been attempts to identify the different hydrogen species present at elevated pressures on supported rhodium (9) and platinum (10-14) catalysts by IR spectroscopy. On alumina supported platinum catalysts three different modes of IR absorption have been reported. The mode at 950 cm⁻¹ has been associated with strongly bound hydrogen while the mode at 2120 cm⁻¹ has been associated with a weakly adsorbed hydrogen species. However, the association of the mode at 2060 cm⁻¹ is controversial. Dixon et al. (11) have assigned it to a weakly adsorbed hydrogen species while other researchers (12-14) suggest that it could be due to a CO contamination of the sample. IR study of alumina supported rhodium catalysts reveal only a weakly adsorbed dissociated hydrogen at 2013 cm⁻¹ for pressures of 100 Torr and greater (9). It was concluded that any adsorbed hydrogen species at lower pressures were infrared inactive.

In the present study an *in situ* NMR technique was used to investigate the various hydrogen species adsorbed on the metal catalysts at pressures up to 760 Torr and temperatures up to 473 K. The main advantage of this

technique is that the amounts of hydrogen adsorbed *on the metal* can be quantitatively determined. Unlike the chemisorption method, the NMR technique can distinguish the hydrogen adsorbed on the metal from the hydrogen associated with the silica support (including the spillover hydrogen). Moreover, in contrast to many of the UHV single-crystal studies, the *in situ* NMR technique is applicable to dispersed catalysts and is not limited in pressure or temperature.

EXPERIMENTAL

Catalyst Preparation and Reduction

The catalysts were prepared by incipient wetness impregnation with Cab-O-sil HS5 silica as the support (BET surface area of 300 m²/g). H₂PtCl₆ (AESAR), Ru(NO)(NO₃)₃ (AESAR) and Rh(NO₃)₃•2H₂O were used as the metal precursors to prepare platinum (10 wt%), ruthenium (4 wt%) and rhodium (5 wt%) catalysts. The ruthenium and rhodium catalyst samples were reduced at 450 °C for 2 h in flowing hydrogen, while the platinum catalyst sample was reduced at 350 °C. The catalyst samples were re-reduced in the NMR probe at 225 °C for 2 h in 760 Torr of hydrogen with the hydrogen being evacuated and replaced every 30 min.

NMR Experiments

¹H NMR measurements were performed at 250 MHz on a home-built spectrometer in an *in situ* NMR probe. The probe was attached to a volumetric adsorption apparatus in which the pressure could be varied between 10⁻⁶ to 10³ Torr. The probe was placed in a cryostat (CF1200 Oxford) and could be heated up to 505 K. The probe had a negligibly small background signal. Typically 2,000 scans, with a recycle time of 0.3 s between scans, were averaged for each spectrum. For suppression of baseline artifacts in the spectra, a standard spin-temperature inversion pulse sequence was used for supported ruthenium

catalyst. The hydrogen-to-metal peak intensities were broader (larger linewidths) on the rhodium catalyst. On the platinum catalyst the hydrogen-on-metal peak was close to the peak associated with hydrogen in the silica support. Therefore, for the NMR experiments on rhodium and platinum catalysts the peak associated with the silica support was suppressed to improve the resolution of the hydrogen-on-metal peaks. This suppression was achieved by applying a π - τ - $\pi/2$ pulse. The time delay, τ , was so chosen that the recovering magnetization silanol proton was zero. The hydrogen-on-metal peak intensity was completely recovered, because it has a much smaller spin relaxation time, T_1 . The ^1H NMR shifts are referenced to tetramethylsilane (TMS) using the δ scale with negative values being upfield.

Hydrogen-on-metal peak intensities were measured to quantitatively determine the amount of hydrogen adsorbed on the metal. The NMR peak intensities were calibrated with a lanthanum hydride ($\text{LaH}_{2.6}$) internal reference standard (15). The reference sample was weighed and sealed in a capillary tube and placed *in situ* with the catalyst in an NMR tube. The amounts of adsorbed hydrogen were determined by comparing the integrated peak areas with that of the $\text{LaH}_{2.6}$ standard. Calibration problems associated with temperature variations were avoided by using this method (16).

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RESULTS

The catalyst dispersions were determined from strong hydrogen chemisorption measurements. The dispersions were determined to be 29%, 20% and 21% for the ruthenium, platinum and rhodium catalysts, respectively.

The ^1H NMR spectra of a silica supported ruthenium, platinum and rhodium catalysts, under 50 Torr of hydrogen at 400 K and are given in Figure 1. Two distinct peaks were observed: a resonance at ~ 3.5 ppm due to hydrogen associated with the silica support (17) and the internal standard (16), and an upfield peak which was labelled as α . The α peak was observed at -60 ppm on ruthenium, -110 ppm on rhodium and -25 ppm on platinum. This peak was attributed to hydrogen dissociatively adsorbed on the metal particles (18, 19).

For silica supported rhodium and ruthenium catalysts, at pressures greater than 100 Torr, a third distinct peak was observed. Representative NMR spectra of adsorbed hydrogen at an elevated pressure of 760 Torr and 400 K are given in Figure 2. This peak, labelled β , resonates between the α peak and the peak due to hydrogen associated with the silica support. With increasing pressure the β peak shifted downfield. The two distinct upfield peaks, α and β , were present over the entire temperature range (300 K to 473 K) investigated in this study. On the silica supported platinum catalysts no β peak was observed.

The hydrogen coverage on the metal surface were determined from the

Figure 1. NMR spectra of: (A) platinum, (B) ruthenium and (C) rhodium catalysts under 50 Torr of hydrogen at 400 K.

Figure 2. NMR spectra of: (A) platinum, (B) ruthenium and (C) rhodium catalysts under 760 Torr of hydrogen at 400 K.

integrated NMR intensities and were used to plot the adsorption isotherms.

The hydrogen adsorption isotherms are given in Figures 3, 4 and 5, for supported ruthenium, rhodium, and platinum catalysts, respectively.

Hydrogen adsorption isotherms for ruthenium and rhodium catalysts (Figures 3 and 4) indicate that the α population saturated at a pressure below 100 Torr, while the β hydrogen population became observable at 100 Torr and continued to increase for the entire pressure range studied (up to 760 Torr). With increasing temperature, considerable desorption from the higher pressure β state was observed on ruthenium catalyst. On the rhodium catalyst, no significant desorption occurred even when the temperature was increased up to 450 K. In contrast, on the platinum catalyst, the net hydrogen adsorbed per surface metal increased with temperature (Fig. 5). An apparent activation energy of approximately 13 kJ/mol was estimated from the isotherms.

The isotherms in Figures 3 to 5, determined from the NMR upfield peak intensities, represent an upper limit to the hydrogen coverage on the surface. The β peak may result from a fast exchange between the hydrogen chemisorbed on the metal and the gaseous hydrogen in the catalyst bed void (20). Therefore, part of the β peak intensity may result from the hydrogen in the gas phase hydrogen (the same may be true for the single peak observed on the platinum catalyst). The β hydrogen is, however, not identical with the free gas phase hydrogen which resonates at ~ 0 ppm. A lower limit of the hydrogen population on the metal surface was determined by subtracting the amount of

H/R_{surface}

Figure 3. Isotherms of hydrogen adsorption on supported ruthenium catalysts at 323 K (●), 400 K (○) and 473 K (■).

H/Rh_{surface}

Figure 4. Isotherms of hydrogen adsorption on supported rhodium catalysts at 323 K (○), 400 K (□) and 450 K (●).

$H/P_{t\text{surface}}$

Figure 5. Isotherms of hydrogen adsorption on supported platinum catalysts at 323 K (●), 400 K (○) and 450 K (■).

gaseous hydrogen present in the sample void volume from the isotherms.

For comparison, the reevaluated isotherms at 323 K are plotted for the platinum, rhodium and ruthenium catalysts in Figure 6. The total hydrogen per surface metal is much higher on the ruthenium and rhodium catalysts than on the platinum catalysts, because of the availability of adsorbed β population.

H/M_{surface}

Figure 6. Hydrogen adsorption isotherms on supported platinum (■), rhodium (●) and ruthenium (○) catalysts at 323 K.

