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The Effect of Carbon on the Reducibility of Rhenium in Pt–Re/Al_2O_3 Catalysts

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The oxidation states of Re in three catalysts (0.4 wt% Pt + 0.6 wt% Re/Al_2O_3, 2.4 wt% Pt + 2.7 wt% Re/Al_2O_3, and 2.4 wt% Re/Al_2O_3) were evaluated with X-ray photoelectron spectroscopy (XPS). Reduction of the bimetallic catalysts with hydrogen at 500°C and 1 atm gave predominantly Re(+4). Addition of small amounts of water to the hydrogen feed resulted in the reduction of the rhenium to Re(0) with complete chloride removal from the Pt–Re/Al_2O_3 samples. Reduction of the bimetallic catalysts in butane + hydrogen at 500°C gave Re(0) without significant chloride removal. The 0.4 wt% Pt + 0.6 wt% Re/Al_2O_3 catalyst with Re in the +4 oxidation state also underwent reduction to give Re(0) in the presence of butane + hydrogen at 500°C. In contrast, under identical conditions, the Re in the Re/Al_2O_3 catalyst was reduced to Re(+4), which indicates that Pt is necessary for the complete reduction of the Re with butane + hydrogen at 500°C. These results suggest that rhenium is present predominantly as the zerovalent metal in the bimetallic reforming catalyst under reaction conditions.

INTRODUCTION

The addition of Re to Pt/Al_2O_3 catalysts used for reforming of petroleum distillates greatly enhances their resistance to deactivation resulting from coke deposition (*1*). Although these catalysts have been investigated extensively, the role of Re in stabilizing the catalyst is still not well understood.

The determination of the oxidation state(s) of Re in the catalyst is crucial to understanding its function. Both chemical (*2, 3*) and physical (*4, 5*) methods have been applied in attempts to determine the oxidation state, and a majority of the investigators have concluded that rhenium is present predominantly as Re(0) or Re(+4). There is a persistent disagreement about which of these prevails, or whether both are present. Several explanations have been offered for the apparent discrepancy, including differences in Re loading (*6, 7*), chloride concentrations (*8*), temperature of calcination prior to reduction (*9, 10*), and partial pressures of water in the hydrogen used for reduction (*6, 7*). Recent results obtained by temperature-programmed reduction suggest that differences in the initial degree of surface hydration are responsible for most of the disagreement; extensive dehydration (similar to that employed in industrial reforming processes) was inferred to favor incomplete reduction of the Re at 500°C under 1 atm of hydrogen (*9*).

All of the above-cited investigations have been concerned with the catalyst as reduced, prior to its exposure to hydrocarbon reactants such as petroleum naphtha. Our goal, in contrast, was to characterize the reducibility of rhenium on alumina in the presence of hydrocarbons. The specific objective was to determine oxidation states of Re by X-ray photoelectron spectroscopy (XPS), accounting for the effects of Re loading and the presence of water in the initial reduction step. The results demonstrate that hydrogen, in the presence of water or butane, reduces the Re to the zerovalent state in Pt-Re/Al_2O_3 catalysts.

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EXPERIMENTAL METHODS

Catalyst preparation. Catalysts were prepared by wet impregnation of γ-Al_2O_3 (Catapal, surface area $\approx$ 250 m^2/g) with an aqueous solution of tetrammine platinum chloride (Colonial Metals) and/or ammonium perrhenate. The suspension was allowed to stand for 24 h; the solid was then dried in air at 110°C for 12 h, calcined in flowing dry air at 500°C for 12 h, and then stored under nitrogen in a Vacuum Atmospheres drybox.

Reduction experiments. The reduction experiments were performed with the sample of catalyst powder (about 70 mg) in the prechamber of the XPS instrument (Physical Electronics Model 551). The reduced samples were transferred into the vacuum chamber without exposure to air. Unless otherwise noted, samples were first evacuated in the prechamber (10^{-5} Torr) at 500°C for 2 h to ensure dryness. Hydrogen (Matheson, UHP, 99.999%) was then allowed to flow through the prechamber at atmospheric pressure and 500°C at a rate of 35 ml/min for 4 h. The samples were then cooled under hydrogen to 150°C (~15 min), evacuated (10^{-5} Torr), and introduced into the vacuum chamber at a temperature of 90°C. This procedure prevented excessive condensation of water on the samples reduced in water (5 Torr) + hydrogen and prevented oxidation of the samples containing Re(0). Samples were allowed to cool to room temperature in the vacuum chamber before data acquisition.

