**REACTIVE CHARACTERIZATION AS A PROBE
OF THE NATURE OF CATALYTIC SITES**

FINAL REPORT

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I. Research Objectives

This research program had two sets of objectives. For the first three years, the project was titled *Reactive Characterization as a Probe of the Nature of Catalytic Sites*. The last year of funding was for *Novel Selective Heterogeneous Catalysts*. Due to no cost extensions, the grant did not officially end until February, 1993.

The first stage of the research program was primarily concerned with achieving a better understanding of the nature of active sites on heterogeneous catalysts. *Reactive characterization* is the technique whereby patterns of activity are used to infer information about catalyst morphology and chemical state. This approach is essentially the converse of the normal approach which uses detailed characterization to infer catalytic properties. Active sites often account for only a very small fraction of the surface of a catalyst. The classical method of selective poisoning yields an upper limit to the number of active sites, but there is no lower bound. Spectroscopic techniques typically assay the dominant surface species without regard to what is the active component. This research program developed a novel method to gain information on the nature of active sites for some reactions. It was also an objective to provide for the first time a tabulation of the activities for H_2 - D_2 exchange over metals and metal oxides in such a manner that meaningful comparisons of the different types of catalysts could be made.

The primary goal of the last year of the research program was to create a new type of selective heterogeneous catalyst. The catalysts consisted of supported metals which had been carefully poisoned by molecular compounds, thereby inducing site isolation between the active metal centers. Essentially, a homogeneous-like heterogeneous catalyst would be synthesized which can combine the advantages of a heterogeneous catalyst (different phase from reactants and high thermal stability) and a homogeneous catalyst (improved selectivity). This is an unusual approach in which poisoning has been addressed from the molecular viewpoint, rather than just the destruction of active sites and resulting modification of heat and mass transport properties. The new catalysts were synthesized, their unusual selectivity assessed by a model reaction, and some of the parameters which are important in creating unusual selectivity in these catalysts determined.

Near the end of this proposal, considerable excitement was generated by the discovery of high temperature superconductors. Some early investigators claimed that these materials had improved catalytic activity. However, in general catalytic activity does not correlate with bulk properties, so it was decided to briefly investigate the activity of some superconductors and related cuprates. This research was done in concert with a project funded by Ford Motor Company. Catalysts were investigated for two reactions useful in pollution control: CO oxidation and NO reduction. In addition, some stoichiometric measurements of the oxygen content of superconductors and related cuprates were made using a TPR apparatus in the lab.

In addition, some experiments were done with the objective of preparing novel Mo-Pd/ Al_2O_3 catalysts in which the Mo and Pd were in close contact. These catalysts have the potential of replacing much more expensive rhodium containing catalysts which are currently used for emissions control. This work in turn led to some studies on the selective reduction of nitric oxide using the equipment which had been developed with the DOE funding.

II. H_2 - D_2 Exchange On Transition Metals

H_2 - D_2 exchange has been studied for many years as a model reaction which requires cleavage of the H-H bond. This reaction is catalyzed by metals, metal oxides, and a few

homogeneous catalysts and hydride complexes, but it has not been possible to compare the activities. In many cases the work with metals has involved metal crystals at low pressures and a wide range of conditions have been employed. Also, the density of active sites has rarely been determined for either metal or metal oxide catalysts. Consequently, we measured the rate and site density for H_2 - D_2 exchange over many bulk metals.

BET surfaces areas were measured and used in conjunction with crystallographic data to calculate the number of surface metal atoms. CO poisoning was done to determine the number (upper limit) of active sites. Reaction was done in a flow system at a total pressure of 1 atm and 10 torr each of H_2 and D_2 (balance He). Analysis of the reaction products was done by a computer controlled mass spectrometer.

Table 1 summarizes the results. This is the first compilation in which a large number of metals have been studied at standard conditions. Of particular interest is that the site density for the noble metals (Ru, Os, Rh, Ir, Pd, Pt) averages 27% of the surface atoms, but the value for the base metals (Mo, W, Re, Fe, Co, Ni) averages only 3.3%. These results suggest that a multiplet of sites might be necessary to efficiently catalyze H_2 - D_2 exchange. The activation energies of all catalysts was very low, usually <1 kcal/mol. Consequently, all of the catalysts (except Cu, Ag, and Au) are also active at 78 K. Also, the specific activity (activity per unit surface area) of the metals is about 10^3 -fold higher than for the oxides, but the turnover frequency is only about 10-fold more, reflecting the lower site density on the oxides.

