SAND98-0879C
SAND--98-0879C

CONF-980908-- RECEIVED
APR 23 1998

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Preparation and Evaluation of Novel Hydrous Metal Oxide (HMO)-Supported Noble Metal Catalysts

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ABSTRACT

Hydrous Metal Oxides (HMOs) are chemically synthesized materials that, because of their high cation exchange capacity, possess a unique ability to allow the preparation of highly dispersed supported-metal catalyst precursors with high metal loadings. This study evaluates high weight loading Rh/HMO catalysts with a wide range of HMO support compositions, including hydrous titanium oxide (HTO), silica-doped hydrous titanium oxide (HTO:Si), hydrous zirconium oxide (HZO), and silica-doped hydrous zirconium oxide (HZO:Si), against conventional oxide-supported Rh catalysts with similar weight loadings and support chemistries. Catalyst activity measurements for a structure-sensitive model reaction (n-butane hydrogenolysis) as a function of catalyst activation conditions show superior activity and stability for the ZrO₂, HZO, and HZO:Si supports, although all of the Rh/HMO catalysts have high ethane selectivity indicative of high Rh dispersion. For the TiO₂-, HTO-, and HTO:Si-supported Rh catalysts, a significant loss of both catalyst activity and Rh dispersion is observed at more aggressive activation conditions, consistent with TiO_x migration associated with SMSI phenomena. Of all the Rh/HMO catalysts, the Rh/HZO:Si catalysts appear to offer the best tradeoff in terms of high Rh dispersion, high activity, and high selectivity.

1. INTRODUCTION

Hydrous Metal Oxides (HMOs) are chemically synthesized materials that contain a homogeneous distribution of ion exchangeable alkali cations that provide charge compensation to the metal-oxygen framework. For catalyst applications, the HMO material serves as an ion exchangeable support which facilitates the uniform incorporation of catalyst precursor species. Because of their high cation exchange capacity with respect to conventional oxide supports these materials possess a unique ability to allow the preparation

^{*} This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

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of highly dispersed supported-metal catalyst precursors with high metal loadings via cation exchange.

Considerable previous work on HMO materials has emphasized various forms of hydrous titanium oxides (HTO) as catalyst supports for direct coal liquefaction, hydrotreating, hydrogenolysis, and hydrogenation/dehydrogenation applications.¹⁻⁸ These studies have yet to show a definitive advantage for HMO-supported metal catalysts at high weight loadings relative to conventional oxide-supported metal catalysts, although HMO-supported noble metal catalysts have not systematically been investigated. Our recent study compared high weight loading (> 10 wt.%) HTO- and conventional oxide-supported Rh catalysts,⁹ showing that although high Rh dispersions could be attained under certain low temperature activation conditions in H₂, exposure to higher temperature reduction conditions resulted in strong-metal-support-interaction (SMSI) phenomena similar to that reported for highly dispersed titania-supported Rh catalysts.¹⁰⁻¹¹

Our current work represents an extension of our previous supported Rh catalyst work to other HMO support compositions, such as silica-doped hydrous titanium oxide (HTO:Si), hydrous zirconium oxide (HZO), and silica-doped hydrous zirconium oxide (HZO:Si). Catalyst activity and selectivity measurements for a structure-sensitive model reaction (n-butane hydrogenolysis) will be correlated with hydrogen chemisorption measurements and microstructural analysis via high resolution transmission electron microscopy (HREM). The sensitivity of these HMO-supported Rh catalysts to different activation conditions and HMO support chemistry will be examined, with the overall goal of preparing stable, highly dispersed supported noble metal catalysts with a range of metal loadings.

