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Characterization and Catalytic Function of Re^0 and Re^{4+} in Re/Al_2O_3 and $PtRe/Al_2O_3$ Catalysts

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Electron spin resonance (ESR) spectroscopy and CO adsorption measurements have shown that Re^0 and Re^{4+} species coexist on the surface of reduced 0.2 wt% Re/Al_2O_3 and 0.3–0.2 wt% $Pt–Re/Al_2O_3$ catalysts. The catalysts were prepared by incipient wetness impregnation with metallic salt precursors, calcined in air at 500°C, and dried in He at 500°C prior to reduction. The Re^{4+} species, which is stabilized by the Al_2O_3 and resists reduction up to 500°C, yields an ESR signal which exhibits hyperfine splitting and accounts for less than 20% of the total Re in Re/Al_2O_3 and less than 10% of the Re in $PtRe/Al_2O_3$. This species does not chemisorb CO but interacts weakly with O_2. The Re^0 does not give rise to a resonance signal, but adsorbs CO strongly. The double bond shift (DBS) of 1-pentene, hydrogenation of 1-pentene, and the skeletal isomerization (SI) of 3,3-dimethyl-1-butene were tested using mild reaction conditions. The results indicate that Re^{4+} slightly enhances the Brønsted acidity in Re/Al_2O_3, although this effect is negligible in comparison with the acidity induced by Cl^- ions. The Re^0 sites are very active for olefin hydrogenation; however, after presulfiding the Re/Al_2O_3, this hydrogenation activity is drastically lowered, but the DBS activity is still high which indicates that surface Re–S species are active for the DBS at the conditions employed.

INTRODUCTION

It is well known that $PtRe/Al_2O_3$ is a better reforming catalyst than the original Pt/Al_2O_3 (*1, 2*). The presence of Re in the bimetallic system results in greater reformate yield and in a longer catalyst life. It has been proposed (*3, 4*) that the improved performance of the bimetallic catalyst compared with the monometallic catalyst is primarily due to the presence of sulfided Pt–Re alloy particles in which sulfur preferentially interacts with the Re surface atoms. Indeed, bulk Re forms stronger bonds with S than does Pt (*5*) and several independent studies have shown that $PtRe/Al_2O_3$ retains more S than Pt/Al_2O_3 (*6, 7*).

In this alloy model, the Re–S species divide the Pt surface into smaller ensembles which are large enough to function as hydrogenation/dehydrogenation sites, but are too small to act as hydrogenolysis sites, thereby reducing cracking and increasing selectivity to desirable products. The enhanced activity maintenance of the bimetallic catalyst is rationalized by assuming that Re–S species impede the reorganization of hydrocarbon fragments to pseudographitic entities which deactivate the metal function of the catalyst. Recent work in this laboratory on the conversion of *n*-hexane and *n*-heptane at atmospheric and elevated pressures supports this model (*8–10*).

Although the superior performance of the bimetallic catalyst can be explained by this PtRe–S alloy model in which both the Pt and Re are completely reduced and are in intimate contact, evidence has been reported that various other Re species coexist in $PtRe/Al_2O_3$ catalysts, with the relative

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amounts of each dependent upon the preparation and pretreatment conditions employed. In particular, a number of physical techniques including XAS (*11–13*), XPS (*12–13*), and EXAFS (*12*) for $PtRe/Al_2O_3$, and ESR [14, 15] for Re/Al_2O_3, have been used to identify a cationic state of Re, most likely Re^{4+}, and possibly also Re^{2+} (*15*), which is apparently stabilized through interaction with the Al_2O_3 and resists reduction to the metallic state.

Since we cannot a priori dismiss the possibility that surface Re species other than sulfur-capped PtRe alloy particles might contribute to the superior performance of the bimetallic catalyst, we thought it timely to address three questions: (1) Are Re^0 and Re^{n+} both present in our $PtRe/Al_2O_3$ catalysts after reduction? (2) If so, what is the location of the Re^{n+} species (on the surface and potentially catalytically active, or in the bulk or at the support/metal interface)? (3) If Re^{n+} is on the surface, does it play any catalytic role and, if so, what?

From the known chemistry, it appears that of all the valence states of rhenium, Re^0 and Re^{4+} are the most stable ones under the conditions of severe reduction which prevail both under industrial reforming conditions and under the conditions of catalyst preparation and testing as described in refs. (*3–10*). Therefore, our work has primarily been focused on the detection and identification of any Re^{4+} coexisting with Re^0. Our approach was first to use ESR spectroscopy to determine if Re^{4+} was indeed present in our reduced catalysts. Re^{4+} is a d^3 ion and should in principle be paramagnetic if the species is sufficiently magnetically isolated.