DISCUSSION

On silica supported ruthenium and rhodium catalysts, hydrogen adsorption at pressures greater than 100 Torr revealed two different hydrogen-on-metal resonance lines. The presence of two separate resonance lines, α and β , indicates that the two hydrogen populations are distinct and not in fast exchange with each other on the NMR time scale (i.e., on the order of ≈ 0.05 ms). The upfield Knight shifts clearly suggests that both hydrogen populations are interacting with the metal (21). The appearance of the β peak on supported ruthenium catalysts above 100 Torr coincides with the reported drop in the heat of adsorption to a plateau of ≈ 10 kJ/mole (16). On supported rhodium catalysts, no significant desorption occurred up to temperatures of 450 K (Figure 4). The weakly adsorbed β species was altogether absent on the supported platinum catalyst.

The isotherms on platinum catalyst revealed an apparent activation energy. Robell et al. (22) have reported activated hydrogen adsorption on carbon supported platinum. It was concluded that the adsorbed hydrogen diffuses slowly to carbon. The activated slow process being the surface diffusion of hydrogen on carbon. In the present study, the adsorbed hydrogen is associated with platinum and not with the support, as indicated by the Knight shifts. The activated process must therefore be associated with the hydrogen adsorption on platinum metal. However, from studies of hydrogen chemisorption on platinum single crystals (22) at coverages less than a

monolayer there is no evidence of activated. It is therefore probable that the activated process is the surface diffusion of hydrogen on platinum.

It has been postulated that the first hydrogen atoms adsorb preferentially on and near the steps (23). The kinetics of adsorption are strikingly different on defect-like sites as compared to that on the basal planes. For Pt[997] an increase in the initial sticking probability by almost a factor of 5 was reported (24). Salmeron et al. demonstrated the catalytic activity for stepped surfaces by angle dependent molecular beam (25). Since the first hydrogen atoms preferentially adsorb at the defect-like sites, the activated process may be the diffusion from the defect-like sites to the basal planes.

From the results of the present study, it is clear that hydrogen adsorption on platinum, rhodium and ruthenium result in different adsorbed species. Although the different hydrogen effects in skeletal reactions of hydrocarbons may have several different causes, the availability of β hydrogen can play a dominant role. For example, it is generally expected that the surface hydrogen concentration regulates the degree of dehydrogenation of hydrocarbons adsorbed on the surface. Consider for example ethane hydrogenolysis. The generally accepted mechanistic scheme is,

In this case, the rate expression is,

$$Rate = \frac{kK_E P_E}{K_H P_H^{3/2}} \frac{1}{[1 + (K_H P_H)^{1/2} + \frac{K_E P_E}{(K_H P_H)^{3/2}}]^2}$$

In this case, the highest negative order with respect to the partial pressure of hydrogen can be -2.5.

This explanation is probably valid for platinum catalysts, but for rhodium and ruthenium catalyst the availability of β hydrogen can open new pathways. In a previous study we have shown that β hydrogen is highly delocalized and does not adsorb on the same sites as α hydrogen or the adsorbed hydrocarbons (16). Therefore the hydrogen released from the defragmented hydrocarbons does not compete for the same sites as the hydrocarbons. An alternate mechanistic scheme could be

The rate expression is

$$Rate = \frac{kK_E P_E}{K_{\beta} P_H^{3/2}} \frac{1}{[1 + \frac{K_E P_E}{(K_{\beta} P_H)^{3/2}}]^2}$$

The variation of the inhibiting effect with temperature and partial pressure of hydrogen are dominated by the equilibrium of β hydrogen with

with respect to partial pressure of hydrogen is -1.5 in this scheme. It can be postulated that with the inhibition of β hydrogen on ruthenium catalyst, the order of reaction should shift from -1.5 toward -2.5. In a previous study (26) we have shown that on the silica supported ruthenium-silver catalyst the β hydrogen adsorption is suppressed. The order of reaction is known to shift from -1.5 to -2.5 with the addition of silver to the ruthenium catalyst (27).

CONCLUSION

In situ ^1H NMR spectra of adsorbed hydrogen revealed two separate peaks, α and β , on ruthenium and rhodium catalysts. Both of these peaks represent adsorbed hydrogen interacting with the metal. The β hydrogen observable only at pressures greater than 100 Torr is a weakly adsorbed hydrogen species. The weakly adsorbed β hydrogen is not present on the platinum catalysts. The availability of the β hydrogen on ruthenium and rhodium can open reaction pathways that would not be available on platinum catalysts.

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GENERAL SUMMARY

The present study has identified two distinct adsorbed hydrogen states, α and β , on supported ruthenium and rhodium catalysts. However, β hydrogen was not detected on supported platinum catalyst. The β hydrogen, a weakly adsorbed species, was found to exist only at pressures greater than 100 Torr. The heat of adsorption of weakly adsorbed β hydrogen on supported ruthenium catalyst was determined to be about 10 kJ/mol. The β hydrogen is highly delocalized and its adsorption could not be fixed to specific surface sites. From the study of ruthenium-silver catalyst (silver being inactive for hydrogen adsorption), it was found that β population was sharply reduced when silver preferentially populated the edge and corner sites. The equilibrium amounts of β hydrogen on the surface were therefore determined to be structure sensitive. A larger β population was correlated with a higher ratio of surface defects.

The β state can, however, be populated even when the transition metals are saturated with carbonaceous residues. Catalytic reactions are generally thought of as occurring between species adsorbed on different surface sites or between adsorbed species and gases. The participation of delocalized β hydrogen can provide alternate routes for catalytic reactions. The availability or unavailability of such large amounts of structure sensitive "weakly" chemisorbed β hydrogen can explain some of the well noted hydrogen effects on metal catalysts. For example most noble metals catalyze hydrogenolysis and isomerization reactions, although with different selectivity. Both

hydrogenolysis and isomerization reactions, are generally postulated to occur due to different hydrogen surface coverage. Ruthenium and rhodium that can accommodate large amounts of delocalized, weakly adsorbed β hydrogen, while no such state is adsorbed on platinum. Also it is known that ruthenium and rhodium are more selective towards the hydrogenolysis reaction, whereas the platinum catalyst is more selective toward isomerization reaction.

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APPENDIX A

AN INTERNAL REFERENCE STANDARD FOR ^1H NMR SPIN COUNTING

AN INTERNAL REFERENCE STANDARD FOR ^1H NMR SPIN COUNTING

^1H Nuclear Magnetic Resonance is an effective spectroscopic technique for the characterization of supported metal catalyst. It has been successfully used to identify and quantify different hydrogen states adsorbed on the metal (see Papers I, II and III), determine adsorption isotherms (Papers I, II and III) study spillover effects, measure dispersion (1), and in certain cases determine surface compositions of bimetallic catalysts (2). The main advantage of ^1H NMR is that with this technique hydrogen adsorbed on the metal surface can be observed and quantified. In contrast traditional volumetric chemisorption measurements determine hydrogen uptake by both the metal and the support.

The amount of adsorbed hydrogen on the metal surface can be determined from the NMR intensities. The NMR intensity measurement, often referred to as spin counting, involves the measurement of the total integrated area under the NMR adsorption peak and comparing it with that of a standard. Most commonly, a sealed sample of precisely determined amount of water is used as an external standard.

Several experimental conditions need to be satisfied to achieve the highest possible accuracy of spin counting by NMR: (i) both the sample and the standard need to be measured using direct excitation, after reaching equilibrium with the lattice, under identical experimental conditions like the probe and spectrometer tuning and the temperature, (ii) to maintain constant

magnitude of the applied B_1 field, the size shape and positions of both the samples within the NMR coil should be kept as close as possible, and (iii) the loss of signal intensity due to probe ring down and receiver dead time have to be minimized and if possible included in the calculation. In practice an accuracy of more than 95% can be achieved.

However for variable temperature in situ NMR experiments, the accurate quantification of intensities becomes more complex. The calibration of intensities involve Boltzmann factor, changes of the probe Q factor and other temperature dependent effects which cannot all be precisely determined. Furthermore, a water sample as an external reference standard cannot be used for NMR intensity calibration at elevated temperatures.

A more effective way of measuring the NMR peak intensities under such conditions is to calibrate them to an *internal* standard. An *internal* standard would minimize the possible experimental errors provided: (i) the standard is stable at the temperatures used, (ii) the NMR line of the standard can be easily distinguished from other features in the spectrum, and is of comparable intensity, and (iii) the spin-lattice time, T_1 , is fast in a broad range of temperatures. The last feature is particularly important in the studies of very weak signals on supported metal catalysts, where short T_1 's are usually encountered, allowing for fast data acquisition.

In this work, we report the use of Lanthanum hydride ($\text{La}_{2.6}$) doped with 25 ppm of gadolinium to be a suitable internal reference standard for

calibrating the ^1H NMR peak intensities.