For "wet" reduction experiments with $H_2 + H_2O$, the hydrogen was bubbled through a glass vessel containing distilled and deoxygenated water at 0°C ($P_{H_2O} \approx 5$ Torr), from which it passed directly into the prechamber.

In experiments involving reduction by hydrogen in the presence of *n*-butane (Matheson, Instrument Purity, 99.5%; no impurities were detected by gas chromatography with a flame ionization detector), the butane and hydrogen flowed to the prechamber in a 10 : 1 molar ratio (H_2 : butane) at a rate of 35 ml/min. Butane was chosen because it is representative of the largest (aliphatic) fraction of components in petroleum naphtha (*1*), and it gave acceptably low amounts of carbonaceous deposits (surface carbon lowers the intensity of metal peaks in the spectra) under reduction conditions. The butane was passed through a trap containing 5A molecular sieve that had been activated at 350°C to remove any traces of water. All other experimental conditions were identical to those described above for reduction in hydrogen alone.

X-Ray photoelectron spectroscopy. The spectrometer utilized nonmonochromatized Mg$K\alpha$ radiation (1253.6 eV), with the anode operated at 10 kV and 40 mA. The base pressure of the instrument was always $<5 \times 10^{-9}$ Torr, with typical operating pressures $<5 \times 10^{-8}$ Torr. To minimize sample charging, a neutralization gun was used at an emission current of 0.05 mA and zero-applied voltage. Samples were finely ground and mounted as powders by packing into aluminum holders in a 10 mm (diam) × 1 mm cavity with an aluminum press (hand pressure was applied). The sample holders were attached to a heatable sample probe with screws and copper clips. The sample temperature was monitored by a thermocouple adjacent to the sample on the probe tip.

For catalyst samples, the Al 2*p* line (74.5 eV) of the alumina support was used as an internal reference for determination of binding energies. The average C 1*s* binding energy found for γ-Al_2O_3 and the catalyst samples was 285.0 eV. Therefore, binding energies for all standard compounds were referenced to the C 1*s* line (285.0 eV). Binding energies were measured with a precision of ±0.2 eV or better. XPS intensity ratios were obtained from the appropriate total integrated peak areas. In the peak area computations, the background was assumed to be linear over the peak width. Intensity ratios were reproducible to ±5% (r.s.d.) or better.

X-Ray fluorescence. The platinum, rhenium, and chlorine contents of the solids were determined by X-ray fluorescence spectroscopy with a Philips PW 1410/80 automated spectrometer equipped with a XRG-31000 generator. In analyzing for chlorine, corrections were made for the interference of the LY8 line of platinum.

X-Ray diffraction. The bulk purity of certain standards and the presence of metal crystallites on selected catalysts were determined by X-ray diffraction with a Philips APD 3500.

Raman spectra. Laser Raman spectra were obtained with a Spex Ramalog spectrometer interfaced to a Nicolet 1180 data system and equipped with a Spectra Physics Model 164 Ar^+ laser. The 514.5-nm line was used as the excitation source.

RESULTS AND DISCUSSION

The binding energies of several rhenium standards were measured (Table 1), and the results agree well with literature values (*11, 12*). The bulk purity of the reference compounds was confirmed by Raman spectra of NH_4ReO_4 (Strem) and Re_2O_7 (Aesar) that showed no evidence of impurities. An X-ray powder pattern of ReO_2 (Aesar) gave only those lines reported (*14*) for the pure compound. However, the XP-spectrum of ReO_2 indicated the presence of Re_2O_7 (Fig. 1c), which we attribute to a surface layer of higher oxides resulting from the slow reaction of ReO_2 with air (*12*). This oxidation may have shifted the signal to slightly higher binding energies; other authors (*12, 14*) have reported lower values (42.5 eV vs our 43.3 eV).

