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Distribution of Pt and Re in Pt–Re : Al_2O_3 Naphtha Reforming Catalysts

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The benefit of Re in Pt–Re : Al_2O_3 naphtha-reforming catalysts is clear, but its disposition and function are not. We report here results of surface analysis of ion-scattering spectroscopy and microanalysis by energy-dispersive X-ray spectroscopy in a scanning transmission electron microscope. On both reduced and reduced and sulfided commercial-type catalysts, we found that Re is not significantly associated with Pt, but rather is widely dispersed on the support surface. Sulfiding essentially covers the Re, but leaves most of the Pt exposed.

INTRODUCTION

It is now more than 10 years since the use of Pt–Re : Al_2O_3 to replace Pt : Al_2O_3 as a catalyst for naphtha reforming was announced (*1*). Re addition is clearly beneficial, giving greater stability and higher average reformate yield than Pt-only catalysts (*2*). How Re addition brings about such benefits and how it is disposed in the catalyst remain the subject of considerable discussion, despite some 20 reported studies. We present here the results from applying advanced instrumental techniques to physically characterize commercial-like catalysts.

PREVIOUS STUDIES

Re Valence State

Researchers have sought to establish Re's valence state and whether it is alloyed with Pt in reduced, active catalyst. Early studies relied heavily on chemical probes, such as H_2 uptake during reduction; more recently advanced instrumental characterization techniques have contributed new insights.

Re_2O_7 dissolved in water is a common Re source for catalyst preparations; all investigators assumed that Re remains in the 7+ valence state when such a solution dries on a high-area alumina support. The H_2 taken up per Re atom during reduction is then a measure of how far the Re is reduced. When the water formed from this H_2 is not removed, Re is reduced only to 4+ (*3*), which is expected thermodynamically (*4*). In very dry systems where this water is continually removed, H_2 uptake corresponds to complete reduction to metal for Re alone (*5, 6*) and Pt–Re (*7–9*) supported on alumina, so long as the Re loading is less than 70% of the Pt (*9*) or the catalysts are dried prior to reduction at low temperature only (*10*). Reoxidation stoichiometry agrees with the H_2 uptakes (*9*).

There have been a few efforts to establish Re's valence state directly using physical characterization techniques. X-Ray absorption spectroscopy applied to the Re L_{III} edge showed features interpreted as a mixture of valence states (*11*), though few experimental details were provided. A more recent X-ray absorption study examined both the same edge and the associated extended fine structure (EXAFS) and concluded that Re is in the 4+ state in reduced catalysts (*12*). The valence state problem seems natural for XPS, since the binding energy shifts for the intense 4f peak are large and well known (*13*). However, at the low loading accompanied by Cl on alumina

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typical of commercial catalysts, an apparent oxygen 2s satellite interferes with the Re 4f and the Cl 2s peak interferes with the next most intense peaks, 4d3/2 and 4d5/2 (*14*). Improved signal-to-noise ratio and data treatment will hopefully make use of the less intense peaks practical in the future.

Alloy Formation

Whether Pt and Re form an alloy when supported on alumina as they do when they are bulk metals has attracted more attention than Re's valence state. Here "alloy" is understood to mean that both metals are in the zero-valent state and bonded to each other; it is not necessarily identical to a bulk alloy. Evidence for some substantial interaction, possibly alloy formation, comes from the shift to lower temperature of the H_2 uptake corresponding to Re reduction when Pt is present (*8*). The effect was absent, however, when the catalysts were severely dried (*7*) prior to reduction or when reduced catalysts were severely oxidized and then rereduced (*9*). The reduction temperature shift may require that the two metals be near each other initially or able to surface diffuse, perhaps assisted by water. Catalysts showing a large reduction temperature shift also had greater activity for cyclopentane hydrogenolysis than those showing little shift (*10, 15*), indicating that the shift is associated with a real catalytic difference.

H_2/O_2 titrations have provided evidence about Pt–Re interactions. Compared to the separately supported metals, the bimetallics showed reduced H_2 and increased O_2 uptake (*16*). A later study showed that O_2 chemisorbed on Re can be readily removed when even a small amount of Pt is present, but the Pt is also effective for a mechanical mixture of the separate metals (*17*), showing that interaction cannot be equated with alloy formation. More recently, the same researchers have interpreted enhanced O_2 reducibility as evidence for alloy formation, without reference to their earlier results for the mechanical mixture (*10*).