2. EXPERIMENTAL PROCEDURE

2.1. HMO Synthesis Chemistry

HTO- or HTO:Si-supported catalyst preparation involves a multiple step chemical procedure that begins with the synthesis of a bulk Na form HTO or HTO:Si powder.^{2-4,12} Previous work has demonstrated that SiO₂ additions (Ti:Si mole ratio = 5:1) to HTO materials act to stabilize support surface area at high temperature (≥ 773 K)³⁻⁶ without altering the ion exchange behavior.^{3,13} A brief review of the synthesis of both HTO and HTO:Si materials with a maximum cation exchange capacity (Na:Ti mole ratio = 0.5) will be given here as an example. In both cases, changes in the Na:Ti stoichiometry ($0 < \text{Na:Ti} < 0.5$) are easily accommodated. The first step of the reaction scheme involves adding the Ti (or mixed Ti-Si) alkoxide to a dilute (~10 wt.%) solution of sodium hydroxide in methanol, resulting in the production of a soluble intermediate species. Structural studies completed to date indicate that the soluble intermediate is composed of a highly crosslinked Na-Ti (or Na-Ti-Si) polymer with alkoxides bridging the various metal centers.¹⁴ To prepare bulk Na form HTO or HTO:Si powders, the soluble intermediate is hydrolyzed in a water/acetone solution. The amorphous HTO or HTO:Si precipitate is filtered, washed, and vacuum dried at room temperature to produce the material for subsequent acidification/ion exchange processing.

HZO and HZO:Si supports are prepared initially in Na form utilizing similar alkoxide/sol-gel chemistry to that described above, with zirconium n-propoxide used as a Zr precursor. An alcohol exchange reaction between zirconium n-propoxide and ethanol (2:1 mole ratio of C₂H₅:C₃H₇) is used to facilitate the formation of zirconium ethoxide.⁴ The synthesis and

hydrolysis of the soluble intermediate to form the bulk Na form HZO or HZO:Si powder is identical to that previously described for the HTO or HTO:Si systems.

2.2. Catalyst Preparation

High weight loading Rh/HTO and Rh/HTO:Si catalyst precursors were prepared utilizing a controlled ion exchange procedure. First, a Na form HTO or HTO:Si/H₂O slurry was acidified to pH 4 using 10 wt.% HNO₃, resulting in the exchange of a significant portion of Na⁺ with H⁺. Subsequently, a concentrated (~10 wt.% Rh) Rh(NO₃)₃ solution was added in small (1-2 ml) aliquots to affect Rh⁺³ ion exchange with H⁺ or Na⁺. Sufficient Rh(NO₃)₃ was added to ensure a 50% excess beyond the total cation exchange capacity of the Na form HTO or HTO:Si. Because of the extreme acidic nature (4-6 M excess HNO₃) of the concentrated Rh(NO₃)₃ solution (pH < 1), small (1-2 ml) additions of 0.6 M NaOH were required between Rh(NO₃)₃ aliquots to return the slurry pH to the optimum value of ~4. After complete addition of the Rh(NO₃)₃, a 1 h mixing period at pH 4 (with further NaOH additions as necessary) facilitated complete ion exchange. These solution chemistry conditions (*i.e.*, pH) were chosen to maximize the cation exchange capacity of the HTO/HTO:Si support while avoiding precipitation of Rh(OH)₃, which occurs at pH values > 4.5.¹⁵ After washing (with H₂O and acetone) and filtering, the catalyst was dried at room temperature under vacuum (75-130 mm Hg) for a minimum of 16 h. Similar procedures were used to prepare ion exchanged Rh/HZO and Rh/HZO:Si catalyst precursors, although initial acidification was performed at pH 6 due to the higher isoelectric point of the HZO and HZO:Si materials.