TABLE 1

XPS Binding Energies (eV) for Reference Compounds[a,b]

Sample	Re $4f_{7/2,5/2}$	O 1*s*
Al_2O_3	—	531.7
Re foil	40.5, 42.9	—
ReO_2[c]	43.3, —	531.8
NH_4ReO_4	46.5, 48.8	531.9
Re_2O_7	46.8, 49.0	532.1

[a] All binding energies were referenced to C 1*s* = 285.0 eV.

[b] Binding energies were measured with a precision of ±0.2 eV or better.

[c] Partially oxidized.

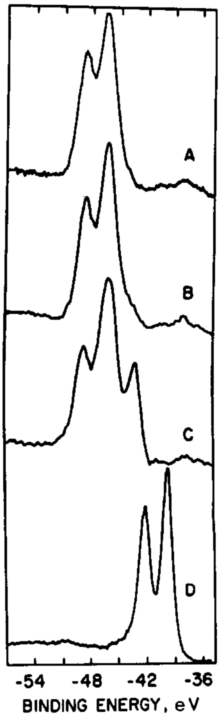

FIG. 1. X-Ray photoelectron spectra of Re reference materials: (A) Re_2O_7; (B) NH_4ReO_4; (C) ReO_2; (D) Re foil.

The binding energies measured for all the catalyst samples are summarized in Table 2; there are data characterizing bimetallic catalysts of two different metal loadings and a rhenium catalyst without platinum. Also reported are values of the chloride contents of the samples determined by XRF and the Re 4*f*/Al 2*s* intensity ratios, which can be taken as indicators of changes of dispersion.

Preliminary experiments were performed to determine the oxidation state of the rhenium in the calcined samples (as prepared). The unreduced catalysts gave broad spectra, each with a peak maximum indicative of Re(+7) (Figs. 2A, B; Fig. 3A). Similar broadening has been observed previously

TABLE 2

XPS Binding Energies (eV), Integrated Peak Intensity Ratios, and Chlorine Contents for Pt-Re/Al$_2$O$_3$ and Re/Al$_2$O$_3$

Sample[a]	Re $4f_{7/2}$	Re $4f$/Al $2s$	wt% Cl[b]
2.4% Pt/2.7% Re (as is)	46.5	0.25	1.8
2.4% Re (as is)	46.3	0.24	0.1
2.4% Pt/2.7% Re (vac)	46.3	0.28	—
2.4% Pt/2.7% Re (H_2O/H_2, air)	46.7	0.21	0.4
0.4% Pt/0.6% Re (as is)	46.7	0.084	0.5
2.4% Pt/2.7% Re (H_2)	42.5	0.14	−0.2
2.4% Pt/2.7% Re (vac, H_2)	42.9	0.28	—
2.4% Pt/2.7% Re (H_2O/H_2)	40.5	0.11	0.4
0.4% Pt/0.6% Re (H_2O/H_2)	40.8	0.037	0.0
2.4% Pt/2.7% Re (vac, HC/H_2)	40.7	0.16	1.8
2.4% Re (vac, HC/H_2)	42.4	0.077	0.1
0.4% Pt/0.6% Re (vac, HC/H_2)	41.0	0.060	0.5
0.4% Pt/0.6% Re (vac, H_2, HC/H_2)	41.0	0.056	0.6

[a] Notation: the comma implies a sequence and the slash implies a mixture; for example, (vac, HC/H_2) signifies 2 h under vacuum followed by 4 h in a hydrocarbon + hydrogen mixture.

[b] ±0.5 wt%, determined by XRF.

(*4, 11, 15*) and is attributed to the interaction of $[ReO_4]^-$ tetrahedra with Lewis acid sites (*11, 15*); Raman spectra (*16, 17*) support this interpretation. Also, sample charging and the O $2s$ energy loss peak, which lies directly beneath the Re $4f$ envelope of the oxidized catalyst and appears as a high-energy shoulder in the reduced spectra (*15*), may contribute to spectral broadening. To evaluate the effect of drying the calcined catalysts, a spectrum of the 2.4 wt% Pt and 2.7 wt% Re sample after 2 h at 500°C under vacuum was obtained and found to be indistinguishable from the original spectrum (Fig. 2B).