Table 1. H_2 - D_2 Exchange Over Metals[#]

Catalyst	Activity		CO sites [‡] ($10^{14}/cm^2$)	θ^*
	(10^{15} HD/cm ² ·s)	(HD/site·s)		
Rh	140	200	7	0.25
Ru	22	47	4.7	0.20
Ir	6.7	18	3.8	0.12
Mo	5	111	0.5	0.01
Pd	3.3	2.1	16	0.36
Os	2.8	4.0	7.1	0.56
Fe	1.8	71	2.6	0.06
W	1.6	46	0.3	0.02
Pt	0.4	2.0	2.2	0.13
Re	0.2	2.2	0.9	0.03
Co	0.2	1.3	1.4	0.05
Ni	0.2	0.18	12.2	0.03
Cu	0	-	-	-
Ag	0	-	-	-
Au	0	-	-	-

[#] Reaction conditions: 273 K, P = 1 atm, flowing gas mixture of 1.33% H_2 , 1.33% D_2 , and 97.3% He.

[‡] Number active sites determined by CO poisoning.

^{*} Fraction of surface metal atoms which are active.

III. A New Method of Determining the Number of Active Sites

A unique contribution of this study is that both a lower and upper limit to the number of

active sites have been determined for metal oxides. Thus, *for the first time the true number of active sites can be bracketed between two bounds*. It is well known that the classical technique of selective poisoning will yield an upper limit to the number of active sites since some of the gas can adsorb on inactive sites. Chemisorption of CO was used to obtain an upper limit to the number of active sites. The exchange of surface OH groups ($\sigma\text{-OH}$) with $\text{D}_2(\text{g})$ was used to obtain a lower limit to the number of active sites. *This is possible because of the very unusual case that any site capable of undergoing this stoichiometric reaction must also be a site for the catalytic reaction*. This is readily seen by the following scheme.

The appearance of $\text{HD}(\text{g})$ can be monitored with great sensitivity using a mass spectrometer, so an accurate count of the lower limit of the active sites can be obtained. Table 2 shows that the ratio of the lower limit to the upper limit of active sites varies from 1 to 0.005 (column 4).

Column 5 shows that only a small fraction of the total $\sigma\text{-OH}$ is involved in the exchange reaction. The last column shows that only roughly 1% of the surface metal cations are active.

Table 2. Site Densities for $\text{H}_2\text{-D}_2$ Exchange Over Metal Oxides

Catalyst	CO sites [‡] ($10^{12}/\text{cm}^2$)	Exch OH ^Δ ($10^{12}/\text{cm}^2$)	(Exch OH) (CO sites)	(Exch OH) $\times 10^3$ (Total OH)	$\theta^* \times 10^2$
V_2O_3	15	0.07	0.005	--	7
MoO_2	14	0.08	0.006	--	5
Cr_2O_3	7.3	.46	0.063	20	1
ZnO	5.8	4.0	0.69	6	1.
NiO	5.5	0.06	0.011	1.5	0.8
MgO	3.5	3.4	0.97	7	0.3
Co_3O_4	3.2	0.03	0.009	0.03	0.4
CuO	0.7	< 0.01	< 0.01	< 4×10^{-5}	0.1
Fe_2O_3	0.4	.10	0.25	3	0.05
TiO_2	0.3	.14	0.47	2	0.004
Mn_2O_3	0.3	< 0.01	< 0.03	< 4×10^{-5}	0.04

[‡] Active sites determined by CO poisoning.

^Δ Amount of $\sigma\text{-OH}$ which rapidly exchanges with $\text{D}_2(\text{g})$ at 273 K.

* Fraction of surface metal cations which are active.

IV. A New Method of Determining the Hydroxyl Content of Catalysts

It will be shown that the activity for $\text{H}_2\text{-D}_2$ exchange of oxide catalysts is strongly

dependent on the hydroxyl content of the surface. It was therefore necessary to determine this dependence so activity could be measured after the optimum pretreatment. Although in many cases studies of hydroxyl content have been done by others, the results are quite sensitive to the exact sample and procedures used. Hence, it is preferable to determine the coverage of σ -OH for the specific sample being used. A major problem with such experiments is that some of the techniques used are quite laborious and it is necessary to differentiate between true σ -OH and adsorbed H_2O . The latter is especially a problem, since at low temperatures the amount of adsorbed H_2O substantially exceeds a monolayer equivalent of σ -OH, so a small error in the determination of adsorbed H_2O causes a large error in the amount of σ -OH at the low coverages which are catalytically interesting.