Lanthanum hydride is stable at higher temperatures (up to 1000 K). A typical NMR spectrum of lanthanum hydride is given in Figure 1. As can be seen, only one resonance at 3 ppm is observed. The shifts are referred to the tetramethylsilane (TMS) standard and the positive shifts are deshielded (downfield). The linewidth of this resonance is 0.85 KHz. The linewidth of the resonance due to the protons associated with the silica support is 2.5 KHz (2). The silanol protons resonate at $\sim 3\text{ppm}$ (2, 6), but because its lineshape is much broader than the resonance due to lanthanum hydride, the two peaks can be easily resolved for intensity calculations, see Figure 2.

The spin relaxation time (T_1) data of lanthanum hydride doped with 25 ppm of gadolinium is presented in Table 1. Typically the T_1 of hydrogen adsorbed on ruthenium metal is 20 ms (this depends on the metal, dispersion of the catalyst,). Lanthanum hydride ($\text{La}_{2.79}$, $\text{La}_{2.9}$) has a higher T_1 $\sim 1\text{-}2\text{ s}$ (3) but lanthanum hydride doped with gadolinium has a much smaller T_1 . The T_1 relaxation mechanisms in lanthanum dihydrides containing controlled levels of gadolinium have been reported in detail by Phua et al. (4). It was demonstrated that Gd^{3+} ions provide a strong relaxation mechanism arising from the dipolar coupling between the impurity and the proton magnetic moments. At temperatures above 300 K proton magnetization is transported to relaxation centers via atomic diffusion. A smaller T_1 for the protons in the internal standard is desirable for catalyst characterization because it allows for

selective suppression of the intensity of the silanol protons, which have a $T_1 \sim 3-5$ s (1), without distorting the intensity of hydrogen adsorbed on the supported metal.

The peak due to protons in the internal standard could be resolved from the peak due to the silanol protons. The intensity due to the internal standard's protons was measured and is presented in Table 2. The ratio of the intensities is in good agreement with the temperature correction for intensities using the Boltzmann distribution, according to which the ratio of intensities is inversely proportional to the ratio of their absolute temperatures.

Table 1. Spin Lattice Relaxation Time (T_1) for Internal Standard Protons

Temperature (K)	T_1 (ms)
300	37.5
323	39.4
348	40.9
373	42.6
400	43.9
423	45.6
448	49.9
473	54.2

Figure 1. NMR spectrum of lanthanum hydride, $\text{LaH}_{2.6}$, doped with 25 ppm of gadolinium.

Figure 2. A typical NMR spectrum of a silica supported ruthenium catalyst with the internal standard.

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APPENDIX B

CALCULATION OF GAS PHASE HYDROGEN IN THE NMR SAMPLE TUBE

CALCULATION OF GAS PHASE HYDROGEN IN THE NMR SAMPLE TUBE

A sample calculation to estimate the gas phase hydrogen present in the catalyst void in the NMR sample tube is given below. The estimated hydrogen in the gas phase is compared to the adsorbed hydrogen, given in Figure 1, estimated from in situ NMR analysis.

Catalyst used was 4% Ru/SiO₂ with a dispersion of 29% (measured from strong hydrogen chemisorption).

Weight of the catalyst in the NMR tube	=	35.5 mg
NMR sample volume	=	0.18 cm ³
Moles of hydrogen (H ₂) at 760 Torr	=	PV/RT
	=	(1 atm x 0.18 cm ³)/(82.05 atm-cm ³ xT)
	=	2.2E-03/T
Moles of Total Ruthenium	=	(35.5/1000)x(0.04)x(1/101.07)
	=	1.405E-5
H _{gas} /Ru _{total}	=	313.2/T

Table 1. The $H_{\text{gas}}/Ru_{\text{total}}$ ratios at 760 Torr with temperature in the NMR sample tube assuming all volume is occupied by the gas phase hydrogen.

Temperature (K)	$H_{\text{gas}}/Ru_{\text{total}}$
323	0.97
400	0.78
473	0.66

Figure 1. Hydrogen adsorption isotherm (●) and the amount of gas phase hydrogen in the catalyst void per surface ruthenium at 323 K.

APPENDIX C
GENERAL KINETICS OF HYDROGEN EFFECTS

INTRODUCTION

Catalytic reactions involving hydrocarbons such as hydrogenolysis, isomerization and deuterium exchange, exhibit a negative pressure dependency with respect to the partial pressure of hydrogen. The surface is composed of a limited number of sites and all sites are potentially available to both reactants. Langmuir (1, 2) developed the first concepts, making it possible to formulate rate equations able to account for such inhibiting effects which were subsequently applied by Hinshelwood (3). This important concept involves competition for chemisorption and appears in the rate equation in the form of an inhibiting term. It has been shown by Kemball (4) that simple competition or adsorption cannot account for the observed inhibiting effects in the frame of these concepts. From a Langmuir type adsorption isotherm,

$$\theta_s = \frac{1}{1 + (Kp_H)^{1/2}}$$

where θ_s is the fraction of free surface sites. At high hydrogen coverage this equation reduces to

$$\theta_s = (Kp_H)^{-1/2}$$

It is thus clear that the maximum negative pressure dependency to be expected in that case is -1/2. On the other hand, it is well known many catalytic reactions exhibit a much more stronger inhibiting effect in hydrogen pressure (5). We will consider ethane hydrogenolysis as a model reaction, since a wide

range of information can be obtained from the numerous studies on this reaction. In general, the order in hydrogen pressure, b , in the rate equation

$$Rate = k(p_H)^a(p_E)^b$$

is generally negative and may be as large as -2.5 (6-8). Several reaction schemes have been proposed. The classical procedure is summarized as follows. One step is considered to be the rate-determining step (RDS), all steps preceding the RDS are in equilibrium and all steps following the RDS are kinetically insignificant. Therefore, if the RDS follows a series of dehydrogenation steps, each of these steps contributes to the inhibiting effect in hydrogen pressure.

Some of the popular interpretations are listed below and described briefly.

Cimino et al. (9) proposed a scheme in which the RDS is the breaking of the C-C bond of a dehydrogenated C_2 radical involving a H_2 molecule.

The rate of hydrogenolysis is then developed as,

$$Rate = k(p_E)^n(p_H)^{1-n(6-x)/2}$$

where p_E is ethane pressure and p_H is hydrogen pressure. This mechanism has been used by several authors with modifications. For example, Sinfelt (10) left out the molecular hydrogen from the RDS to get

$$Rate = k(p_E)^n(p_H)^{-n(6-x)/2}$$

Leclercq et al. (11) came up with

$$Rate = k \frac{K p_H p_E}{(p_H)^{(6-x)/2 + K p_E}}$$

Boudart (12) introduced the concept that the site on which the hydrocarbon radical is chemisorbed is not the same as the one on which hydrogen atoms are chemisorbed.

Hydrogen is dissociatively chemisorbed in equilibrium with sites S which are not the same as the sites * on which the hydrocarbon reacts. The adsorption of ethane is considered to be irreversible. The rate is a function of $(1-\theta_H)^Y$, θ_H being the hydrogen coverage in equilibrium with the gaseous hydrogen and Y being the number of H atoms by the hydrocarbon that are held on Y neighboring S sites. At saturation coverage of hydrogen, the function reduces to $(K P_H)^{Y/2}$.

An additional improvement is due to Gudkov et al. (13). The new feature considered that the RDS is not independent of the experimental conditions: the degree of dehydrogenation of the most abundant surface intermediate (MASI) is dependent on the amount of hydrogen. The scheme

considered is

from which the following rate equation is derived,

$$\text{Rate} = k \frac{p_\text{E}(p_\text{H})^{1/2}}{(p_\text{E} + k'p_\text{H})^2}$$

If there is not enough hydrogen on the surface, the C_2H_5 radical dehydrogenates and the MASI becomes a C_2H_2 radical. The corresponding rate equation becomes

$$\text{Rate} = k \frac{p_\text{E}(p_\text{H})^2}{[p_\text{E} + k'(p_\text{H})^{2.5}]^2}$$

In all the interpretations of the negative order characteristic of the hydrogen pressure, the striking feature is that the inhibiting effect is related to the degree of dehydrogenation of the MASI (most abundant surface intermediates). But when analyzing the experimental data, for example of ethane hydrogenolysis on metals, it appears that the value of the inhibiting effect in hydrogen pressure is not independent of the experimental conditions (14). The inhibiting effect, varies continuously with both pressure and temperature conditions. In effect, the inhibiting effect is increasing both when the hydrogen pressure increases and when the temperature is lowered!