Second, as a comparison, in addition to the conventional incipient wetness impregnation technique employing an aqueous solution of a metallic salt, we prepared both Re/Al_2O_3 and $PtRe/Al_2O_3$ catalysts using an alternate method in which the Re was put on the support using a dirhenium decacarbonyl precursor dissolved in a pentane solvent. Preparation of $PtRe/Al_2O_3$ catalysts via decomposition of carbonyl compounds has been described in the patent literature (*16–18*). In addition, a number of different carbonyl precursors (e.g., (*19*)), including $Re_2(CO)_{10}$ (*20, 21*), have recently been used in preparing various supported metal catalysts. In the current study, care was taken in selection of conditions for pretreatment of the Al_2O_3, and for activation of the catalyst, that the Re would remain primarily in the zero-valent state following removal of the CO ligands.

Since it is known that Al_2O_3-supported Re does not adsorb H_2 at room temperature (*22–28*), we chose to use CO adsorption as a relative indication of the percentage exposed of Re in the monometallic Re/Al_2O_3 catalysts which were prepared by the two different methods.

To investigate the catalytic function of the Re species present in the conventionally prepared catalysts, several test reactions were chosen. The double bond shift (DBS) of 1-pentene at mild conditions is a very facile reaction and therefore the activity can be greatly affected by small changes in the catalyst. It is also a very selective reaction, as the product *cis*/*trans* ratio is indicative of whether the reaction is occurring over Brønsted acid or base sites. Under the same mild conditions, the hydrogenation of 1-pentene was studied. For both reactions the effect of sulfur poisoning was determined.

The skeletal isomerization (SI) of 3,3-dimethyl-1-butene at mild conditions was used as a probe for Brønsted acid sites and the effect of Re on the acidity of Al_2O_3 was compared to that of chloride.

EXPERIMENTAL

Catalyst Preparation and Pretreatment

Catalysts were prepared by conventional incipient wetness impregnation of high purity γ-Al_2O_3 (Cyanamid), PHF-4, surface area 180 $m^2\ g^{-1}$, pore volume 0.5 $cm^3\ g^{-1}$, mesh size 60–80) with solutions of NH_4ReO_4 (Aldrich No. 20416-1) and/or $Pt(NH_3)_4(NO_3)_2$ (Alfa No. 88960) in deionized water. A solution of NH_4NO_3 (Aldrich No. 25,606-4) was used to prepare an Al_2O_3 "blank" and it received the same subsequent treatment as the metal-containing catalysts. The Al_2O_3 was cleaned prior to impregnation using the procedures of Kobayashi *et al.* (*29*). After impregnation, the catalysts were dried overnight at 100°C in an oven, calcined in flowing tank air at 500°C for 2 hr, and stored in bottles at ambient conditions for at least 2 weeks prior to use.

The loadings of these catalysts were 0.3 wt% Pt/Al_2O_3, 0.2 wt% Re/Al_2O_3, and 0.3–0.2 wt% $PtRe/Al_2O_3$, all with negligible halide content. To study the effect of Cl^- on the acidity of the support, NH_4Cl (Mallinckrodt No. 3384) was used to impregnate blank Al_2O_3 to 1 wt% Cl^-.

These conventionally prepared catalysts were dried in flowing He at 500°C, 60 ml min^{-1}, 1 hr, reduced in flowing H_2 at 500°C, 2 hr, and cooled in flowing H_2 from 500°C to room temperature, *in situ*. It should be noted that these standard pretreatment conditions are the same as those used prior to reforming reaction studies which have been performed in this laboratory (*8–10*).

For the alternate preparation method, special reactor cells were designed so that the catalyst samples (1.5 g) were prepared, pretreated, and analyzed (by ESR or CO adsorption) *in situ*, avoiding contact with ambient conditions. The Al_2O_3 (same as described previously) was first either dehydroxylated in flowing He at 900°C, or partially dehydroxylated at 500°C, and then contacted under inert conditions with $Re_2(CO)_{10}$ dissolved in pentane. $Re_2(CO)_{10}$ (Alfa No. 62108) was purified by vacuum sublimation at 25°C and the pentane was distilled under inert atmosphere. In the case of the bimetallic catalyst, the conventionally prepared Pt/Al_2O_3 was used as the starting material and subjected to the standard pretreatment conditions prior to contact with $Re_2(CO)_{10}$/pentane. The metal loadings ranged from 0.3 to 0.6 wt% Re for the nonmetallic samples and was 0.3 wt% Pt–0.5 wt% Re for the bimetallic catalyst. The solvent was then removed under a slow flow of He at 25°C. The activation treatment (decomposition of the carbonyl complex) was performed in flowing H_2 (unless otherwise noted) using the following temperature program: (1) 25 to 100°C, 1 hr; (2) 100 to 200°C, 0.5 hr; (3) 200 to 500°C, 1 hr; (4) 500°C, 0.5 hr. For the ESR studies the sample was then cooled to 25°C in flowing H_2, whereas for the CO adsorption studies the sample was first purged with Ar, 500°C, 1 hr, and then cooled to 25°C in flowing Ar. ESR and CO adsorption characterization studies were performed on these catalyst samples after these specific treatments and again after a "redox" treatment which consisted of oxidation in O_2, 300 or 500°C, 0.5 hr, followed by reduction in flowing H_2, 500°C, 2 hr, and cooling/purging as described above for the two different methods.