The reducibility of the rhenium in the Pt-Re/Al$_2$O$_3$ catalysts in pure hydrogen was determined; a spectrum (Fig. 2C) of the sample containing 2.4 wt% Pt and 2.7 wt% Re after 2 h under vacuum followed by 4 h in H_2 at 500°C had a maximum at 42.9 eV. As before, the spectrum was broadened, which is indicative of an interaction between Re(+4) oxide and surface Lewis acid sites. Several authors (*4, 18, 19*) have inferred that this interaction is strongest for Re(+4), which gives an extremely stable surface rhenium species. When the pretreatment under vacuum was omitted, a similar spectrum was observed, now shifted 0.4 eV to lower binding energies. The shift could be an indication of more extensive reduction; however, no additional broadening was observed, which ar-

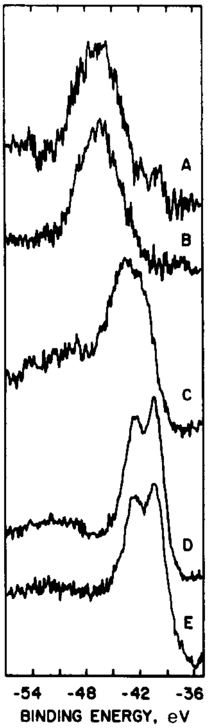

FIG. 2. X-Ray photoelectron spectra of a 2.4 wt% Re/Al$_2$O$_3$ catalyst: (A) as calcined; (B) and a 2.4 wt% Pt + 2.7 wt% Re/Al$_2$O$_3$ catalyst, as calcined; (C) after 2 h under vacuum followed by 4 h in hydrogen at 500°C; (D) after 4 h in hydrogen + water at 500°C; (E) after 2 h under vacuum followed by 4 h in hydrogen + butane at 500°C.

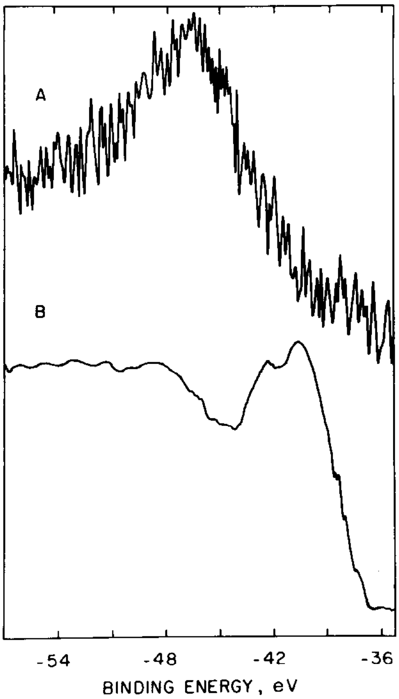

FIG. 3. X-Ray photoelectron spectra of a 0.4 wt% Pt + 0.6 wt% Re/Al_2O_3 catalyst; (A) as calcined; (B) after 2 h under vacuum followed by 4 h in butane + hydrogen at 500°C (data have been smoothed).

gues against this interpretation. A more likely explanation is a weakened interaction of the Re with the Lewis acid sites on the alumina surface, associated with a higher hydroxyl group concentration. Consistent with this hypothesis, the decrease in the Re 4*f*/Al 2*s* intensity ratio (Table 2) can be interpreted as an indication of the formation of a three-dimensional ReO_2 phase with an observed binding energy (42.5 eV) that is identical to the value reported for bulk unoxidized ReO_2 (*12, 14*). On the basis of results reported below and those of Isaacs and Petersen (*9*), the lack of complete reduction of the ReO_2 to Re(0) on the undried sample is inferred to be an indication that water uptake was minimal during sample loading.

The addition of water (5 Torr) to the hydrogen stream led to reduction to the zerovalent state of the rhenium in the catalyst containing 2.4 wt% Pt and 2.7 wt% Re (Fig. 2D). Significant reduction also occurred with the catalyst having a metal loading representative of industrial catalysts, namely, 0.4 wt% Pt and 0.6 wt% Re; however, the spectrum lacked sharp features, which suggests that a mixture of oxidation states of Re was present and makes the assignment of binding energies difficult. The value reported in Table 2 is interpreted as the average over a range of oxidation states. In the XPS experiments with samples having both high and low Re loadings, a decrease in the Re 4*f*/Al 2*s* intensity ratio was observed, which indicates that some loss of surface area had occurred.