According to Frennet (15, 16), this leads to the difficulty that the degree of dehydrogenation should increase when the hydrogen pressure is increased or when the temperature is lowered! Other types of models have been previously developed and are briefly discussed next.

Multisite Effect

This analysis is based on the observation according to which at saturation of surface by the hydrocarbon, a fraction of the surface sites are still available for hydrogen chemisorption (15). Therefore the idea is that some chemisorbed radicals are larger than the surface site, the ensemble size for adsorption being derived from the number of hydrogen atoms that may be chemisorbed per unit surface area. This model, developed by Frennet et al. (16), distinguishes three types of sites: (a) the sites to which the chemisorbed radicals are bonded, (b) the sites that are covered by the large chemisorbed radical and where no adsorption can occur and (c) the sites that are hindered for chemisorption of large radicals, but that can adsorb hydrogen.

In the rate equation there is a requirement to find an ensemble of X free sites (17) expressed as $(1-\theta_H)^X$. When the partial pressure of ethane is maintained constant, the resulting rate equation is written as

$$Rate = k(1 - \theta_H)^X$$

This model also has some weaknesses. To determine X, correlations are

made with the number of bonds formed by chemisorption of the hydrocarbon fragments on the metal. These correlations are derived from magnetic measurements which are conducted in the absence of gaseous hydrogen, whereas hydrogenolysis measurements are conducted in the presence of a large excess of hydrogen. It would be surprising that the degree of dehydrogenation should be the same under such different conditions. Furthermore it is very hard to accept that the hydrocarbon undergoes a complete cracking at once. It is generally accepted that cracking is a result of a series of successive steps of dehydrogenation and of C-C bond breaking. Also the high mobility of hydrogen on the surface, at the temperature where hydrogenolysis proceeds, makes it difficult to understand why all these X sites should be found as an ensemble in the framework of the reaction scheme.

PROPOSED MODEL

In light of our investigations of hydrogen adsorption on supported metal catalysts (18, 19), we propose a different kinetic model using the classical approach. Consider a modified version of Gudkov's scheme. In this scheme (Scheme A) the MASI is considered to be the ethylidyne radical rather than the ethyl radical (20).

an implicit assumption here is that

From this the rate is determined to be

$$Rate = \frac{kK_E P_E}{K_H P_H^{3/2} [1 + (K_H P_H)^{1/2} + \frac{K_E P_E}{(K_H P_H)^{3/2}}]^2}$$

In this case, the highest negative order with respect to the partial pressure of hydrogen can be -2.5.

We know from our investigations (18, 19) that at elevated pressures another adsorbed hydrogen species, β , becomes available. The β hydrogen is in equilibrium with the gas phase hydrogen and the adsorbed α hydrogen. The presence of β hydrogen may provide an alternate path for the hydrogenolysis reactions. Using these facts, we propose an alternate scheme (Scheme B) to be

For the MASI to be ethylidyne radical, $x = 3$. In this mechanistic scheme we consider that the surface coverage by components other than the MASI (C_2H_x) is negligible. Hydrogen that becomes available from the dehydrogenation of the hydrocarbon fragment does not compete with the hydrocarbon for the same sites, S. The S surface sites are those that are accounted for by strong hydrogen chemisorption. We have shown that at higher pressures with the

availability of additional adsorbate atoms (or molecules) the surface concentrations of adsorbed species can far exceeds the coverage expected at low pressures (18). It is postulated that the additional adsorbate atoms (representing β hydrogen species) are weakly adsorbed and make room by squeezing themselves on the surface. These species are delocalized and highly mobile and no fixed geometry can be assigned to them. It is further shown that when the hydrocarbons are chemisorbed on surface sites, S, the β hydrogen may still be weakly adsorbed on to the surface (18).

From the reaction scheme B,

$$Rate = \frac{kK_E P_E}{K_\beta P_H^{3/2}} \frac{1}{\left[1 + \frac{K_E P_E}{(K_\beta P_H)^{3/2}}\right]^2}$$

The inhibiting effect in this scheme is still related to the degree of dehydrogenation. However the variation of the inhibiting effect with temperature and partial pressure of hydrogen are dominated by the equilibrium of β hydrogen with gaseous hydrogen. From the rate equation the order of reaction with respect to partial pressure of hydrogen can vary between 1.5 to -1.5. Clearly at high pressures of hydrogen the order of reaction with respect to partial pressure of hydrogen is -1.5 in this scheme.

Previous results indicate that the apparent orders of reaction with respect to hydrogen for silica-supported iridium and ruthenium catalysts are -1.6 and -1.3 respectively, while that for platinum catalyst is -2.5 (3). Smale

and King have postulated that these contradictory results were due to a different proportion of defect-like corner and edge sites on the surface (8). The role of defect-like sites is also suggested from the fact that with the addition of inert silver to ruthenium the order of reaction with respect to hydrogen changes from -1.3 to that of -2.5.

From our proposed model, we postulate that the differing orders of reaction are due to the availability of weakly bound β hydrogen. The amounts of adsorbed β hydrogen depends upon the proportion of defect-like sites (18, 19). Therefore the edge and corner atoms do play a role in determining the order of reaction with respect to hydrogen. We have previously reported that with the addition of silver to ruthenium, the amount of β of hydrogen is greatly diminished (19). This shifts the reaction mechanism from scheme B to scheme A, with the apparent order of reaction moving toward -2.5. For the platinum catalyst, β hydrogen was not observed. Therefore the order of reaction (from scheme A) would be expected to be -2.5.

CONCLUSIONS

The order of reaction with respect to hydrogen for ethane hydrogenolysis has been generally reported to be between -1.5 to -2.5. These strongly negative orders of reaction cannot be explained from Langmuir-Hinshelwood kinetics by simple site blocking by hydrogen. It has been previously postulated that sites for hydrocarbon chemisorption are different from that of hydrogen

chemisorption. The edge and corner atoms which are kinetically more active for hydrogen dissociation were assumed to be sites for hydrogen adsorption and not hydrocarbon chemisorption. We postulate that the order of reaction on ruthenium and platinum differ because of the availability of a weakly bound β hydrogen species on ruthenium but not on platinum. This allows for a different mechanistic scheme to be operable on ruthenium catalysts allowing the order of reaction with respect to hydrogen to be close to -1.5. The β hydrogen is greatly influenced by the surface defect-like sites. Blocking of these sites by inert silver diminishes the β hydrogen population making the order of reaction closer to -2.5 on supported ruthenium-silver catalysts.

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APPENDIX D
DYNAMICS OF HYDROGEN AT THE SURFACE OF A SUPPORTED
RUTHENIUM CATALYST

DYNAMICS OF HYDROGEN AT THE SURFACE OF A SUPPORTED
RUTHENIUM CATALYST

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ABSTRACT

One- and two-dimensional NMR exchange measurements were performed to probe the dynamics of hydrogen adsorption on highly dispersed silica-supported ruthenium particles at pressures from 10^{-4} to 600 Torr and temperatures between 292 K and 400 K. We found three distinct NMR resonances, α_i , α_M , and β , representing hydrogen interacting with the metal surface. The character of motion of the three hydrogen species was inferred from 1D and 2D NMR experiments. Also, two types of exchange processes were found: a slow chemical exchange occurring on a submillisecond time scale between α_M and β and a fast exchange between weakly adsorbed hydrogen and hydrogen in the gas phase, with both hydrogen species contributing to the β NMR line.

INTRODUCTION

Interactions between hydrogen and metal surfaces have been a subject of intense investigation because of the considerable scientific interest in hydrogen-metal systems and their practical importance in catalysis. Hydrogen adsorption over well-defined single crystal ruthenium surfaces was studied under ultra-high vacuum (UHV) conditions by temperature programmed desorption (TPD)¹⁻³, vibrational spectroscopy³⁻⁵, angle-resolved photoemission spectroscopy⁶, low-energy electron diffraction (LEED)^{1,3,7-10}, and measurements of the surface diffusion of hydrogen atoms¹¹⁻¹³. In addition, the hydrogen adsorption on ruthenium surfaces was a subject of theoretical investigation using ab initio calculations^{14,15}.