ESR Spectroscopy Studies

Spectra were recorded at room temperature and at liquid N_2 temperature on a Varian Associates E-4 spectrometer that operates at a frequency of 9 GHz (X band) and on a Varian E-109 spectrometer that operates at a frequency of 35 GHz (Q band). Liquid He temperature spectra were recorded on a modified E-4/E-9 spectrometer in the X band. The g values were measured by comparison with crystalline diphenylpicrylhydrazyl (DPPH) ($g = 2.0036 \pm 0.0003$) and Varian weak pitch standard was used for signal integration.

The sample tubes used for ESR analysis were high purity quartz of 3 mm outer diameter. A sample tube was attached as a sidearm to the reactor. The entire cell was isolated from possible O_2 contamination by a He buffer volume which was valved off from the ambient at both the gas inlet and outlet. After pretreatment of a catalyst sample, it was transferred into the sidearm for analysis. It could then be transferred back to the flow-through reactor for further treatment and subsequent analysis.

CO Adsorption Measurements

The CO adsorption capacity of the monometallic Re/Al_2O_3 catalysts was measured at 25°C using a static volumetric technique. Accurate pressure measurements were made using a Datametrics Type 590 Differential Barocel Pressure Sensor. The reference side of this variable capacitance transducer was maintained in the 10^{-7} Torr region while the differential pressure in the system was measured.

The conventionally prepared Re/Al_2O_3 catalyst received the standard pretreatment except that instead of cooling in H_2 the catalyst was purged in Ar, 1 hr, 500°C, and cooled to 25°C in flowing Ar. The *in situ* treatments given the carbonyl-derived Re/Al_2O_3 catalysts were detailed above. Prior to adsorption of CO, each sample was degassed for 20 min at 25°C (to a final pressure of approximately 10^{-6} Torr).

Catalytic Studies

Catalytic studies were performed in a conventional fixed-bed continuous-flow microreactor operated at a total pressure of 1 atm. Reaction products were analyzed on-line using a Hewlett-Packard 5794A gas chromatograph and peak areas determined using a HP 3390A integrator.

Conversion of 1-pentene (Aldrich No. 24,199-7) was studied at 100°C using either He (DBS reaction only) or H_2 (DBS and hydrogenation reactions) as the carrier gas, with a carrier gas/1-pentene ratio of 2.5. Conversion of 3,3-dimethyl-1-butene (Fluka No. 39832) was performed at 150°C with a He/3,3-DM-1-B ratio of 4. No impurities were detected in the 3,3-dimethyl-1-butene by gas chromatography. The purity of the 1-pentene was determined to be 99+% by GC analysis and no further purification methods were employed.

For sulfidation, the catalysts were exposed to a 10 ppm H_2S/H_2 stream at 500°C for 20 hr, after the reduction step of the standard pretreatment. This was followed by a 200–500°C purge in H_2 and cooling to 25°C in flowing H_2.

RESULTS AND DISCUSSION

Characterization Studies

a. ESR spectroscopy studies. After the standard pretreatment, both the Re/Al_2O_3 and $PtRe/Al_2O_3$ catalysts that were prepared using the incipient wetness impregnation method yielded a complex hyperfine resonance pattern characteristic of a paramagnetic Re ($I = \frac{5}{2}$) species. A typical *X* band (9 GHz) ESR spectrum, recorded at 77 K, is given in Fig. 1 for Re/Al_2O_3. It should be noted that no hyperfine pattern due to Re was ever detectable at room temperature, and yet no significant resolution of the signal was obtained by lowering the detection temperature to 4 K. Preliminary analysis of this spectrum and others taken at the higher microwave frequency (35 GHz) yields $g_x = 2.01$, $g_y = 1.82$, $g_z = 1.78$ with hyperfine splitting constants $A_x \sim 170$ G, $A_y \sim 490$ G, and $A_z \sim 910$ G. We attribute this signal to paramagnetic Re^{4+} entities. Further discussion of this assignment will be given below.

Several other resonance signals overlap the Re hyperfine signal and deserve mention. The sharp signal at low field, $g = 4.16$, is due to Fe^{3+} impurities in the support. The intense and narrow signal at $g = 2.0$ is due to mobile electrons within the Al_2O_3, a phenomenon which has been observed by

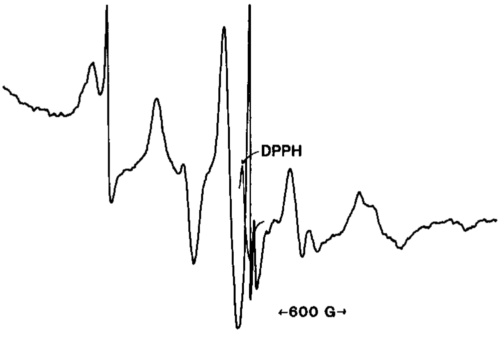

FIG. 1. Typical ESR spectrum of Re/Al_2O_3 (*X* band, 77 K).

others, including (*15, 30*), for various Al_2O_3 supports.