A new approach to this problem has been developed which is simple and accurate. A sample is heated to such a high temperature (about 1000 °C) that there is no further weight loss detected by TGA (it is necessary that the sample not decompose). This is assigned a hydroxyl content of zero. Additional weight at moderately lower temperatures is then attributed to σ -OH. From knowledge of the crystal structure, it is also possible to calculate the weight of a monolayer of σ -OH and hence determine at what temperature a monolayer is formed. It is assumed that additional weight at temperatures below this value is due to adsorbed H_2O . In the cases of MgO, NiO, and ZnO, separate mass spectrometric analysis of the desorbed gases allowed a correction for the small amounts of NO_x (from the nitrate salt precursors) desorbed. Figure 1 shows the hydroxyl content determined in this manner for Fe_2O_3 , NiO, Co_3O_4 , Cr_2O_3 , ZnO, TiO_2 , MgO, Mn_2O_3 , and CuO.

V. H_2 - D_2 Exchange On Metal Oxides

An important aspect of this work is that the activity of metal oxides for H_2 - D_2 exchange was determined as a function of activation temperature. *It is found that the activity varies tremendously with the activation temperature, and thus earlier data in the literature are often incomplete or misleading.* In particular, all of the catalysts are inactive when either 100% or 0% hydroxylated and the activity shows a single maximum at an intermediate level of hydroxylation. The data in Table 3 show the temperature of activation in vacuo, termed T_{max} , which yielded the maximum activity for each metal oxide. By way of example, Figure 2 shows the data for two samples of MgO (one commercial and one prepared in-house). It is interesting that except for the rather inactive catalysts TiO_2 and Fe_2O_3 , the hydroxyl content of the catalysts at T_{max} is in the narrow range of 20% to 40%. Powder XRD spectra were also acquired for the fresh samples and after activation at T_{max} . Initially the materials were primarily either hydrous hydroxides or amorphous, but after activation showed partial conversion to crystalline oxides.

Figure 1. Hydroxylation of Metal Oxides

Table 3. Temperature of Activation Giving Maximum Activity for H₂-D₂ Exchange

Catalyst	T _{max} (°C)
Co ₃ O ₄	300
Fe ₂ O ₃	400
Mn ₂ O ₃	550
CuO	550
MoO ₂	600
MgO	700
TiO ₂	700
ZnO	700
NiO	800
Cr ₂ O ₃	1000
V ₂ O ₃	1000

Figure 2. Activity of MgO as a Function of the Temperature of Activation

Table 4 shows the activity of metal oxides for $\text{H}_2\text{-D}_2$ exchange when activated at the temperature yielding the maximum activity. It is notable that when the activity is expressed per unit surface area (as is normally done), the oxides are roughly 10^3 -fold less active than metals. However, it is seen that much of this difference is due to a roughly 10^2 -fold lower density of active sites. Hence, the turnover frequency of the metal oxides is only about 10-fold less than for the metals. This surprising result suggests that *perhaps oxide catalysts can be synthesized with much higher site densities and activities*. The activation energy for $\text{H}_2\text{-D}_2$ exchange was measured for a few of the oxides. As also reported by others, the activation energy is very low, ~ 2 kcal/mol.

Figure 3 displays the activity of the first row transition metal oxides as a function of the number of d electrons of each cation. As has been previously reported in less exhaustive studies, a bimodal curve is observed. However, contrary to earlier reports which claimed no activity for a catalyst with a d^5 electronic configuration, when properly activated such a catalyst is quite active. A surprising result is that when the activity is expressed as a turnover frequency, there is only about a 20-fold range in the activities of the catalysts, far less than when the activity is expressed per unit surface area. This is due to the wide variation in site densities and a compensation effect.