The results of single-crystal studies cannot always be extrapolated to high-pressure conditions and highly dispersed systems. For example, at elevated pressures steady-state concentrations of various "weakly" bound species can exist that may be important for catalytic processes. In addition, interaction of these species with the surface of highly dispersed metal particles, residing on a support material, may be strongly modified by the presence of "defect-like" sites (e.g., edges and corners).

Recently IR studies have identified different hydrogen species interacting with rhodium¹⁶ and platinum¹⁷⁻²¹ in alumina-supported catalysts at elevated pressures. NMR spectroscopy has been increasingly used to study the surfaces of metal particles²²⁻²⁹. The influence of support materials on the adsorption of

hydrogen on rhodium has been studied by deuterium NMR³⁰. In supported hydrogen-metal systems at elevated pressures, NMR permits quantifying the amount of hydrogen present in the system and can distinguish different hydrogen species based on their respective Knight shifts and dynamic properties^{22,31-34}. In general, the time scale of dynamic processes accessible to NMR ranges from 10^{-9} to 10^5 s, which encompasses the time scale of the motion of molecules interacting with metal surfaces and other important catalytic processes^{24-27,32-33}.

Recently we have noted the presence of three types of hydrogen, called α_1 , α_M , and β , interacting with the surface of highly dispersed ruthenium particles by means of *in situ* ^1H NMR³⁵ (see Fig. 2). In the present paper we report the results of *in situ* ^1H exchange-NMR experiments, performed to elucidate the dynamic behavior of these hydrogen species. We will show that a slow exchange process (on a submillisecond time scale) takes place between the mobile species α_M and β at 400 K, whereas the strongly bonded hydrogen species, α_1 , does not undergo motions measurable by these NMR experiments. The β hydrogen is found to consist of two rapidly exchanging species: weakly adsorbed hydrogen and hydrogen in the gas phase.

EXPERIMENT

The catalyst sample was prepared by incipient wetness impregnation of $[\text{Ru}(\text{NO})(\text{NO}_3)_3]$ in distilled water with a dried Cab-O-Sil HS5 (300m² BET area)

silica support as described previously³³. For the present study we used a catalyst with a ruthenium loading of 8% and a dispersion (number of metal surface atoms/total number of metal atoms) of 0.30. The sample was reduced at 450° C for 2 hours in flowing H₂ and re-reduced in the NMR probe at 225° C for 5 hours in 760 Torr of H₂ with the hydrogen evacuated and replaced every 30 minutes.

A home-built spectrometer was operated at 250 MHz for proton resonance. The NMR probe was connected to a vacuum/dosing manifold allowing variable hydrogen pressure and then inserted in an Oxford CF1200 cryostat connected with a temperature controller (Oxford 3120) to regulate the temperature between room temperature and 500 K. The proton background signal of the NMR probe (including an empty glass tube) was determined separately under the conditions used in the study and found to be negligibly small. The chemical shift scale was referenced to tetramethylsilane (TMS) with negative values upfield.

The basic pulse sequences used to monitor exchange processes are sketched in Fig. 1:

(i) 2D exchange-NMR measurements³⁶ (Fig. 1(a)) with acquisition of data in the time-domain t_2 , as a function of t_1 and fixed mixing time τ_m

(ii) spin-population saturation by selective excitation (DANTE-type pulse sequence³⁷, Fig. 1(b)), with the exchange process being monitored through the development of magnetization as a function of the recovery time τ_m

(iii) spin population inversion by means of the 2D exchange-NMR sequence³⁶ (Fig. 1(a)) with the evolution time t_1 set to a fixed value, and a series of spectra taken with various mixing times τ_m

In the 2D exchange-NMR experiment (Fig. 1(a)) we employed quadrature detection of the signal (FID) in the time-domain t_2 (dwell time 5 μs) as a function of the time variable t_1 (varied between 10 and 1280 μs in 10 μs increments), while the mixing time τ_m was fixed at 2 ms. The resulting complex-valued interferogram was Fourier transformed, with respect to the t_2 dimension, and phase corrected. Only the real part of the resulting spectra was then Fourier transformed with respect to t_1 , yielding the final 2D NMR spectrum.

A DANTE sequence (Fig. 1(b)) consisted of 36 short pulses with total duration of approximately 300 μs and width of excitation of ≈ 1 kHz, which corresponded to 40% of the width (FWHM) of the β resonance. The selectivity was tested by Fourier transformation of the pulse sequence itself and by applying it to the silica peak at 3 ppm. After readjusting the resonance offset and the rf field strength to selectively saturate the β line, a set of spectra was acquired using a variable evolution time τ_m between the DANTE sequence and a subsequent nonselective $\pi/2$ pulse. The spectra taken at short recovery times τ_m (≈ 10 μs) after DANTE excitation showed that it was not possible to achieve a selective saturation or inversion ("hole burning") within the β peak, i.e., the whole β resonance (FWHM 2.5 kHz) was saturated by the DANTE

sequence. Also, the intensity of the α resonance decreased slightly. Both of these observations indicate a magnetization exchange occurring during the 300 μ s irradiation of the DANTE sequence. Therefore, after completion of the pulse sequence, the initial values of the magnetization (for $\tau_m = 0$) are not given by the experimental conditions alone (ideally, zero magnetization for β , or part of β , and maximum magnetization for α), but are also determined by the dynamic processes taking place in the system during the selective excitation.

The time period for spin-population labeling can be reduced considerably using the basic 2D pulse sequence (Fig. 1(a)) in a series of 1D NMR experiments. By choosing the frequency in resonance with the β peak and applying the initial $(\pi/2)_x$ pulse, the magnetization of β hydrogen remains aligned in the $+y$ direction in the rf rotating frame, whereas the α magnetization vector rotates in the xy plane with an angular frequency $\Delta\omega$ corresponding to the offset between α and β ($\Delta\omega/2\pi \approx 6$ kHz). Therefore, after a time $t_1 \approx 80$ μ s the magnetization vectors for α_M and β are 180° out of phase. The second $(\pi/2)_x$ pulse converts these two $\pm y$ magnetizations into $\pm z$ magnetizations creating population differences, which develop during the mixing time τ_m . The final $\pi/2$ pulse monitors the resulting magnetizations as a function of τ_m . The above experiment is referred to as the spin-population inversion experiment throughout this work.

The difference between selective saturation and spin-population inversion experiments is that they create different initial conditions at $\tau_m = 0$.

The initial magnetizations, after selective saturation of the β resonance using DANTE, deviate significantly from the initial magnetizations in an ideal experiment (β intensity zero, α_M intensity maximum) because of the relatively long duration (300 μ s) of the saturation sequence. This is also true for the $\pi/2$ pulse sequence of Fig. 1(b), but to a lesser extent because the evolution period t_1 (80 μ s) is shorter. Regardless of the special technique for the preparation of the initial spin populations, in the time periods τ_m the evolution of the magnetization is governed by the same processes of exchange and spin-lattice relaxation.

Figure. 1 Basic pulse sequences to monitor exchange processes by spin-population labeling and two-dimensional NMR.

RESULTS

Figure 2 shows representative single-pulse *in situ* ^1H NMR spectra of the silica-supported ruthenium catalyst (dispersion 0.30, Ru loading 8 weight%) obtained under various pressures. The NMR peak near 3 ppm originates from OH protons in the silica support. Under vacuum conditions (10^{-5} to 10^{-1} Torr) a hydrogen resonance α_1 , shifted upfield, was found at ~ -60 ppm (Fig. 2(a)). This hydrogen species, interacting with the metal surface as indicated by the Knight shift, could not be removed by short (several-minute) evacuation at 400 K. With increasing pressure a second hydrogen species α_M appeared. It exhibited a narrow NMR peak (~ 2 kHz FWHM, full width at half height) at -55 ppm, as shown in Fig. 2(b), with intensity growing as the pressure increased from 10^{-1} to 100 Torr. The α_M species could be easily evacuated in the temperature range studied (292 to 400 K). At a pressure of ~ 100 Torr a third hydrogen species, denoted β , became observable at -45 ppm (Fig. 2(c)). Further elevation of pressure above 150 Torr led to an intensity increase of β , whereas the α_M intensity remained constant above ~ 100 Torr (Figs. 2(d) and 2(e)).