Yao and Shelef (*15*) report the existence of a narrow axial signal in 1.21 wt% Re/Al_2O_3 after certain treatments and attribute it to surface Re^{2+} cations. Although they do not report the *g* value, we observed a very similar axial signal (with the same peak-to-peak width), both in the presence and absence of the Re, which changed slightly upon different pretreatment conditions. We prefer to assign the signal to weak paramagnetic impurities in the Al_2O_3 support.

The Re^{4+} signal was more intense in the case of the monometallic catalyst than in the bimetallic catalyst. This is in accord with studies in the literature in which Re has been found to reduce more easily in the presence of Pt (*11, 13, 31–34*). The signal accounted for less than 20% of the Re present in the monometallic catalyst and less than 10% of the Re in the bimetallic. No signal due to any Re species was present prior to reduction or after a subsequent reoxidation treatment.

For the carbonyl-derived catalysts, no resonance signal due to a Re species was observed after activation in H_2, or after the subsequent redox treatment. Since it appears that the Re in the carbonyl-derived catalysts is present primarily in the zero-valent state after activation and can be oxidized (O_2, 300°C) and then fully reduced (H_2, 500°C), this Re may have a weaker interaction with the support than the tetravalent Re species present in the conventionally prepared catalysts, for these particular preparation and pretreatment conditions. However, the same Re^{4+} signal found in the reduced conventionally prepared catalysts was observed for two carbonyl-derived samples which were exposed to different conditions.

After the redox treatment and ESR analysis (no signal observed), one sample was allowed to "age" (1 month, ambient conditions). After subsequent drying (He, 500°C, 1 hr) and reduction (H_2, 500°C, 2 hr), a resonance signal was obtained that was very similar to the one produced by the reduced conventionally prepared catalysts. A possible explanation for the absence of a signal prior to aging (Re^0) and the presence of a signal after aging is that a rearrangement of the Re particles has occurred which leads to a stronger interaction with the support (for at least some of the Re present) and thus to enhanced stabilization of Re^{4+}.

A study involving 1.1 to 1.9 wt% Re/SiO_2 catalysts prepared by impregnation with aqueous perrhenic acid using TEM to detect redispersion of Re particles during air aging at ambient temperatures (*35*). Presumably, the formation of a Re oxide layer (on the surface and in several adjacent layers of Re crystallites) induces a strain energy in the crystallites. At a critical point, this energy is partially relaxed by splitting the primary particles. These researchers also observed that the H_2 and O_2 adsorption capacity for freshly prepared samples was smaller than that for a catalyst air-aged for even a few days.

As mentioned, if the Re^0 particles in the H_2-activated carbonyl-derived catalysts have a relatively weak interaction with the support, it is possible that these particles would behave as the Re particles in the Re/SiO_2 catalysts and redisperse upon aging at ambient conditions. These smaller (more highly dispersed) particles could interact more strongly with the support, and resist complete reduction. Further, the oxidic species formed during aging on the now fully hydroxylated support may actually be very similar to the oxidic species in the (calcined) conventionally prepared catalysts which were stored prior to use. The treatment given the "aged" carbonyl-derived sample and the conventional catalysts prior to ESR analysis was the same.

Another Re/Al_2O_3 sample was prepared from the carbonyl precursor, but the activation step was done with flowing He, rather than H_2. ESR analysis was performed after a subsequent redox treatment and a Re^{4+} signal was obtained. It appears that the state of Re obtained is dependent on the atmosphere of activation. The results of other studies (*17, 21, 36*) would support this conclusion.

Hucul and Brenner (*36*) prepared a 0.37 wt% Re/Al_2O_3 sample on partially dehydroxylated Al_2O_3 using $Re_2(CO)_{10}$. Temperature-programmed decomposition studies showed that the average oxidation number per metal atom after activation in He to 600°C is 5.4, indicating that a significant amount of the Re was oxidized to the tetravalent and heptavalent states due to the redox reaction occurring on the support. Kosinskii and Shmidt (*21*) decomposed $Re_2(CO)_{10}$ (0.37 wt% Re on partially dehydroxylated Al_2O_3) by thermoevacuation. XPS studies indicated that the average oxidation state of the Re was +1 or +2, after thermoevacuation at 453 K. However, IR studies which were performed after thermoevacuation at the same temperature indicated that the carbonyl complex had not yet been fully decomposed and several CO ligands still remained on each Re atom. Significantly higher temperature was required before the IR bands due to the CO ligands completely disappeared, quite possibly accompanied by further oxidation of the Re. In a patent to UOP (*17*), Antos describes the decomposition of $Re_2(CO)_{10}$ on $Pt-Zn/Al_2O_3$. Pyrolysis (activation) conditions were designed to decompose substantially all of the rhenium carbonyl material, without oxidizing either the Pt or the decomposed rhenium carbonyl component. Best results were obtained when the pyrolysis was performed using an anhydrous H_2 stream at about 400–750°F, rather than in an inert atmosphere or *in vacuo*.