High weight loading oxide-supported Rh catalysts precursors were also prepared by wet impregnation using an aqueous Rh(NO₃)₃ solution and as-received TiO₂ (Degussa, P25 grade), ZrO₂ (Degussa, VP grade), and SiO₂ (Cabot Corporation, Cab-O-Sil, HS-5 Grade) as raw materials. A fresh 0.3 M Rh(NO₃)₃ aqueous solution (from Rh(NO₃)₃•2H₂O) was used for impregnation rather than the Rh(NO₃)₃ solution described above. Oxide support dissolution was minimized at the pH of this impregnating solution (~1.8), while extensive Rh hydrolysis was avoided due to the minimal time between solution preparation and use. The preparation procedure consisted of aqueous slurry (salt solution + oxide) preparation, drying at 373 K, grinding/mixing via mortar and pestle, and sieving to < 250 μm particle size. Table 1 shows the final high weight loading catalyst compositions produced for this study. The Rh loadings obtained for the Rh/HTO and Rh/HTO:Si catalyst samples roughly correspond to 100% Rh⁺³ exchange for Na⁺, while the yields for the Rh/HZO and Rh/HZO:Si samples were less than theoretical. The Rh⁺³ ion exchange procedure removed/replaced virtually all of the Na⁺ (> 99 %) from the original Na form HMO ion exchangers. The compositions of the oxide-supported Rh catalysts prepared by incipient wetness impregnation were targeted to match the composition of the HMO-supported Rh catalysts prepared by ion exchange.

2.3. Catalyst Activation, Testing, and Characterization

Catalyst activation was performed *in situ* in a microflow reactor system prior to catalyst activity measurements. The microflow reactor system was composed of a 0.635 cm OD quartz U-tube packed with quartz wool supporting the catalyst (fine powder form). For all activation procedures and activity measurements, total gas pressure in the reactor was 630 mm Hg. For these activity studies, a single as-prepared catalyst sample (0.020-0.050 g) was activated in flowing UHP H₂ (20 sccm), and evaluated intermittently as a function of time (1-32 h) at a given activation temperature, with the activation temperature increased stepwise

Table 1.
Supported Rh Catalyst Compositions

Catalyst	Wt. % Rh ⁺	Wt.% Na ⁺	Wt.% Rh (Final)*
Rh/SiO ₂	9.2	NA	11.5
Rh/TiO ₂	9.8	NA	12.4
Rh/ZrO ₂	7.1	NA	8.9
Rh/HTO	12.7	0.03	15.0
Rh/HTO:Si	13.8	0.09	16.0
Rh/HZO	7.3	0.04	9.0
Rh/HZO:Si	7.6	0.02	9.4

⁺ Elemental compositions determined by AAS, with weight loadings expressed on an as-prepared basis.

* Final catalyst compositions assume the removal of all volatiles and that all Rh exists in the metallic state.

from 423 K, to 573 K, to 673 K. In certain cases, oxidative heat treatments at various temperatures utilizing He:O₂ gas mixtures (20:2 sccm He:O₂) were either performed prior to H₂ reduction or used as part of additional oxidation/reduction cycling experiments.

The model reaction used to determine the activity of the catalyst materials was n-butane hydrogenolysis, a known structure-sensitive reaction.^{16,17} Under steady state reactor conditions, UHP H₂ and research purity n-butane flow rates to the reactor were 20.0 and 1.0 sccm, respectively, and were selected to prevent catalyst deactivation. Reaction temperatures investigated ranged from 393 to 503 K, depending on the particular catalyst and its state of activation. After 10 min of reactant flow over the catalyst at the desired reaction temperature, product gas analysis (relative to the pure n-butane reactant feed) was determined by on-line gas chromatography with a flame ionization detector. For all activity measurements, the reactor was assumed to operate in a differential mode. After careful passivation, selected catalyst samples were characterized by x-ray diffraction and/or HREM.⁹

H₂ chemisorption measurements were performed at room temperature (after evacuation to ~10⁻⁵ Pa) using an automated gas chemisorption unit (Coulter Omnisorp 100CX). Catalyst activation treatments were performed *in situ* on as-prepared supported Rh catalyst samples (0.5-0.7 g) using flowing UHP H₂ (~30 sccm) with an activation temperature/time sequence identical to that used for n-butane hydrogenolysis activity testing. Rh dispersion values were calculated from the total H₂ chemisorption monolayer capacity.