The role of water in promoting the reduction of the rhenium is not yet clear. It has been suggested (*9, 10*) that the Re_2O_7 becomes hydrated, giving a mobile rhenium surface phase. The hydrated Re_2O_7 might then migrate to the platinum, where it could be reduced. The mobility of the Re_2O_7 might be interpreted as an indication of the protonation of ReO_4^- by water to give $HReO_4$, which would be mobile in water and hence readily reduced.

A related interpretation is that water, by stripping chloride from the surface or by dissociative adsorption on Lewis acid sites, poisons the interaction between the Re(+4) oxide and the alumina surface. The weakened interaction would allow the two-dimensional oxide layer to rearrange into crystallites, which are easily reduced to Re(0) (*12, 18*). Consistent with this latter interpretation, all the chloride was removed from the sample containing 2.4 wt% Pt and 2.7 wt% Re which was reduced in hydrogen + water to give Re(0) (Table 2); however, complete stripping of chloride from the sample reduced in pure hydrogen to give Re(+4) was also observed (Table 2). These results suggest that although the loss of chloride may favor reduction, it is not sufficient for complete reduction to Re(0) by pure hydrogen at 500°C, even with samples containing high loadings (2.7 wt%) of rhenium.

Reduction in wet hydrogen maximizes

the concentration of hydroxyl groups on the alumina surface. The rate of hydrogen spillover on Pt/Al_2O_3 is reported to be directly proportional to the hydroxyl group concentration (*20*), and an enhanced spillover rate might be responsible for the reduction of the rhenium. However, the calculations of Isaacs and Petersen (*9*) show that the total amount of hydrogen spillover during reduction cannot account for all the rhenium reduced. Using the same method (*9*), we calculate that the amount of hydrogen spillover during 4 h at 500°C is 2 orders of magnitude too small to account for the reduction of the Re. However, this calculation neglects the autocatalytic nature of metal oxide reduction and therefore may underestimate the reducing effect of atomic hydrogen generated on the platinum.

Whatever the correct explanation for the role of water in reducing the rhenium, the experimental results suggest that the reduction of Re in Pt–Re/Al_2O_3 catalysts can be made thermodynamically favorable at 500°C [bulk Re_2O_7 is reduced at 300°C in hydrogen (*12*)] . Further support for this inference is provided by the results obtained in experiments performed with butane (76 Torr) + hydrogen at 500°C. Both the bimetallic catalyst with a high metal loading and that with a low metal loading were reduced to give Re(0) (Figs. 2F and 3B) by treatment under vacuum for 2 h followed by treatment in butane + hydrogen for 4 h at 500°C. The binding energy of the Re(0) in the samples with low Re loadings (Table 2) is shifted to slightly higher values than that characterizing bulk Re metal (Table 1). Comparable shifts (~0.5 eV) have also been observed for other highly dispersed metal catalysts (*21, 22*). The shift is attributed to the final state effect (*21*) which, due to a lessened screening of the created core hole by the electrons on a smaller number of neighboring atoms, predicts higher apparent binding energies for small Re crystallites than for bulk Re. The presence of small amounts of Re (below the detection limit of XPS) in oxidation states other than zero on the reduced catalysts, especially those with low metal loadings, cannot be excluded.

An additional experiment, in which a 4-h period in pure hydrogen immediately followed the pretreatment step, was performed with the bimetallic catalyst having the lower metal loading. As shown above and by others (*4*), the pretreatment followed by reduction in hydrogen gives the highly stable Re(+4) species. The spectrum recorded after the three-step sequence was indistinguishable from that obtained when the step involving pure hydrogen was omitted (Fig. 3B); evidently the additional stability gained by first kinetically stabilizing the Re(+4) state is not sufficient to prevent reduction with hydrocarbon at 500°C. Furthermore, no chloride loss from the catalysts reduced with butane + hydrogen was observed, which demonstrates that the stabilizing effect of chloride on ReO_2 can also be overwhelmed by the hydrocarbon. However, it is inferred that the chloride may still have minimized sintering, since the decrease in the Re 4*f*/Al 2*s* intensity ratio for both bimetallic catalysts reduced in butane + hydrogen is not as great as that observed for those reduced with water + hydrogen, in which complete removal of chloride occurred.