Table 4. Activity of Metal Oxides for H₂-D₂ Exchange[#]

Catalyst	Activity	
	(10 ¹² HD/cm ² ·s)	(HD/site·s) [‡]
NiO	71	12.9
Cr ₂ O ₃	38	5.2
MoO ₂	15	1.1
Co ₃ O ₄	14	4.5
MgO	13	3.7
ZnO	6.4	1.1
V ₂ O ₃	4.5	0.3
Fe ₂ O ₃	0.7	1.8
TiO ₂	0.2	0.7
Mn ₂ O ₃	0.2	0.5
CuO	0.2	0.3

[#] Reaction conditions: 273 K, P = 1 atm, flowing gas mixture of 1.33% H₂, 1.33% D₂, and 97.3% He.

[‡] Number of active sites determined by CO poisoning.

Figure 3. Activity of the First Row Transition Metal Oxides for H₂-D₂ Exchange

Another notable result is substantially revised values for the activity and site density of MgO. It had been reported that the site density was extremely low ($10^9/\text{cm}^2$) and the activity was extremely high, the turnover frequency being 10^3 s^{-1} at 78 K. This activity is far higher than found for metals and thus is out of line with the patterns of activity observed in this study. Also, it was suggested that the active site involves a triangular array of three O^- ions and an adjacent $\sigma\text{-OH}$, unusual for the lack of participation of a metal cation. For these reasons, a more detailed study of the exchange reaction over MgO was done.

The previous publication was based on a site density determined by epr. We also find that the strength of the epr signal increases as the MgO is dehydroxylated and the activity increases. However, exposure to air and CO has little effect on the epr signal but destroys the activity. Thus, epr does not measure an active site. Using the techniques previously described, a lower and upper limit for the number of active sites have been determined. The site density is about 10^3 -fold higher than previously reported and the turnover frequency is about 10^3 -fold lower than previously reported. The new values are in the expected range.

The data presented here leads for the first time to a unified picture of $\text{H}_2\text{-D}_2$ exchange on metal oxides. This is shown in Figure 4. An essential feature of this mechanism is that a triangular multiplet, termed a Δ site, is involved which includes an exposed cation and adjacent O^{2-} and $\sigma\text{-OH}$. Thus, when a catalyst is 100% hydroxylated the activity is low because there are no exposed cations or bare O^{2-} . When a catalyst is completely dehydroxylated, the activity is low because there is no residual $\sigma\text{-OH}$. It should be noted that the fraction of residual $\sigma\text{-OH}$ which are active sites is very low, roughly 1%. Therefore, there is some unspecified parameter which is also important in creating activity, i.e., a Δ site is a necessary but not sufficient condition for activity.

Figure 4. Unified Mechanism for $\text{H}_2\text{-D}_2$ Exchange Over Metal Oxides

VI. Reactive Characterization and Atomic Isolation of Active Sites

The nature of catalytic hydrogenation of an olefin over a metal is intrinsically different from that for a homogeneous catalyst. Deuterogenation of an olefin over a metal gives extensive scrambling of D in the product alkane. For example, the deuterogenation of ethylene leads to $\text{C}_2\text{D}_n\text{H}_{6-n}$, $n = 0, 1, \dots, 6$ and the yield of the unscrambled product, 1,2-dideuteroethane, (d_2 -ethane), is usually $<50\%$. In contrast, the deuterogenation of olefins over homogeneous catalysts usually yields $>90\%$ of the unscrambled product. The differences in the isotopic distributions between the two types of catalysts can be explained based on their reaction mechanisms. Essentially, scrambling with the metallic catalyst is due to multiple connected sites which provide a pathway for H or D from one site to be reacted at another site. By connectivity is meant the ability of sites (a site is the smallest ensemble capable of effecting a reaction) to influence each other in the course of a reaction by sharing at least one common reactant. On metal surfaces this is readily accomplished by the migration of species between

sites, but there is no equivalent facile means of intersite communication for the isolated metal centers in a solution containing an homogeneous catalyst.

It is also found that ethylene deuteration over metal oxides usually gives >90% d_2 -ethane if the temperature and conversion are not too high. Although a metal oxide has many sites on the surface, due to the heteroatomic nature of the surface and the low density of active sites (usually <1% of the surface) they are not easily connected as is the case on a metal surface. Thus, there is the important result that the seminal parameter is the connectivity of an active center, and not whether it is homogeneous or heterogeneous or even its nuclearity.