3. RESULTS AND DISCUSSION

The results for the various catalysts will generally be grouped in three different sets: titania-supported catalysts (including TiO₂, HTO, and HTO:Si supports), zirconia-supported catalysts (including ZrO₂, HZO, and HZO:Si supports), and the silica-supported catalyst. Inclusion of the silica-supported Rh catalyst with the other two oxide supports (TiO₂ and

ZrO₂) helps provide a reference point for comparison with the silica-doped HMO (HTO:Si and HZO:Si) supports and to the existing literature.

Figure 1 shows the activation behavior in H₂, with respect to normalized (per g_{Rh}) n-butane hydrogenolysis activity measured at a reaction temperature of 423 K, of several oxide- and HMO-supported Rh catalysts. Single samples of the respective catalysts were used to obtain the complete data set, except in the case of the Rh/TiO₂ catalyst, where separate aliquots were tested as a function of time at 423 K, 573 K, and 673 K. Previous work with high weight loading Rh/HTO catalysts has shown little difference in catalyst activity between these two testing protocols with the n-butane hydrogenolysis model reaction.⁹ For the oxide-supported Rh catalysts, catalyst activation in H₂ was fairly rapid at low temperature (423 K), which was consistent with TGA data that showed TiO₂-supported Rh(NO₃)₃ decomposition in H₂ is complete within 1 h at 423 K. Once fully activated, both the TiO₂- and ZrO₂-supported Rh catalysts were relatively stable against deactivation, both as a function of time at a given activation temperature and to some extent with increasing temperature. However, unlike the stable Rh/ZrO₂ catalyst, catalyst activity for the Rh/TiO₂ catalyst was found to decrease significantly at 673 K. In contrast to the extensive data obtained for the other oxide-supported Rh catalysts, a single data point was obtained for the Rh/SiO₂ catalyst after a 573 K/H₂/1h activation treatment. Although this data point is not shown in Figure 1, the normalized n-butane hydrogenolysis activity observed for the Rh/SiO₂ catalyst (~7 μmoles n-butane reacted/g_{Rh}•s) was very similar to that observed for the Rh/TiO₂ and Rh/ZrO₂ catalysts under similar activation conditions.

Figure 1. Normalized n-butane hydrogenolysis activity as a function of activation conditions for various high weight loading oxide- and HMO-supported Rh catalysts.

The activation behavior of high weight loading Rh/HTO and Rh/HTO:Si catalysts proved to be both interesting and complex, and can best be summarized by separation into distinct

regimes. First, similar to the oxide-supported Rh catalysts, both catalysts are easily activated at low temperatures (423 K) and short times (~1 h) in H₂. Catalyst activity is stable as a function of activation time at these temperatures. Second, at higher temperatures (573 K), catalyst deactivation is observed as a function of heat treatment time at a given temperature. Finally, in the case of the Rh/HTO catalyst only, at higher temperatures (673 K) some reversal of catalyst deactivation is observed. In contrast, the activity of the Rh/HTO:Si catalyst continues to decline with increasing activation temperature and time in H₂. Although not shown in Figure 1, the minimum activity observed for the Rh/HTO:Si catalyst was ~2 orders of magnitude lower than the Rh/HTO catalyst at the most aggressive activation conditions. It should be noted that the activity values shown in Figure 1 for the Rh/HTO and Rh/HTO:Si catalysts after activation at 673 K were too low to be accurately measured. Instead, they were calculated from data taken at higher reaction temperatures using the calculated Arrhenius parameters for the specific catalyst at those activation conditions.