b. CO adsorption studies. Two adsorption isotherms were measured for each determination over a pressure range of 50 to 400 Torr. Typical data for the adsorption of CO on the carbonyl-derived Re/Al_2O_3 is given in Fig. 2. Isotherm I is the initial isotherm which includes both weak and strong adsorption, while Isotherm II is that measured after subsequent sample degassing, 0.5 hr, 25°C (to a final pressure of about 10^{-6} Torr), and includes only weak adsorption. The difference between these two isotherms, taken at 150 Torr in all cases, is the amount of strongly adsorbed CO on the catalyst. Correction was made for strong adsorption on the support, by separate adsorption measurements on the blank Al_2O_3, in order to determine ratios of CO uptake to total Re content, CO/Re, for Re/Al_2O_3 catalysts prepared by the two different methods.

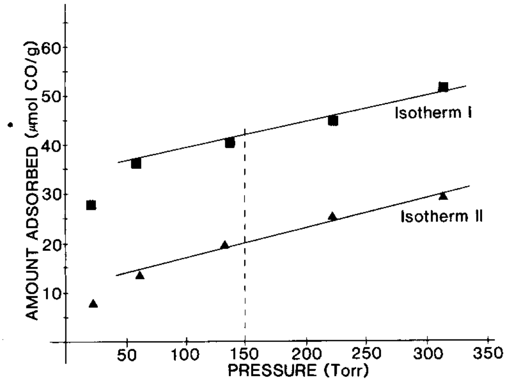

FIG. 2. Typical isotherms for CO adsorption of Re/Al_2O_3 at 25°C.

The CO adsorption capacity of our conventionally prepared Re/Al_2O_3 catalyst was quite small, yielding a CO/Re ratio of 0.20. In comparison, 0.3 and 0.35 wt% Re/Al_2O_3 samples which were prepared using the carbonyl precursor yielded CO/Re values of 1.1 and 0.70, respectively. It is apparent that some of the Re is able to adsorb more than one CO per surface Re species, which is in line with previous studies (*20, 37*). In addition, we know that differences in the amount of Re^0 which is exposed on the surfaces would give rise to different CO/Re ratios, but we must also address the question as to whether Re^{4+}, if present on the surface, would strongly adsorb CO.

From purely Lewis acid/base considerations, it is plausible that cationic Re species would adsorb CO, since the molecule has a lone pair of electrons to donate to the electron-deficient Re species. However, in view of general experience in cluster chemistry and CO chemisorption, it would also seem reasonable that the bonding between Re^{4+} and CO would be substantially weaker than the bonding between Re^0 and CO, since the Re^{4+} cation has fewer electrons to back-donate to the CO ligand. This view is supported by the IR experiments of Guerra (*38*) on CO chemisorption on reduced and oxidized Re/SiO_2 and of Zecchina *et al.* (*39, 40*) on Cr/SiO_2 in which Cr was in the +2 and +3 states.

c. Effect of CO and O_2 *on the* Re^{4+} *resonance signal.* Further ESR studies were performed on the conventionally prepared Re/Al_2O_3 and $PtRe/Al_2O_3$ catalysts to determine the effect of CO and O_2 on the Re^{4+} resonance signal. The catalysts were exposed to CO at 200 Torr, 25°C, and then degassed at the same temperature to remove the weakly bound CO, as in the case of the CO adsorption measurements. The presence of adsorbed CO had no effect on the Re^{4+} resonance signal. The catalysts were then exposed to O_2, 80–160 Torr, 25°C, which caused the resonance signal to completely vanish. However, this effect was reversible upon evacuation at 25°C, indicating that the paramagnetic oxygen was weakly adsorbing on the Re^{4+} species. This experiment also confirms the assignment of Re^{4+} as the paramagnetic species. If the signal was due to Re^0 entities highly dispersed on the surface, these would quickly be oxidized upon admission of O_2 and the signal would not be recovered upon evacuation.

It follows then that the Re^{4+} species must be an exposed surface species since the presence of O_2 would have no effect on a paramagnetic species isolated in the bulk of the material. We also conclude that although Re^{4+} is indeed a surface species, it does not adsorb CO at room temperature.