To investigate further the role of butane in the reduction, a 2.4 wt% Re/Al_2O_3 catalyst was reduced under the same conditions as those used with the bimetallic catalysts. The spectrum obtained lacked definition and was much reduced in intensity, as evidenced by the drop in the Re 4*f*/Al 2*s* intensity ratio relative to that of the oxidic catalyst. We tentatively suggest that the loss of intensity is due to carbon on the surface of the rhenium and that the broad peak is indicative of a mixture of oxidation states. The contrast between this result and that observed with the bimetallic catalysts implies that Pt is necessary for the complete reduction of the Re with butane + hydrogen at 500°C.

An explanation for the reduction of the rhenium with butane + hydrogen can be made on the basis of the work of Somorjai (*23*) and others (*24*), who have demonstrated that carbonaceous layers on the surfaces of metal hydrogenolysis catalysts act to transfer hydrogen via the metal centers to the reactant fragments on the surface. Low hydrogen-to-carbon ratios favor coke formation; depletion of hydrogen from the carbonaceous layer accompanies catalyst deactivation. As an extension of this idea, we suggest that the carbonaceous layer on a Pt–Re/Al_2O_3 catalyst may act to transfer hydrogen not only to organic reactants but also to Re, resulting in its reduction to the zerovalent state. Alternatively, it has been reported (*14, 25*) that olefins at 1 atm and 120 or 500°C reduce Re in Re/Al_2O_3 to the +4 and +6 oxidation states, whereas benzene + hydrogen at 30 atm and 200°C (*12*) reduce Re to a mixture of oxidation states (0 to +4). We suggest that butene, which results from the platinum-catalyzed dehydrogenation of butane, might play a role in reducing the rhenium to Re(0) in the butane + hydrogen reduction experiments with the Pt–Re/Al_2O_3 catalysts.

The relative merits of the two hypotheses stated above can be evaluated on the basis of the observations (*26, 27*) that a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3 exhibits catalytic properties for naphtha reforming similar to those of a Pt–Re/Al_2O_3 catalyst. We expect that the chemical state of the rhenium should be the same in the two cases [we emphasize that in the latter experiment (*27*) the feed did not contain water]; to the extent that this inference is correct, the suggestion that the reduction occurred with butene is favored over the inference that reduction was promoted by carbonaceous deposits because the olefins and aromatics in the feed as well as those produced *in situ* by the platinum under reforming conditions could reduce the Re/Al_2O_3 to Re(0). It is less likely that hydrogen dissociated on the Pt/Al_2O_3 particles could migrate to the Re/Al_2O_3 via carbonaceous deposits to reduce the rhenium. In the absence of atomic hydrogen generated on the platinum, hydrogen transfer from carbonaceous deposits would result in rapid coke formation and incomplete reduction of the rhenium similar to that demonstrated for 2.4% Re/Al_2O_3. The oxidation state of the rhenium in the bimetallic catalyst would then be different from that in the physical mixture of the monometallics, and large differences in the catalytic properties (which were not observed) would be expected.

The presence of Pt(0) in the samples with high metal loadings was verified by X-ray diffraction, which was also used to analyze for Re(0). No Re(0) was observed in any of the reduced samples. Subsequent analysis by XP-spectroscopy revealed that the rhenium in the highly dispersed crystallites had been oxidized back to the +7 oxidation state upon exposure to O_2; similar oxidation has been reported by Yao and Shelef (*18*).

We infer that the reduction of Re to Re(0) with hydrocarbon + hydrogen is consistent with the contention that alloy-like structures form (*28*); however, the presence of Re(0) does not imply that all the rhenium is present in alloy-like structures with platinum; we infer that mixtures of platinum, rhenium, and platinum–rhenium aggregates are present on the surfaces of the industrial reforming catalysts. The reduction of Re under reaction conditions also implies that, at short times, the extent of formation of bimetallic aggregates may depend on the rate of reduction. If this reduction is characterized by positive orders in hydrogen, water, and olefin partial pressures we infer that it would be rapid under practical reforming conditions; for example, the assumption that the rate is directly proportional to hydrogen partial pressure implies a maximum reduction time of 24 min at 500°C and 10 atm vs 4 h at 500°C and 1 atm. This result suggests that the initial transients observed in low-pressure kinetics experiments (*27, 29, 30*) may actually reflect a change in the oxidation state of the catalyst, and therefore the extent of bimetallic aggregate formation, and may not be an accurate indicator (except at very short times) of industrial performance.