The activity data for the Rh/HZO and Rh/HZO:Si catalysts were significantly different from the Rh/HTO and Rh/HTO:Si catalysts. Both of these catalysts showed no degradation in activity with more aggressive activation conditions. In fact, a increase in catalyst activity was observed upon increasing the activation temperature from 423 to 573 K. The Rh/HZO:Si catalyst was significantly more active than the Rh/HZO catalyst, being the most active catalyst tested in this study, even with respect to the oxide-supported Rh catalysts.

It is well known that highly dispersed Rh particles result in preferential central bond scission for both n-butane and n-pentane hydrogenolysis.^{18,19} Therefore, analysis of the product distribution under similar activation conditions can provide helpful insight regarding the state of Rh dispersion on the various supports. For conventionally prepared catalysts, it would be expected that the metal dispersion would decrease significantly with increased metal weight loading due to increases in metal particle size. Since changes in particle size can result in significant changes in the number of surface atoms exposed on various low index crystallographic planes,²⁰ marked changes in product selectivity can result. A recent study has examined the changes in activity and product selectivity for n-butane hydrogenolysis over single crystal and supported Rh catalysts.¹⁸ Ethane selectivity was shown to decrease from ~80 mole % ethane (for highly dispersed Rh) to ~50 mole % ethane (for single crystal Rh (111) surfaces) with increasing Rh weight loading (and therefore particle size).

Table 2 shows the ethane selectivity of the oxide- and HMO-supported Rh catalysts as a function of activation conditions (temperature and time) in H₂. Similar to the data shown in Figure 1, the ethane selectivity values correspond to a reaction temperature of 423 K. Under these conditions, the ratio of methane to propane was approximately unity (~1.0-1.2) in all cases, which is consistent with a single hydrogenolysis event. For low temperature activation (≤ 573 K), ethane selectivity was found to be relatively independent of activation time and extremely low values for ethane selectivity (~10-15 mole % ethane) were observed for the TiO₂- and ZrO₂-supported Rh catalysts. Some improvement in the ethane selectivity of these catalysts was observed with more aggressive activation conditions. In contrast, the ethane selectivity of the Rh/SiO₂ catalyst was higher (~50 mole %), similar to that predicted from previous work.¹⁸

Additional experiments indicated that the abnormally low ethane selectivity data observed for these Rh/TiO₂ and Rh/ZrO₂ catalysts cannot solely be attributed to activation in H₂, since similar data were observed after a more traditional activation procedure (*i.e.*, calcination at 773 K followed by H₂ reduction).⁹ It is therefore likely that the choice of Rh precursor, the

resulting wet impregnation solution chemistry conditions, or the reduction temperature used in the catalyst activation procedure had a significant effect on the resulting ethane selectivities.

Table 2.

Ethane selectivity values (mole %) for n-butane hydrogenolysis at a reaction temperature of 423 K for various supported Rh catalysts over a range of activation conditions.

Activation	Rh Catalyst Support						
	SiO ₂	TiO ₂	HTO	HTO:Si	ZrO ₂	HZO	HZO:Si
423 K/1 h	NA	10.1	70.5	71.7	14.8	47.1	47.9
423 K/8 h	NA	11.5	NA	NA	16.8	52.1	61.5
573 K/1 h	49.0	18.2	79.5	79.1	20.6	51.2	66.1
573 K/8 h	NA	18.4	NA	80.4	19.9	51.4	67.3
573 K/32 h	NA	16.3	76.6	78.7	18.4	52.1	67.7
673 K/1 h	NA	24.5	54.9	*	18.3	50.1	69.9
673 K/8 h	NA	25.9	56.0	*	18.1	43.6	69.5

NA Not applicable. Testing not performed for these specific activation conditions.

* Catalyst activity was too low to allow testing at a reaction temperature of 423 K.