The occurrence of the α_1 , α_M , and β resonance lines has been correlated with the heats of adsorption obtained from microcalorimetric measurements³⁵. At low pressures (10^{-5} to 10^{-1} Torr), when only α_1 hydrogen is present on the surface, the heat of adsorption was found to be ≈ 70 kJ/mole. In the pressure range from 10^{-1} to 100 Torr the heat of adsorption decreased to values of 60 to 30 kJ/mole (α_M hydrogen). Above 100 Torr there was an additional drop of the

Figure. 2 In situ ^1H NMR spectra of hydrogen on silica-supported Ru particles (loading 8%, dispersion 0.29) at various H_2 pressures.

heat of adsorption to a value of ≈ 10 kJ/mole, coinciding with the appearance of the β resonance in the NMR spectrum. From these results and the behavior upon evacuation mentioned above, the following terminology seems to be adequate: α_1 is termed as strongly bound hydrogen, whereas α_M and β hydrogen are relatively weakly adsorbed hydrogen species.

Two-dimensional exchange-NMR lineshapes and linewidths provide information about the hydrogen dynamics even if no resolved resonances can be observed. The 2D NMR *absorption* spectra taken at various temperatures and pressures with a mixing period of 2 ms are shown in Fig. 3. Since no exchange was found between the hydrogen residing at or near the Ru surface and the hydrogen on the support, only the spectral region representing the former is shown. Figs. 3(a) and 3(b) show the contour plot of α_1 type hydrogen characteristic for pressures below 0.1 Torr and at temperatures of 292 K and 400 K. The two-dimensional lineshape did not change in this temperature range and extended along the main diagonal. After increasing the hydrogen pressure to 80 Torr at $T=400$ K the hydrogen species α_M appeared, superimposed on α_1 , and was characterized by the circular contour shown in Fig. 3(c). Further elevation of the pressure to 160 Torr yielded an asymmetrical peak (Fig. 3(d)), indicating the occurrence of β type hydrogen (compare with Fig. 2(c)). At pressures between 200 and 300 Torr sufficiently resolved cross peaks became visible which were *in phase* with the two peaks on the main diagonal (Fig. 3(e)). Similarly, the cross peaks were observed at the

Figure. 3 Two-dimensional exchange-NMR spectra at various temperatures and H_2 pressures: a) 292 K, 10^{-4} Torr, b) 400 K, 10^{-4} Torr, c) 400 K, 80 Torr, d) 400 K, 160 Torr, e) 400 K, 300 Torr, f) 400 K, 600 Torr.

final H_2 pressure of 600 Torr (Fig. 3(f)).

The presence of 2D-NMR cross peaks (Figs. 3(e,f)) at elevated pressures reveals that the two species α_M and β , both interacting with the ruthenium surface, are in a slow exchange limit, i.e., the correlation time for the exchange $\tau_c > (\Delta\omega_{\alpha\beta})^{-1} \approx 0.05$ ms, where $\Delta\omega_{\alpha\beta}/2\pi$ is the difference of resonance frequencies of α_M and β . In order to obtain a value for the exchange rate, the one-dimensional selective saturation and spin-population inversion experiments described above were performed. The results of these two experiments, obtained at a temperature of 400 K and an external hydrogen pressure of 300 Torr are plotted in Figs. 4 and 5. In Fig. 4 the quantity $X_i'(\tau_m)$, defined by the relations

$$X_i'(\tau_m) = \exp(\tau_m/T_1)X_i(\tau_m), \quad X_i(\tau_m) = \frac{M_{eqi} - M_i(\tau_m)}{M_{eqi}}, \quad (1)$$

($i = \alpha_M, \beta$) is plotted versus the recovery time τ_m after irradiation the DANTE sequence with $M_i(\tau)$ being the intensities (magnetizations) of α_M and β , and M_{eqi} the equilibrium values for $\tau_m \rightarrow \infty$. The spin-lattice relaxation time T_1 has been determined in a separate saturation-recovery experiment and found to be $T_1 = (15 \pm 3)$ ms for α_M and β hydrogen. The quantity $X_i'(\tau_m)$ was obtained according to Eq. (1) to separate the influence of spin-lattice relaxation from the experimental values $(M_{eqi} - M_i(\tau_m))/M_{eqi}$ (*vide infra*, section IV). Clearly the initial time dependence in the selective saturation experiment indicated a

Figure. 4 Time dependences of α_M and β intensities after selective saturation of the β resonance line. Note that the contribution of spin-lattice relaxation has been eliminated from the data.

Figure. 5 Time dependence of α_M and β in the spin-population inversion experiment. As in Fig. 4, the contribution of spin-lattice relaxation has been eliminated.

magnetization transfer from α_M to β . While the β intensity M_β was increasing continuously (i.e., X_β' is decreasing), the intensity of the α_M resonance line M_α was initially decreasing (X_α' increasing) for short recovery times τ_m of less than 2 ms.

The results of the spin-population inversion experiment (Fig. 1(b)), corrected for the spin-lattice relaxation according to Eq. (1), are shown in Fig. 5. Since the initial intensity of the β resonance at the mixing time $\tau_m = 0$ was chosen to be positive, the renormalized intensity X_β' increases its value. As explained above, this initial value is not equal to the equilibrium value because during the time period t_1 spin-spin relaxation (including magnetization exchange) cannot be neglected. The same holds for the intensity of the α_M peak, which is initially 180° phase shifted and shows a negative initial intensity: thus $X_\alpha'(0)$ is greater than $X_\beta'(0)$ and decreases with τ_m . The curve at the bottom of Fig. 5 represents the difference $X_\alpha' - X_\beta'$, and the upper curve represents the sum $X_\alpha' + X_\beta'$. The approximate exponential behavior of the quantities X_α' and X_β' for mixing times $\tau_m < 2$ ms again demonstrates the magnetization exchange between the two spin populations α_M and β . The data of Figs. 4 and 5 will be used in the next section to determine the rate of magnetization exchange between the two species.

It was noted that the resonance shifts of α_M and β depend on the pressure of hydrogen. A plot of the upfield NMR shifts δ versus hydrogen pressure for 323 and 400 K (Fig. 6) shows that the variation of the resonance

Figure. 6 Variation of the upfield NMR shifts of α_M and β versus pressure at two temperatures, $T = 323$ K and $T = 400$ K.

shift for α_M is weaker than for β . Because β hydrogen becomes visible in the NMR spectra as a separate peak at pressures above 100 Torr where the corresponding heat of adsorption is rather low (10 kJ/mole), it is likely that this type of hydrogen is in fast exchange with hydrogen in the gas phase, present within the sample and normally resonating near 0 ppm. To confirm this hypothesis experimentally, we utilized a standard inversion recovery experiment (π - τ - $\pi/2$ -acquisition) and chose the time delay τ such that the silanol proton magnetization was zero and the intensities of α_M and β hydrogen or hydrogen gas were completely recovered. This was easy to accomplish since the spin-lattice relaxation time T_1 of silanol protons is typically two orders of magnitude longer than the T_1 value of hydrogen gas (10 ± 1 ms) and the T_1 value for both hydrogen species α_M and β (15 ± 3 ms). Figure 7 represents the results of this experiment for silica without and with ruthenium, respectively. Both samples were pretreated under the same conditions as described earlier. Spectrum A shows the inverted OH resonance and a completely recovered, narrow resonance line near zero ppm assigned to H_2 gas. The assignment was verified by measurement of the pressure dependence of this peak and comparison with 1H NMR spectra of the probe filled with hydrogen gas only at corresponding pressures, as well as measurement of relaxation times T_1 . Spectrum B shows the H_2 resonance alone (the recovering OH intensity is zero), and spectrum C, obtained at longer recovery times, shows the OH resonance line superimposed with the H_2 peak. Spectra D, E, and F were

Figure. 7 *In situ* ^1H NMR spectra of silica without a catalyst (left) and with a catalyst (right) under a hydrogen pressure of 400 Torr at $T = 400$ K, T_1 inversion recovery experiment. A: partly inverted OH intensity. The narrow peak with positive intensity represents H_2 gas in the sample. At longer recovery times, B: OH intensity zero, C: positive OH intensity superimposed with the H_2 resonance. D, E, F: silica + catalyst (same conditions as for pure silica, however, no H_2 resonance near 0 ppm is observed).

obtained under the same conditions for the catalyst sample. Note the absence of the narrow, fast-relaxing peak near 0 ppm if ruthenium is present (compare spectra B and E).

DISCUSSION

There are several dynamic processes involving hydrogen interacting with the metal surface as shown by our NMR measurements. In the following sections we will discuss these processes, the type of motions revealed by the NMR lineshapes, time scales of the exchange phenomena, and other properties of the hydrogen species adsorbed on the surface of the ruthenium particles.