Nevertheless, low-pressure kinetics experiments do contribute to the understanding of the catalyst and can be interpreted in terms of the results stated above. In the work of Coughlin *et al.* (*27*) the feed to a flow reactor consisted of a 1/9/9 mixture of methylcyclohexane/hydrogen/nitrogen at 1 atm and 500°C. In the first 10 h of the experiment, a gradual increase in conversion to toluene with a concomitant decrease in conversion to benzene was observed. According to a published model (*28, 31, 32*) these results can be interpreted as indicating a decrease in the Pt ensemble size, which, we suggest on the basis of our results, may be provided by hydrocarbon-reduced Re that migrates to the Pt. However, the alternative explanation that selective coke poisoning of cracking sites is responsible for the selectivity change to toluene cannot be excluded on the basis of the results of this investigation. Coughlin *et al.* also observed that regenerating the coked catalyst with pure hydrogen gave a catalyst that was much more selective for hydrogenolysis than the fresh catalyst when the methylcyclohexane feed was reintroduced. We suggest that the high hydrogenolysis activity is provided by the reduced and now relatively coke-free Re, which is as much as five orders of magnitude more active for hydrogenolysis than Pt (*33, 34*). Transient behavior different from that described above was observed in the presence of sulfur (*30*). This result is not surprising since sulfiding may affect the amount, extent, and rate of reduction of the Re.

SUMMARY AND CONCLUSIONS

The results of this investigation extend previous work on the reducibility of Re in Pt–Re/Al_2O_3 catalysts to include the effect of hydrocarbon reactants on the oxidation state of the Re.

Initial experiments were conducted to provide a framework in which the role of the hydrocarbon could be evaluated. Consistent with the report of Onuferko *et al.* (*4*), reduction in dry hydrogen at 500°C gave predominantly Re(+4). Addition of water to the hydrogen resulted in the reduction of rhenium to Re(0) in the bimetallic catalysts, in agreement with the report (*9*) that high concentrations of surface hydroxyl groups favor the reduction of rhenium to the zerovalent state in Pt–Re/Al_2O_3 catalysts. This interpretation is different from that proposed earlier (*6*), according to which water inhibits the reduction of the rhenium. The present results and those of Isaacs and Petersen (*9*) suggest that the high calcination temperature employed in the earlier work (*6*), which was in excess of the reduction temperature, was responsible for the lack of reducibility of the catalyst.

Reduction of the Pt–Re/Al_2O_3 catalysts in a butane + hydrogen stream at 500°C gave Re(0), both in samples with high (2.7 wt%) and low (0.6 wt%) Re loadings. Reduction with butane + hydrogen of a catalyst containing 0.4 wt% Pt and 0.6 wt% Re, initially stabilized with Re in the +4 oxidation state, also yielded Re(0). This result demonstrates that even the most difficult-to-reduce catalyst (*4, 6, 7, 18*) could be reduced to give Re(0) in the presence of the hydrocarbon at 500°C.

Other workers have observed the partial reduction of Re/Al_2O_3 in the presence of aliphatic and aromatic hydrocarbons (*12, 14, 25*), and we have suggested two related interpretations to account for the complete reduction of Re to Re(0) in Pt–Re/Al_2O_3 catalysts. Each explanation is based on the concept of hydrogen transfer via unsaturated hydrocarbons to the metal center. The observation that a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3 has catalytic properties similar to those of Pt–Re/Al_2O_3 (*26, 27*) favors the interpretation that reduction occurs by gas-phase unsaturated hydrocarbons generated on the Pt and present in the naphtha feed, rather than by carbonaceous deposits on the surface.

The results of this work indicate that the

Re in Pt–Re/Al_2O_3 catalysts is reduced to the zerovalent state in the presence of hydrocarbon + hydrogen feeds at 500°C and suggest that the transients in activity/selectivity observed in low-pressure kinetics experiments (*27, 29, 30*) may not be directly extrapolated to steady-state industrial operation.

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