For all activation conditions, the HMO-supported Rh catalysts proved to be fairly selective to ethane. The minimum and maximum ethane selectivity values observed were ~50 mole % (for Rh/HZO) and ~80 mole % (for Rh/HTO:Si). In contrast to the oxide-supported Rh catalysts, these high ethane selectivities were obtained under mild activation conditions and found to be relatively stable after exposure to more aggressive conditions. These high ethane selectivities are indicative of well dispersed Rh particles.¹⁸ At the highest activation temperature (673 K), the ethane selectivity of the Rh/HTO and Rh/HZO catalysts decreased, but was still superior to that of the Rh/TiO₂ and Rh/ZrO₂ catalysts. The decrease in ethane selectivity at these conditions may be consistent with some Rh particle growth.

H₂ chemisorption measurements were performed on the oxide- and HMO-supported Rh catalysts to determine the Rh dispersion and the total number of active sites as a function of catalyst activation in H₂. The Rh dispersion data for the different supported Rh catalysts are shown in Figure 2, and illustrate several interesting trends. First, under low temperature (423 K) activation conditions in H₂, the Rh dispersions are fairly high (~25-60 %) for all of the catalysts, and remain stable as a function of activation time. The Rh dispersion for the Rh/HMO catalysts is superior to the oxide-supported Rh catalysts at these low temperature activation conditions. Significant differences are observed among the different support chemistries upon exposure to more aggressive activation conditions. For the TiO₂-, HTO-, and HTO:Si-supported Rh catalysts, Rh dispersion is observed to significantly decrease with increasing activation temperature and time at a given activation temperature. This behavior is most pronounced for the Rh/HTO and Rh/HTO:Si catalysts, which both exhibit large decreases in Rh dispersion (factors of 20-50x) after 673 K activation relative to 423 K activation in H₂. For comparison, the Rh/TiO₂ catalyst exhibits a factor of ~2.5x decrease in Rh dispersion over the same range of activation conditions.

Figure 2. The effect of activation conditions on dispersion values for various high weight loading oxide- and HMO-supported Rh catalysts.

In contrast to the behavior observed for the TiO₂-, HTO-, and HTO:Si-supported Rh catalysts, the Rh dispersion of the Rh/ZrO₂, Rh/HZO, and Rh/HZO:Si catalysts was very stable over a wide range of activation conditions, comparing well with that of the Rh/SiO₂ catalyst. The HZO- and HZO:Si-supported Rh catalysts appear to offer a slight benefit in terms of higher dispersion than the Rh/ZrO₂ catalyst. Combining this data with the n-butane hydrogenolysis activity data shown in Figure 1 clearly indicates that the Rh/HZO and Rh/HZO:Si catalysts are superior to the Rh/HTO and Rh/HTO:Si catalysts for applications requiring catalyst stability in reducing environments. Compared to the oxide-supported catalysts, the Rh/HZO:Si material offers enhanced selectivity with no penalty in terms of catalyst activity. Considering that the trends and magnitudes of change between Figures 1 and 2 are very similar over the range of activation conditions, one could infer that turnover frequency values for n-butane hydrogenolysis based on the number of active sites determined by H₂ chemisorption would not be significantly different for the various supported Rh catalysts at any selected activation condition, which was indeed the case.

Two explanations exist which could possibly explain the significant decrease in both catalyst activity and Rh dispersion at the higher temperature activation conditions for the TiO₂-, HTO-, and HTO:Si-supported Rh catalysts: 1) strong metal-support interaction (SMSI) phenomena; and 2) significant changes in Rh particle size. The existence of SMSI phenomena in transition metal oxide-supported metal catalysts after high temperature reduction was first characterized by a near total loss of metal chemisorption capacity for H₂ and CO.^{10,11,21} As a consequence of the reduced chemisorption in the SMSI state, large decreases in reaction rates, often several orders of magnitude, have been observed for alkane hydrogenolysis reactions utilizing transition metal oxide-supported metal catalysts.^{22,23} For Rh/TiO₂ catalysts, it has been shown by numerous investigations that high temperature reduction at 773 K results in significant TiO_x migration onto Rh particles, thereby blocking active sites and causing a loss of activity in a number of catalytic reactions.²⁴⁻²⁷ SMSI