Our earlier work with ethylene deuteration over Mo catalysts has been extended and studies have now been made of Rh, Ni, NiO, Co, Ru, and Pt supported on alumina and bulk CoO and Co₃O₄. As expected, NiO and Co₃O₄ (CoO is inactive) give high yields of d_2 -ethane (>80%), but the metals give low yields (<50%).

It was hoped that mild activation and the use of a very low loading would yield a catalyst in which the metal particles were atomically dispersed. Such a material might then give a high yield of d_2 -ethane and low activity for H₂-D₂ exchange, as expected for a catalyst with discrete sites. Thus, this would be a novel homogeneous-like heterogeneous catalyst. A catalyst of 0.0080% Ru/Al₂O₃ was prepared by thermal activation at 115 °C of Ru(CO)₅/Al₂O₃. Unfortunately, the catalyst only gave a yield of 20% d_2 -ethane. In another experiment, 0.22% Mo/Al₂O₃ was prepared by the photolysis at 40 °C of Mo(CO)₆/Al₂O₃. This catalyst gave a normal high activity for H₂-D₂ exchange and a normal low yield (29%) of d_2 -ethane. These results are indicative of others in which attempts to make atomically isolated metal catalysts which would behave as a homogeneous catalyst failed. However, homogeneous-like heterogeneous catalysts were prepared by the method of selective poisoning.

VII. Site Isolated Catalysts Synthesized by Selective Poisoning

This group recently reported the first example of a supported metal catalyst giving a very high yield of d_2 -ethane under reaction conditions that would normally yield extensive scrambling. As shown in Table 5, ethylene deuteration over Ni/Al₂O₃ gave the expected isotopic smear of deuterated ethanes, with only 28% of the product being d_2 -ethane. However, by poisoning the catalyst with CO the yield of d_2 -ethane increased to 94%. An important corollary is that this indicates that the CO is not leaving islands of bare Ni, *which would result in lower activity but would not appreciably change the isotopic product distribution*. In a flow system the CO slowly desorbed and concurrently the activity increased and the percent d_2 -ethane dropped. The reversibility of the poisoning makes it clear that the reaction is occurring on the Ni and not on NiO possibly formed by reaction with CO. Thus, reactive characterization not only identifies a catalyst having unusual selectivity, but also provides information on the morphology of the catalyst and its poison. It is believed that the CO is acting like a picket fence to effectively site isolate the Ni atoms. Thus, the partially poisoned Ni catalyst is a homogeneous-like metal catalyst.

Table 5. Ethylene Deuteration Over Ni/Al₂O₃ *

Pretreatment	Conversion	Mole % d _n -ethane						
	(%)	d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆
reduction at 900 °C	32.1 ^a	17.0	38.4	28.3	10.1	4.8	1.3	0.0
above plus 28 torr CO during reaction	2.6 ^b	6.2	0.0	93.8	0.0	0.0	0.0	0.0

* D₂/C₂H₄ = 1; T = 0 °C; P = 1 atm

^a flow system

^b circulating system

The effect of amount of poison is illustrated in Table 6. When the catalyst is heavily poisoned, it changes from a typical heterogeneous catalyst to giving a homogeneous-like product distribution. Most of the change occurs when the ratio of poison molecules to surface metal atoms is moderately greater than one. It should be noted that much of the poison is probably adsorbed on the support. Fortunately, the activity of a heterogeneous metal catalyst for olefin hydrogenation is often about 10³- to 10⁴-fold higher than for a homogeneous catalyst of the same metal, so considerable reduction in rate is feasible.

Table 6. Effect of Amount of Poison in Inducing Site Isolation on Ni/Al₂O₃ Catalysts

Poison	Poison Molecules Surface Metal Atoms	% Poisoning	% d ₂
none	0	0	27
CS ₂	3	99	38
CS ₂	30	99	94
CS ₂	1300	99	97

The nature of the poison is expected to be crucial for several reasons: the poison must remain on the surface during reaction, the poison must block intersite communication, and the poison must not leave patches of open metal on the surface. An important point is that an atomic poison may be ineffective since even though active sites are geometrically isolated, a reactant might be able to migrate across the poison to yield a conventional selectivity. For example, it is well known that Cu-Ni alloys are surface enriched in Cu and have a small Ni ensemble size which suppresses the activity for hydrogenolysis relative to the activity for hydrogenation. Nonetheless, there is considerable experimental evidence that the Ni exists in patches. It is therefore notable that even at high levels of Cu, bulk Cu-Ni alloys gave low yields of d₂-ethane. However, Al-Ni alloys gave about 85% d₂-ethane. Both alloys were first reduced in H₂, which will reduce CuO to Cu(0), but will not reduce Al₂O₃ on the surface of an Al-Ni alloy. These results underscore the difference between the concept of site isolation being pursued here and the substantial work which has already been done on using inactive metals to reduce the ensemble size of active metals.