Catalytic Tests

Catalytic studies involving paraffin isomerization, dehydrocyclization, and cracking tests performed over the same conventionally prepared catalysts after the same pretreatments are reported in Refs. (*8–10*).

The results of the double bond shift (DBS) experiments for unsulfided conventionally prepared catalysts are shown in Fig. 3. The overall conversion of 1-pentene is higher over Re/Al_2O_3, than over Pt/Al_2O_3 or blank Al_2O_3, and higher still over $PtRe/Al_2O_3$. The results suggest that the higher conversion obtained with Re/Al_2O_3 and $PtRe/Al_2O_3$ relative to Al_2O_3 is due to the increasing amount of Re metal, as it is certain that more Re is reduced to Re^0 in the bimetallic than in the monometallic catalyst samples. However, the *cis/trans* ratio for the 2-pentene was 0.5 for all the experiments, which does not distinguish between metal or Brønsted acid sites.

The skeletal isomerization (SI) of 3,3-dimethyl-1-butene was used to probe for Brønsted acidity of the catalysts. The only major products formed were 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene in a 3/1

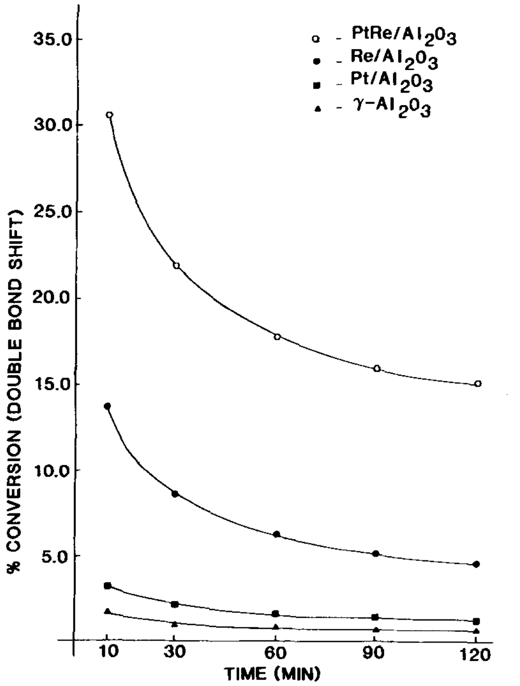

FIG. 3. Percent double bond shift conversion vs time over Al_2O_3, Pt/Al_2O_3, Re/Al_2O_3, and $PtRe/Al_2O_3$.

TABLE 1

Skeletal Isomerization Conversion Data for 3,3-Dimethyl-1-Butene/He over Unsulfided Al_2O_3, Re/Al_2O_3, Pt/Al_2O_3, and $PtRe/Al_2O_3$ at 150°C

Time (min)	% Conversion (±0.1%)			
	Al_2O_3	Re/Al_2O_3	Pt/Al_2O_3	$PtRe/Al_2O_3$
10	2.85	3.55	2.95	3.05
30	2.30	2.85	2.30	2.50
60	2.15	2.55	2.15	2.20
90	2.05	2.50	2.05	2.10
120	2.05	2.45	2.00	2.05
150	2.00	2.40	1.85	2.05
180	1.95	2.35	1.85	2.05

ratio. The results of these experiments are given in Table 1. Re/Al_2O_3 exhibits a SI conversion about 15–20% greater than those of Pt/Al_2O_3, $PtRe/Al_2O_3$, and blank Al_2O_3, which all have very similar conversions. These results show that Re somewhat enhances the Brønsted acidity of the Al_2O_3 in Re/Al_2O_3, but not appreciably in $PtRe/Al_2O_3$. So, the enhanced acidity apparently is lower as the extent of Re reduction increases, implying that the increase in acidity is due to Re in an oxidation state greater than zero. This is, however, insufficient to account for the enhancement in the DBS activity in the Re/Al_2O_3 compared with the Al_2O_3, which must therefore be primarily due to the presence of Re metal.

Since the acidity of a commercial PtRe/Al_2O_3 reforming catalyst is generally promoted by about 1 wt% Cl^-, we also checked the isomerization activity of 3,3-dimethyl-1-butene over a chlorided Al_2O_3 sample under the same conditions. The conversion was almost 100%, so it is apparent that although the presence of the Re^{4+} surface species does increase the Brønsted acidity of the Al_2O_3, this effect is negligible under reforming conditions. Similar results have been reported by Jossens and Petersen (*41*).

The effect of sulfur on the conversion of 1-pentene and 3,3-dimethyl-1-butene was quite different. Unsulfided Re/Al_2O_3 was active for hydrogenation of 1-pentene, whereas presulfiding reduced this activity by at least an order of magnitude as shown in Fig. 4. This behavior is characteristic for Re^0. However, the conversion of 1-pentene in hydrogen over presulfided $PtRe/Al_2O_3$ was still very high due to the activity of the Pt, which is only partly deactivated at the low H_2S/H_2 ratio used. This partial deactivation of Pt is known to be largely reversible.