phenomena has primarily been observed with highly dispersed Rh/TiO₂ catalysts, since smaller Rh particle size allows more rapid active site blockage by TiO_x migration. However, the work of Miessner, *et. al.*,²⁸ has shown that SMSI effects are observable via H₂ chemisorption even for very high weight loading (> 25 wt.% Rh) Rh/TiO₂ catalysts. The lack of observed SMSI phenomena in this study for the ZrO₂-, HZO-, and HZO:Si-supported Rh catalysts is indicative of a lack of reducibility of the zirconia support, consistent with previous work.²¹

In order to further probe these potential explanations, HREM was performed on both the Rh/TiO₂ and Rh/HTO catalyst samples exposed to both low (423 K) and high (673 K) temperature activation in H₂. These microstructural results, which are not shown herein due to space limitations, did not show a significant difference in Rh particle size with increasing activation temperature for either the high weight loading Rh/TiO₂ or the Rh/HTO catalysts.⁹ If the decrease in H₂ chemisorption uptake observed on increasing the activation temperature from 423 to 673 K was due solely to Rh particle growth, large increases in Rh particle size (at least of a factor of ~4x) would have been expected. Since no significant increase in Rh particle size was observed by HREM, the decrease in H₂ chemisorptive uptake can most likely be attributed to SMSI-related phenomena, i.e., TiO_x migration over Rh particles. Another supporting factor for the lack of significant Rh particle growth is that relatively little change was observed in ethane selectivity values for the Rh/HTO and Rh/HTO:Si catalysts as activation temperature was increased. An interesting aspect of the HTO and HTO:Si supports is that both of these initially amorphous materials are easily reducible and susceptible to the TiO_x migration associated with SMSI phenomena even at low temperatures (573 K) relative to conventional crystalline TiO₂ supports.^{9,29,30} Consistent with previous work,^{25,27,31} various oxidation procedures, followed by low temperature reduction, were used to destroy the SMSI state, resulting in normal catalytic activity and higher Rh dispersions. In the case of the Rh/HTO catalysts, we believe that the partial reversal of the SMSI state also results from crystallization of the amorphous HTO support into anatase or rutile, which explains the reversal of the decrease in n-butane hydrogenolysis activity observed as a function of activation time at 673 K (see Figure 1).⁹ No such reversal occurs for the Rh/HTO:Si sample because it remains amorphous under these activation conditions due to the presence of the SiO₂ dopant.

4. SUMMARY

This purpose of this study was to evaluate high weight loading HMO- and conventional oxide-supported Rh catalysts. Over a wide range of HMO support compositions, highly dispersed supported Rh catalysts were produced after low temperature activation in H₂ as evidenced by high n-butane hydrogenolysis activity, high ethane selectivity, and high H₂ chemisorptive uptake. In particular, the ethane selectivity values were significantly higher for the HMO-supported Rh catalysts than the TiO₂- and ZrO₂- supported Rh catalysts. For the TiO₂-, HTO-, and HTO:Si-supported Rh catalysts, a significant loss of both catalyst activity and Rh dispersion was observed at more aggressive activation conditions, consistent with TiO_x migration typically associated with SMSI phenomena. Superior activity and stability were observed for the ZrO₂-, HZO-, and HZO:Si-supported Rh catalysts over a wide range of activation conditions in H₂. Of all the Rh/HMO catalysts, the Rh/HZO:Si catalysts appear to offer the best tradeoff in terms of high Rh dispersion, high activity, and high selectivity.

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M98005780

Report Number (14) SAND--98-0879C
CONF-980908--

Publ. Date (11) 199804

Sponsor Code (18) DOE/MA, XF

UC Category (19) UC-900, DOE/ER

19980702 088

DTIC QUALITY INSPECTED 1

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