It is expected that a poison which is large (such as thiophene or a phthalocyanine) will leave patches of metal on the surface and hence would be less effective for inducing site

isolation. Table 7 shows that the linear molecule CS_2 was much better than the flat molecule thiophene for inducing site isolation in $\text{Ni}/\text{Al}_2\text{O}_3$.

Table 7. Effect of Identity of Poison on Site Isolation on $\text{Ni}/\text{Al}_2\text{O}_3$

Poison	Poison molecules	% Poisoning	% d2
	Surface metal atoms		
none	0	0	27
thiophene	810	99	43
CS_2	30	99	94

VIII. Catalysts Prepared from High Temperature Superconductors

The oxygen content and reducibilities of four base metal oxides, six non-conducting cuprates and three superconducting cuprates were investigated by temperature programmed reduction (TPR) from 30 to 900 °C. Cuprates are multimetallic oxides composed of copper and one to five more electropositive metals which are usually alkalies, alkaline earths and rare earths. It was shown that the copper, bismuth, and thallium ions of these oxides were reduced to the zero valence state. Thus, TPR is a useful technique for determining the actual oxygen stoichiometry of cuprates. For multiphase $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{8+x}$ and $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_{8+x}$ superconductors pretreated in air, x was found to be 2 ± 0.2 and 1 ± 0.2 , respectively. Both values are significantly higher than previously reported. The reduction of superconducting and related cuprates required higher temperatures than CuO , but the reducibility of CuO decreased when it was calcined in air at 940 °C. The Bi- and Y-based superconducting cuprates exhibited the lowest reducibility among the samples investigated.

In another study, the catalytic activities of five non-conducting and three superconducting cuprates were measured for the decomposition of NO and the reduction of NO by CO. The concentration of the reactants and the space velocities approximated the conditions of automotive catalysts. In contrast to earlier results, obtained at 20 to 30 times higher partial pressures of NO and 20 to 100 times lower space velocities, none of the catalysts, including five perovskite-like cuprates, showed significant activity for the decomposition of NO at reaction temperatures up to 700 °C. All catalysts were fairly active for the reduction of NO. At temperatures above about 400 °C on the perovskite-like cuprates $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Ba}_2\text{CuO}_{3.5-x}$, the rates for NO reduction were higher than on CuO . All catalysts lost activity for NO reduction in the presence of oxygen (oxidizing conditions).

The catalytic activity of cuprates was first reported in 1977, but interest increased in 1987 after the discovery of high temperature superconductors. In spite of the very large number of cuprates, reports of catalytic activity are largely limited to perovskite-like compounds of La and Y. Due to the disparate results in the literature, we further investigated the relationship between structure, electrical conductivity, and catalytic activity of cuprates for CO oxidation. Two superconductors, $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{10\pm x}$ and $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_{9\pm x}$, and two insulating compounds, $\text{Y}_2\text{Cu}_2\text{O}_5$ and $\text{Ba}_2\text{CuO}_{3.5\pm x}$, were studied. In contrast to the good activity of $\text{Y}_2\text{Cu}_2\text{O}_5$, the perovskite-like insulator $\text{Ba}_2\text{CuO}_{3.5\pm x}$ has low activity. It was also shown that the non-conducting cuprates, $\text{Ba}_2\text{Cu}_3\text{O}_5$, BaCuO_2 , and Y_2BaCuO_5 are among the most

active catalysts for the oxidation of CO. In summary, the studies on superconductors gave the expected result that, contrary to early reports, neither they nor cuprates with a perovskite structure have special catalytic activity.