Origin of the Lineshapes

From Figs. 3(a) and 3(b) the homogeneous line width of α_1 (width perpendicular to the main diagonal) was determined to be ~ 2 kHz (FWHM), significantly less than the width of ~ 12 kHz along the main diagonal. Hence, the line width appearing in the 1D NMR spectrum (see Fig. 2(a)) is mainly inhomogeneous, in this case determined by distribution of isotropic and/or anisotropic Knight shifts, variation of magnetic susceptibilities due to a distribution of particle sizes, and by heteronuclear H-Ru dipolar coupling. The coverage of the metal surface (H/Ru_s) at pressures where the α_1 species are best observable is about 0.3 to 0.6. These values were obtained by comparing the α_1 intensity with that of an internal standard (lanthanum hydride³⁵) and taking into account the total number of ruthenium surface sites. Therefore, the average proton-proton distance can be estimated assuming that the hydrogen atoms either a) are randomly distributed at the surface, or b) maximize their mutual distances (with the given H/Ru_s value as a boundary condition).

Assuming that α_1 hydrogen is immobile, one can calculate the homonuclear second moment from the estimated distances and the corresponding (homogeneous) line width. For hydrogen occupying the fcc sites of a ruthenium (0001) surface^{14,15} at a coverage of 0.5, one obtains FWHM of 8.4 kHz and 2.3 kHz for cases a) and b), respectively. If the protons undergo a strict two-dimensional fast motion (fast surface diffusion), partial averaging of the homonuclear dipolar interaction occurs because of the time average of the spatial part of the dipolar Hamiltonian as follows:

$$\overline{r_{jk}^{-3}(t) (3 \cos^2 \vartheta_{jk}(\theta_n, t) - 1)} = \frac{1}{2} R_{jk}^{-3} (1 - 3 \cos^2 \theta_n). \quad (2)$$

$\vartheta_{jk}(\theta_n, t)$ denotes the orientation angles of the internuclear vectors $\mathbf{r}_{jk}$ connecting two proton spins (j, k) relative to the external constant field $\mathbf{B}_0$, and θ_n is the angle between the normal vector of the two-dimensional plane of motion and $\mathbf{B}_0$. The time-dependent distance function $r_{jk}^{-3}(t)$ has been replaced by an average value R_{jk}^{-3} , where R_{jk} is of the order of the internuclear distance for the rigid case. The time average in Eq. (2) yields a factor of 1/2 (i.e., 1/4 for the second moment), therefore two-dimensional isotropic motion with $r_{jk}^{-3}(t)$ replaced by the average value R_{jk}^{-3} reduces the line width by a factor of 2. Such a motional process is *not* indicated by the 2D line shape (Figs. 3a,b) that is almost independent of temperature in the range between 292 K and 400 K. The homogeneous line width of 2.3 kHz can be explained by assuming immobile protons with an average distance of the order of 0.5 nm at the metal

surface, consistent with the threefold hollow adsorption site-to-site distance^{14,15}.

A notably different 2D pattern was observed at the higher pressure of 80 Torr at 400 K (Fig. 3(c)) as the H/Ru_s ratio increases to approximately 1.5. The observed 2D NMR spectrum exhibits a line width of ~3 kHz, which is approximately the same as the 1D NMR line width of Fig. 2(b). Calculation of the homonuclear second moment with H/Ru_s = 1.5 yielded line width values of ~20 kHz for rigid spins and ~10 kHz, assuming fast surface diffusion in two dimensions. We conclude therefore that (i) α_M represents hydrogen which undergoes three-dimensional motion in the vicinity of ruthenium particles, and (ii) this random motional process is fast enough to average out the direct dipolar interaction between protons, i.e., is characterized by a correlation time $\tau_c \ll (2\pi \times 20 \text{ kHz})^{-1} \approx 10 \text{ } \mu\text{s}$. A further indication that the α_M line shape is not due to residual dipolar coupling is its constant line width over a wide range of pressures (1 to 100 Torr). The quasi three-dimensional motion can be understood taking into account the small size of metal particles on which hydrogen adsorption occurs. Assuming the metal dispersion of 30%, their mean diameter is in the order of 5 nm. Fast motion across the surface of such small particles may be regarded as three-dimensional motion of protons across the curved surface of the whole particle. In addition, this kind of motion may likely occur in a surface layer of finite dimension normal to the surface of the metal particle.

The third type of hydrogen β that became observable above 100 Torr

(Figs. 2(c-e) and 3(d-f)) partly overlapped with α_M and was characterized by a similar line shape and line width. At a pressure of 300 Torr the H/Ru_s ratio approached 2 and resolved cross peaks were observed in the 2D NMR-exchange spectrum (Fig. 3(e)). The appearance of cross peaks, indicating a magnetization transfer between α_M and β , can be of various origins: (i) proton-proton spin diffusion (via direct dipolar interaction), (ii) dipolar cross relaxation, and (iii) particle exchange (chemical exchange).

Assuming, as before, a two-dimensional arrangement of immobile protons, a line width of 50 kHz is expected for H/Ru_s = 2, whereas, according to Eq. (2), a fast two-dimensional surface diffusion would result in a line width of 25 kHz. These two values exceed the experimental value by one order of magnitude. Hence, similar to α_M , it is concluded that there is a three-dimensional motion of β -type hydrogen in the vicinity of Ru particles. As a result of such a fast motion, spin diffusion can be disregarded. Although motional averaging of the secular part of the dipolar interaction does not exclude the possibility of dipolar cross relaxation (non-secular part of the dipolar coupling Hamiltonian), as observed in some liquids and polymers, the cross peaks due to cross relaxation would be 180° out of phase to the diagonal peaks and would have much weaker intensity compared to the main diagonal peaks. Thus we attribute the cross peaks in the 2D spectra of Figs. 3(e) and 3(f) to a chemical exchange process. Given the high intrinsic mobility of the exchanging species, this is a remarkably slow process taking place in a time

scale of several hundred microseconds.

Determination of the Rate for the Slow Exchange Between α_M and β

The proton exchange process between hydrogen α_M and β , observable by the approximate exponential time development of the magnetizations $M_{z\alpha}$ and $M_{z\beta}$ after preparation of nonequilibrium initial values, either by selective saturation or spin-population inversion (Figs. 4 and 5), can be described by a system of two coupled, first-order differential equations,

$$\frac{d}{d\tau_m} \vec{M}_z(\tau_m) = \mathbf{K} (\vec{M}_z(\tau_m) - \vec{M}_{eq}), \quad (3)$$

$$\vec{M}_z(\tau_m) = \begin{vmatrix} M_{z\alpha}(\tau_m) \\ M_{z\beta}(\tau_m) \end{vmatrix}, \quad \vec{M}_{eq} = \begin{vmatrix} M_{eq\alpha} \\ M_{eq\beta} \end{vmatrix},$$

with $M_{eq\alpha}$ and $M_{eq\beta}$ being the equilibrium magnetizations for α and β , respectively. $\mathbf{K}$ denotes the dynamic matrix describing the exchange as a first-order process, given by the rate constants $k_{\alpha\beta}$ and $k_{\beta\alpha}$. $\mathbf{K}$ also includes spin-lattice relaxation (time constant T_1).

$$\mathbf{K} = \begin{vmatrix} -R_1 - k_{\alpha\beta} & k_{\beta\alpha} \\ k_{\alpha\beta} & -R_1 - k_{\beta\alpha} \end{vmatrix}, \quad R_1 = \frac{1}{T_1}. \quad (4)$$

The formal solution of the vector differential equation (3) reads

$$\begin{aligned}\vec{M}_{eq} - \vec{M}_z(\tau_m) &= e^{K\tau_m} (\vec{M}_{eq} - \vec{M}_0), \\ \vec{M}_0 &= \begin{vmatrix} M_{z\alpha}(\tau_m=0) \\ M_{z\beta}(\tau_m=0) \end{vmatrix}.\end{aligned}\tag{5}$$