While the hydrogenation activity of Re is poisoned by adsorbed S, the DBS activity of the Re-containing catalysts was not reduced upon sulfidiation and indeed some increase was actually observed. Thus, for the DBS reaction at the conditions used, the Re–S surface species is not inert. The exact nature of this Re–S species cannot be elucidated completely from these experiments. It could be a site similar to those found in bulk ReS_2 and MoS_2, or it could be a Brønsted acid site, –SH, formed during the sulfiding treatment. It is well known that sulfided Mo catalysts retain a large

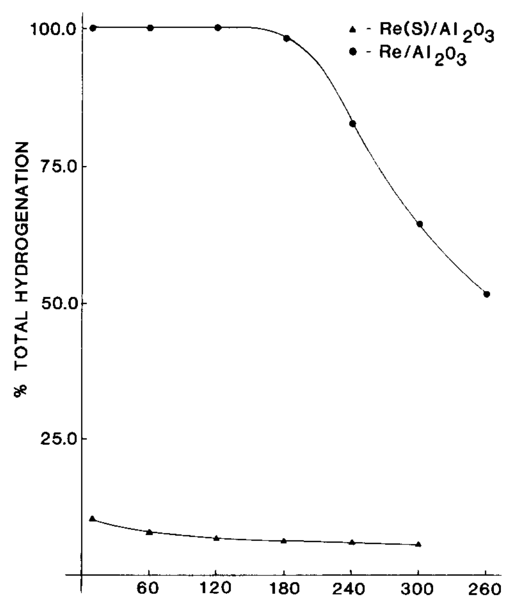

FIG. 4. Percent conversion (hydrogenation) vs time over sulfided and unsulfided Re/Al_2O_3.

amount of H (*42–45*) which is preferentially bound to the sulfur ions (*46*). Since S is strongly bound to Re in Re-containing catalysts, it is possible that a similar phenomenon occurs with them, resulting in Re–SH groups that can function as Brønsted acid sites.

CONCLUSIONS

The surface of the reduced bimetallic $PtRe/Al_2O_3$ catalyst contains both Re^0 and Re^{4+}, although the Re^{4+} could account for only about 10% or less of total Re at the loadings investigated here. Our results show that the Re^{4+} surface sites do not chemisorb CO, whereas Re^0, either separately dispersed or in contact with the Pt (*23, 26*), strongly chemisorbs CO. In addition, while adsorption of dioxygen on the Re^{4+} is weak and reversible, oxygen is strongly chemisorbed on Re^0. Re^{4+} mildly enhances the acidity of Re/Al_2O_3, but the effect is negligible compared to that of conventional acidity promoters such as Cl^- at levels of commercial interest. It seems reasonable therefore to conclude that Re^0 is the valence state of Re which is decisive for the catalytic function of the $PtRe/Al_2O_3$ reforming catalyst.

In earlier studies we had addressed the question of whether this Re^0 on the surface is present as pure Re^0 or in mixed Re–Pt ensembles. This question was answered by work where the mixed ensembles had been identified by their characteristic selectivity for producing methane from hydrogenolysis of *n*-hexane and *n*-heptane (*9, 10*) which distinguished them sharply from pure Re_n and pure Pt_n ensembles.