IX. Mixed Metal Pd-Mo Catalysts

Three different procedures were compared for the preparation of PdO-MoO₃/γ-Al₂O₃ catalysts for the purpose of achieving close proximity of the Pd and Mo oxides. The methods were: 1. adsorption of [PdCl₂(OH)₂]²⁻ anions on MoO₃/γ-Al₂O₃; 2. coadsorption of [Pd(NH₃)₄]²⁺ cations and MoO₄²⁻ anions on γ-Al₂O₃; 3. adsorption of Mo(CO)₆ on PdO/γ-Al₂O₃. Twenty catalysts were prepared and characterized by temperature programmed reduction and X-ray powder diffraction. In general, the first method resulted in large, weakly bounded PdO particles in poor contact with the molybdenum oxide, whereas the other two methods resulted in a strong interaction between finely divided palladium and molybdenum oxides.

X. Selective Reduction of Nitric Oxide

The catalytic activity for the reduction of NO by CO of five PdO-MoO₃/γ-Al₂O₃ catalysts was compared in the presence of varying amounts of oxygen at reaction temperatures from 25 to 550 °C. The samples were prepared by different methods and contained about 2% of Mo and 2% Pd. Results were compared with the activities and selectivities of PdO/γ-Al₂O₃ and PdO-MoO₃/γ-Al₂O₃ containing 2% Pd and 2% Pd + 20% Mo, respectively. All catalysts showed appreciable activity at temperatures between 300 and 550 °C and at stoichiometric ratios (R) of the oxidizing to reducing gases of 0.1 < R < 1.1. The activity of three PdO-MoO₃/γ-Al₂O₃ catalysts with low concentrations of Mo and Pd was found to be significantly higher than the activity of PdO/γ-Al₂O₃ at 1.1 < R < 1.3 and at temperatures between 300 to 500 °C. The improved activity is ascribed to the interaction of the active metals.

In a related study, the catalytic activity and selectivity of three PdO-MoO₃/γ-Al₂O₃ catalysts containing about 2% Pd and 2% Mo were studied for the reduction of NO by H₂ in the presence of varying amounts of oxygen at temperatures from 50 to 550 °C. The results were compared with those for PdO/γ-Al₂O₃, PdO-MoO₃/γ-Al₂O₃ containing 2% Pd and 20% Mo, and a commercial Pt-Rh catalyst. In the absence of oxygen, the conversion of NO to N₂ and N₂O is higher on the three catalysts than it is on PdO/γ-Al₂O₃ at 500 and 550 °C. In the presence of oxygen, the yields of N₂ and N₂O are generally lower on two of the PdO-MoO₃/γ-Al₂O₃ catalysts than on PdO/γ-Al₂O₃.

The above results were extended by comparing the catalytic activity and selectivity of three PdO-MoO₃/γ-Al₂O₃ samples containing roughly 2% Pd and 2% Mo for the reduction of NO by CO and H₂ in the presence of different amounts of oxygen at temperatures from 100 to 550 °C. Data were compared with the activities and selectivities of PdO/γ-Al₂O₃, PdO-

MoO₃/γ-Al₂O₃ containing 2% Pd and 20% Mo, and a commercial Pt-Rh catalyst. In general, the PdO-MoO₃/γ-Al₂O₃ samples were more active for the selective reduction of NO to N₂ and N₂O than the PdO/γ-Al₂O₃ using slightly oxidizing conditions (redox ratios from R = 1.0 to R = 1.2) at temperatures from 300 to 550 °C. Under these reaction conditions, the PdO-MoO₃/γ-Al₂O₃ catalysts are competitive with the commercial Pt-Rh catalyst. The improved activity of PdO-MoO₃/γ-Al₂O₃ is due to the interaction of the Pd and Mo. The effect of O₂ on the activity and selectivity of catalysts is quite different in the reduction of NO by H₂, by CO, and by a mixture of H₂ with CO. Results with the mixture of CO and H₂ cannot be obtained from the addition of results with the single reductants, H₂ and CO.