By calculating the matrix exponential $\exp(K\tau_m)$ and introducing the variables and notations

$$\begin{aligned}X_\alpha(\tau_m) &= \frac{M_{eq\alpha} - M_{z\alpha}(\tau_m)}{M_{eq\alpha}}, \quad X_\beta(\tau_m) = \frac{M_{eq\beta} - M_{z\beta}(\tau_m)}{M_{eq\beta}}, \\ X_{0\alpha} &= \frac{M_{eq\alpha} - m_{0\alpha}}{M_{eq\alpha}}, \quad X_{0\beta} = \frac{M_{eq\beta} - m_{0\beta}}{M_{eq\beta}}, \quad X_0 = X_{0\alpha} + X_{0\beta},\end{aligned}\tag{6}$$

the final solution can be written as

$$\begin{aligned}X_\alpha(\tau_m) &= \frac{e^{-\tau_m/T_1}}{1+\kappa} (\kappa X_0 + (X_{0\alpha} - \kappa X_{0\beta}) e^{-\sigma\tau_m}), \\ X_\beta(\tau_m) &= \frac{e^{-\tau_m/T_1}}{1+\kappa} (X_0 - (X_{0\alpha} - \kappa X_{0\beta}) e^{-\sigma\tau_m}).\end{aligned}\tag{7}$$

The quantities σ and κ are defined by

$$\sigma = k_{\alpha\beta} + k_{\beta\alpha}, \quad \kappa = \frac{k_{\beta\alpha}}{k_{\alpha\beta}}.\tag{8}$$

Because the T_1 time constants can be measured separately, the spin-lattice relaxation can be eliminated from the experimental data by simple multiplication: $X_i'(\tau_m) = \exp(\tau_m/T_1) \times X_i(\tau_m)$ (Figs. 4 and 5). In addition, according to Eq. (7), the difference $X_\alpha'(\tau_m) - X_\beta'(\tau_m)$ should then be monoexponential with the rate σ , and the sum $X_\alpha'(\tau_m) + X_\beta'(\tau_m)$ should be

independent of τ_m . As indicated in Fig. 5, the experimental time dependences for the two magnetizations satisfy (approximately) these two features of the exchange model. At the pressure of 350 Torr used in this experiment, the equilibrium magnetizations of α_M and β were approximately equal ($M_{eq,\alpha} \approx M_{eq,\beta}$), which corresponds to $\kappa \approx 1$ in the model introduced above. The initial values $X'_{0\alpha,\beta}$ and the rate constant $\sigma = (1500 \pm 300) \text{ s}^{-1}$ have been obtained by fitting Eq. (7) to the experimental data, giving a time constant $\tau_{ex} = 1/\sigma \approx 700 \text{ } \mu\text{s}$ (solid curves in Fig. 5). The same model can be applied to interpret the data from the selective-saturation experiment. The solid curves drawn in Fig. 4 were calculated using Eq. (7) with the σ value determined from the data of Fig. 5. Although the agreement with the experimental data is satisfying, we note systematic deviations from the single-exponential model comparable to the experimental error. Clearly, the model for the $\alpha_M \leftrightarrow \beta$ exchange described above has to be regarded as an approximate approach. Because of the heterogeneity of the system, the rate constant σ represents an average value over an unknown distribution of rate constants. Also, the chemical exchange itself may involve dissociation or recombination and adsorption or desorption of hydrogen and not be a simple first order-process.

Fast Exchange Between Gas Phase and Weakly Bound Hydrogen

While α_M hydrogen is assumed to be dissociatively adsorbed^{35,38}, the state of dissociation of β hydrogen cannot be concluded from our present

experimental data. However, the absence of the H_2 resonance line near 0 ppm for the ruthenium catalyst (Fig. 7, spectrum E) indicates that a fast chemical exchange process occurs between non-adsorbed hydrogen and weakly adsorbed hydrogen, most likely hydrogen characterized by the lowest values of the heats of adsorption (10 kJ/mole). Thus the β resonance line can be regarded as representing the fast exchange average between hydrogen gas (H_2) and weakly adsorbed hydrogen on ruthenium, with the observed resonance shift given by the weighted average of the resonance shifts δ_{gas} and δ_{ads} ,

$$\delta_{obs} = \beta_{gas}\delta_{gas} + \beta_{ads}\delta_{ads} \quad (9)$$

where β_{gas} and β_{ads} represent the mole fractions of the exchanging species. The characteristic time scale τ_{ex} for this rapid exchange is given by $\tau_{ex} \ll (2\pi\Delta\nu) \approx 10 \mu s$, with $\Delta\nu = 14$ kHz being the estimated difference of resonance frequencies for H_2 and for weakly adsorbed hydrogen in the zero pressure limit (extrapolated from Fig. 6). Within this short time scale, hydrogen in the gas phase and weakly adsorbed hydrogen can be considered isolated from (non-exchanging with) other hydrogen species present in the sample, e.g., α_M hydrogen and hydrogen in silanol groups: thus $\beta_{gas} + \beta_{ads} = 1$. The proposed exchange process explains the pressure dependence of the β resonance shift, i.e., variation of pressure means changing the mole fractions β_{gas} and β_{ads} . Conversely, from the experimental resonance shift of the β peak versus pressure (see Fig. 6) the mole fractions β_{gas} and $\beta_{ads} = 1 - \beta_{gas}$ can be determined, inferring the "zero pressure" β resonance shift by extrapolation in

Fig. 6 ($\delta_{\text{ads}} \approx -55$ ppm) and assuming $\delta_{\text{gas}} \approx 0$ ppm. In Fig. 8 the mole fraction β_{gas} is plotted as a function of pressure for two temperatures, 323 and 400 K⁴⁹. Although the data of Fig. 8 are insufficient to establish a specific adsorption model operable between the gas and weakly adsorbed species, we note that the observed pressure dependence is consistent with a simple Langmuir type behavior for the adsorbed species and with the ideal gas approximation for H_2 , as is illustrated by solid curves in Fig. 8.

The pressure dependence of the α_{M} resonance shift (Fig. 6) cannot be explained by this model. Postulating an additional fast exchange between α_{M} and gas phase hydrogen would contradict the observation of two separate resonance lines for α_{M} and β hydrogen. The resonance shift of α_{M} (and of the weakly adsorbed fraction of β as well) originates from the interaction with surface ruthenium 3d electrons. At high hydrogen populations on or near the surface, it seems plausible that the presence of an increasing amount of hydrogen may alter the electron density distribution on the metal surface, leading in turn to a variation of the Knight shift. However, there does not appear to be a similar change in the heat of adsorption. Since at pressures above 100 Torr the amount of α_{M} hydrogen remains constant, the change of the Knight shift must be due to the presence of β hydrogen.

In view of the exchange processes discussed above, part of β hydrogen is regarded as present in an intermediate or precursor adsorption state, whereas the α species appears to be the final adsorption state. It should also be noted

Figure. 8 Mole fraction β_{gas} versus pressure, assuming fast exchange between hydrogen gas and weakly adsorbed hydrogen.

that the β species can exist in the absence of the α species when the surface is pretreated with ethylene prior to hydrogen adsorption³⁵. Although α_M and β species are highly mobile, their interaction with the metal surface is structure sensitive^{35,38}. For example, the amount of adsorbed β hydrogen depends on the dispersion of the metal particles and, therefore, on the number of edges and corner sites, and it is influenced by the presence of other metals besides ruthenium (bimetallic particles³⁸).

At present it remains an open question whether or not the weakly adsorbed hydrogen contributing to the β resonance line is dissociated. Whether the two slowly exchanging hydrogen species α_M and β form a multilayered "sandwich" of hydrogen over the metal surface or a (homogeneous) mixture of two different species (e.g., dissociated and non-dissociated hydrogen) is a subject of further investigation.

SUMMARY

Three types of hydrogen species, α_I , α_M , and β , interacting with ruthenium were found on the surface of a Ru/SiO₂ catalyst. Strongly adsorbed hydrogen α_I , which is observable under vacuum conditions, is characterized by a resonance line that is inhomogeneously broadened due to the heterogeneity of the system. At elevated pressures, α_M and β hydrogen species were found with high intrinsic mobility. Using one- and two-dimensional *in situ* ¹H NMR, two different types of exchange processes of hydrogen interacting with the surface

of supported ruthenium particles have been detected. The slow chemical exchange between β and dissociatively adsorbed α_M hydrogen was quantified by measuring the time dependence of the magnetization exchange between the α_M and β NMR peaks (time constant $\tau_{ex} \approx 700 \mu s$). The observed pressure dependence of the β resonance shift and the absence of an NMR signal from hydrogen gas near 0 ppm at elevated pressures indicated a fast exchange process ($\tau_{ex} \ll 10 \mu s$) between weakly adsorbed hydrogen and hydrogen in the gas phase, both contributing to the β NMR peak. Thus, the weakly adsorbed β hydrogen was found to be in an intermediate or precursor adsorption state between free hydrogen gas and dissociatively adsorbed hydrogen species α_M and α_I .

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