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REFERENCES

1. Kluksdahl, H. E., U.S. Patent 3,415,737 (1968).
2. Jacobson, R. L., Kluksdahl, H. E., McCoy, C. S., and Davis, R. W., *in* "Proceedings, 34th Midyear Mtg.," p. 504. Div. Refin., Amer. Pet. Inst., 1969.
3. Biloen, P., Helle, J. N., Verbeek, H., Dautzenberg, F. M., and Sachtler, W. M. H., *J. Catal.* **63,** 112 (1980).
4. Sachtler, W. M. H., *J. Mol. Catal.* **25,** 1 (1984).
5. Kubaschewski, O., and Evans, E. L., *in* "Metallurgical Thermochemistry." Pergamon, Elmsford, NY, 1965.
6. Schay, Z., Matusek, K., and Guczi, L., *Appl. Catal.* **10,** 173 (1984).
7. Mieville, R. L., private communication, 1983.
8. Shum, V. K., Butt, J. B., and Sachtler, W. M. H., *Appl. Catal.* **11,** 151 (1984).
9. Shum, V. K., Butt, J. B., and Sachtler, W. M. H., *J. Catal.* **96,** 371 (1985).
10. Shum, V. K., Butt, J. B., and Sachtler, W. M. H., *J. Catal.* **99,** 126 (1986).
11. Yermakov, Yu. I., Kuznetsov, B. N., Ovsyannikova, I. A., Startsev, A. N., Erenburg, S. B., Sheromov, M. A., and Mironenko, L. A., *React. Kinet. Catal. Lett.* **7** (3), 309 (1977).
12. Short, D. R., Khalid, S. M., Katzer, J. R., and Kelley, M. J., *J. Catal.* **72,** 288 (1981).
13. Onuferko, J. H., Short, D. R., and Kelley, M. J., *Appl. Surf. Sci.* **19,** 227 (1984).
14. Johnson, M. F. L., and LeRoy, V. M., *J. Catal.* **35,** 434 (1974).
15. Yao, H. C., and Shelef, M., *J. Catal.* **44,** 392 (1976).
16. Ohmori, T., Fujiso, T., Yasui, E., Nomura, S., and Aizawa, Y., Fr. Demande FR 2,545,095, 02 Nov. 1984, JP Appl. 83/73,842, 28 Apr. 1983.
17. Antos, G. J., U.S. Patent 4,137,153, 30 Jan. 1979.
18. ELF France, British Appl. 2,096,418A.
19. Burwell, R. L., Jr., and Brenner, A., *J. Mol. Catal.* **1,** 77 (1975/1976); Brenner, A., and Burwell, R. L., Jr., *J. Amer. Chem. Soc.* **97,** 2565 (1975); Ichikawa, M., *Chemtech,* 674 (1982); Yermakov, Yu. I., Kuznetsov, B. N., and Zakharov, V. A., "Catalysis by Supported Complexes." Elsevier, Amsterdam/New York, 1981, and references therein.
20. Sudhakar, C., Yesodharan, E. P., Cichowlas, A., Majer, M., and Brenner, A., Prep. Div. of Pet. Chem., A. C. S., 440, March 1982.
21. Kosinskii, O. L., and Shmidt, F. K., Depos. Doc. 1982SPSTL, 1275, Khp-D82 (English Abstract: CA 60922r (1984)).
22. Freel, J., Prep. Div. Pet. Chem., A.C.S., Dallas Mtg., April 1973, 10 (1973).
23. Bolivar, C., Charcosset, H., Frety, R., Primet,

M., Tournayan, L., Betizeau, C., Leclercq, G., and Maurel, R., *J. Catal.* **45,** 163 (1976).

24. Barbier, J., Charcosset, H., de Periera, G., and Riviere, J., *Appl. Catal.* **1,** 71 (1981).
25. Eskinazi, V., *Appl. Catal.* **4,** 37 (1982).
26. Carter, J. L., McVicker, G. B., Weissman, W., Kmak, W. S., and Sinfelt, J. H., *Appl. Catal.* **3,** 327 (1982).
27. Isaacs, B. H., and Petersen, E. E., *J. Catal.* **85,** 1 (1984).
28. Isaacs, B. H., and Petersen, E. E., *J. Catal.* **85,** 8 (1984).
29. Kobayashi, M., Inoue, Y., Takahashi, N., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **64,** 74 (1980).
30. Berger, P. A., and Roth, J. F., *J. Catal.* **4,** 717 (1965).
31. Bolivar, C., Charcosset, H., Frety, R., Primet, M., Tournayan, L., Betizeau, C., Leclercq, G., and Maurel, R., *J. Catal.* **39,** 249 (1975).
32. Wagstaff, N., and Prins, R., *J. Catal.* **59,** 434 (1979).
33. Isaacs, B. H., and Petersen, E. E., *J. Catal.* **77,** 43 (1982).
34. Mieville, R. L., *J. Catal.* **87,** 437 (1984).
35. Szymura, J. A., and Paryjczak, T., *React. Kinet. Catal. Lett.* **12**(3), 219 (1979).
36. Hucul, Dennis, A., and Brenner, A., *J. Phys. Chem.* **85,** 496 (1981).
37. Guerra, C. R., and Schulman, Jack H., *Surf. Sci.* **7,** 229 (1967).
38. Guerra, C. R., *J. Colloid Interface Sci.* **29**(2), 229 (1969).
39. Zecchina, A., Garrone, E., Ghiotti, G., Morterra, C., and Borello, E., *J. Phys. Chem.* **79**(10), 966 (1975).
40. Zecchina, A., Garrone, E., Ghiotti, G., and Coluccia, S., *J. Phys. Chem.* **79**(10), 972 (1975).
41. Jossens, L. W., and Petersen, E. E., *J. Catal.* **76,** 265 (1982).
42. Bond, G. C., Webb, G., and Wells, P. B., *Trans. Faraday Soc.* **64,** 3077 (1968).
43. Massoth, F. E., *J. Catal.* **36,** 164 (1975).
44. Burch, R., and Collins, A., *Appl. Catal.* **18,** 373 (1985).
45. Hau, P., and Wise, H., *J. Catal.* **78,** 469 (1982).
46. Wright, C. J., Sampson, C., Fraser, D., Moyes, R. B., Wells, P. B., and Riekel, C., *J. Chem. Soc. Faraday I* **76,** 1585 (1980).