XI. Publications

1. P. N. Gonzalez and A. Brenner, "Comments on Ethylene Deuteration as a Probe of Active Sites", "Catalysis: Theory to Practice", M. J. Phillips and M. Ternan, Ed., Chemical Institute Canada, Volume 5, p. 359, 1989.
2. I. Halasz, H-W Jen, A. Brenner, M. Shelef, S. Kao, and K. Y. S. Ng. "Determination of the Oxygen Content in Superconducting and Related Cuprates Using Temperature Programmed Reduction", Journal of Solid State Chemistry, 92, 327 (1991).
3. I. Halasz, A. Brenner, M. Shelef, and K. Y. S. Ng. "Decomposition of Nitric Oxide and its Reduction by CO Over Superconducting and Related Cuprate Catalysts", Catal. Lett. 11, 327 (1991).
4. Y. Gu and A. Brenner, "Hydrogen Activation by Magnesia Catalysts", J. Catal., 136, 222, (1992).
5. I. Halasz, A. Brenner, M. Shelef, and K. Y. S. Ng. "Catalytic Oxidation of Carbon Monoxide Over Superconducting and Related Cuprates", J. Catal., 134, 731 (1992).
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7. I. Halasz, A. Brenner, M. Shelef, and K. Y. S. Ng. "Preparation and Characterization of PdO-MoO₃/Al₂O₃ Catalysts", Applied Catal. 82, 51 (1992).
8. I. Halasz, A. Brenner, and M. Shelef, "Reduction of NO by CO on PdO-MoO₃/Al₂O₃ of Low Molybdena Loading", Catal. Lett. 16, 311 (1992).
9. I. Halasz, A. Brenner, and M. Shelef, "Catalytic Reduction of Nitric Oxide on PdO-MoO₃/Al₂O₃", Appl. Catal. B: Environmental, 2, 131 (1993).
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11. I. Halasz, A. Brenner, and M. Shelef, "Reduction of NO by H₂ and CO on PdO-MoO₃/Al₂O₃ of Low Molybdena Loading", Catal. Lett., 22, 147 (1993).

XII. Presentations

1. A. Brenner, "The Nature of Active Sites on Metals, Metal Oxides, and Homogeneous Catalysts", U. of Michigan, Ann Arbor, MI, February, 1989.
2. Y. Gu and A. Brenner, "Hydrogen Activation by Metal Oxides", 11th N. American Meeting of

The Catalysis Society, Dearborn, MI, May, 1989.

3. A. Brenner, "Characterization of Active Sites by Ethylene Deuteration", 2nd Korea/USA Catalysis Workshop, Dearborn, MI, May, 1989.
4. A. Brenner, "Reactive Characterization as a Probe of the Nature of Catalytic Sites", 7th BES Catalysis and Surface Chemistry Research Conference, Gaithersburg, MD, March, 1990.
5. Y. Gu and A. Brenner, "Hydrogen Activation Over Magnesia Catalysts", 12th Ann. Symp. Michigan Catalysis Soc., Ann Arbor, MI, May, 1990.
6. Y. Gu and A. Brenner, "Hydrogen Activation by Metal Oxides", 22nd Central Regional Meeting, ACS, Midland, MI, June, 1990.
7. H. W. Jen and A. Brenner, "Homogeneous-Like Heterogeneous Catalysts", XIVth Int. Conf. on Organometallic Chem., Detroit, MI, August, 1990.
8. A. Brenner, "Structure-Reactivity Relationships in Heterogeneous Catalysis", Wayne State University Frontiers in Chemistry, Detroit, MI, February, 1991.
9. H. W. Jen and A. Brenner, "Improved Selectivity with Partially Poisoned Heterogeneous Catalysts", 13th Ann. Symp. Michigan Catalysis Soc., East Lansing, MI, April, 1991.
10. H. W. Jen and A. Brenner, "Reactivity Patterns of Ethylene Deuteration Over Nickel-Copper Alloys", 12th North American Meeting of The Catalysis Society, Lexington, KY, May, 1991.
11. H. W. Jen and A. Brenner, "Homogeneous-Like Heterogeneous Catalysts", 12th North American Meeting of The Catalysis Society, Lexington, KY, May, 1991.
12. A. Brenner, "Novel Selective Heterogeneous Catalysts", 3rd DOE/BES Organometallic Chemistry and Homogeneous Catalysis Research Conference, Madison, WI, June, 1991.
13. A. Brenner, "Novel Selective Heterogeneous Catalysts", 8th DOE/BES Heterogeneous Catalysis and Surface Chemistry Research Conference, Santa Monica, CA, March, 1992.
14. I. Halasz, A. Brenner, M. Shelef, and K.Y. S. Ng, "CO Oxidation, NO Decomposition, and NO Reduction by CO on Superconducting and Related Cuprates", 10th Int. Congr. Catalysis, Budapest, Hungary, July, 1992.