Reaction studies are the other major probe of alloy formation. The earliest work showed increased C_5+ yield and slower deactivation compared to Pt only in full-scale industrial use (*2*). Laboratory investigation of several reactions revealed quite complex behavior (*15*). Activity for 1,1,3-trimethylcyclohexane hydrogenolysis declined monotonically as Re was added to a level less than that obtained when the two metals were supported separately. Activity in benzene hydrogenation, cyclopentane hydrogenolysis, butane hydrogenolysis, and benzene–deuterium exchange was a maximum near 70% Re. This behavior was understood as the combination of the monometallic activities with a subtle (undefined) electronic interaction between the metals. The same investigators later confirmed their findings for cyclopentane hydrogenolysis and showed that the magnitude of the activity enhancement was correlated with the extent of Re reduction temperature decrease (*10*). Subsequently they found no activity increase for *n*-heptane decomposition, but increasing selectivity toward aromatics as Re was added (*18*). More recently an extensive study of the effect of Re addition on reactions related to reforming (*19*) showed that rates for production of benzene from methylcyclopentane and of toluene from methylcyclohexane and the rate of self-deactivation by methylcyclohexane (short term) were unaffected. In contrast, the rate for methylcyclopentane ring opening decreased, as did the rates for toluene dealkylation and self-deactivation by methylcyclohexane (long term). The latter reactions are believed to be structure sensitive while the former are not, suggesting that Re directly affects Pt, as would be expected if Pt–Re alloys formed.

A live reforming experiment comparing separately and cosupported Pt and Re provides contrary evidence insofar as no difference was found between the mechanical mixture and the bimetallic (*20*). Moreover, postanalysis of the mechanical mixture established that no metal transfer had taken place. Additional experiments in which suspected coke-promoters were spiked into the feed naphtha showed that Re's chief discernible effect was to promote cyclopentane hydrogenation to innocuous paraffins, thereby blocking its dimerization to coke precursors. Re's effect on cyclopentane was different from that observed in the model study (*19*) discussed above. Possibly Re was indeed alloyed in the model study and separately dispersed in the other, giving rise to different catalytic behavior. Taken together, the reaction experiments show that Re does indeed alter the catalytic behavior of Pt in a manner consistent with the benefits attained in industrial practice. They also suggest that alloy formation, if it occurs, is not necessary.

Infrared absorption spectroscopy of molecules adsorbed on the catalyst surface provides a combined instrumental–chemical probe of these sites. Differences between spectra obtained from bimetallics and the separate monometallics can indicate Pt–Re interactions, perhaps alloying. Extensive comparison of such catalysts in both industrial and laboratory forms using NO and CO as probe molecules as a function of preparation and subsequent treatments found no spectral features for the bimetallics that could not be represented as a reasonable combination of features seen for the monometallics (*21*). In contrast, another study of chemisorbed CO on less rigorously predried catalysts (*17*) found unique features in the bimetallics. Features corresponding to linearly adsorbed CO on Pt and on Re shifted frequency and the relative intensity of the band corresponding to CO multiply adsorbed on Pt decreased. Since these same effects were seen earlier for Ni–Cu : SiO_2 where alloy formation was explicitly established, it was concluded that seeing these features for Pt–Re : Al_2O_3 provided evidence for alloy formation. In a later study (*10*), the same investigators confirmed their earlier findings and showed that the extent of interaction as evidenced by the ir spectral features was correlated with the extent of interaction as evidenced by Re reduction temperature shift.

Infrared spectroscopy of carbonaceous residues on Pt, Re, and Pt–Re : Al_2O_3 catalysts showed substantially less carboxylic carbon when Re was present (*22*). Carboxylic carbon was held to be associated with deactivation of the alumina itself, leading to reduced isomerization activity for the catalyst. As with the reaction studies, the ir findings show that interaction may take place, but do not establish that it is alloying or that it is necessarily associated with Re's catalytic benefit.

Alloy formation, if it occurs, should be reflected in lattice parameter changes as determined by X-ray or electron diffraction. The small metal particles typical of industrial reforming catalysts give X-ray diffraction features so broad that they are not useful for lattice parameter determination. Large particles are obtained when such catalysts are thermally sintered and they show the lattice parameter changes expected for alloy formation (*16*). Efforts to obtain electron diffraction from unsintered catalysts have been unsuccessful (*17*). TEM (transmission electron microscopy) has shown that the bimetallic is more resistant to thermal sintering than either monometallic (*16*). Interatomic distances for Re determined by EXAFS showed no bond lengths characteristic of metals, even after 16 hr reduction at 485°C (*12*).

If Pt and Re form an alloy, an elemental analysis technique with high spatial resolution should find that they are codispersed. Such a technique is provided by using the STEM (scanning transmission electron microscopy) accessory to focus a TEM's electron beam down to dimensions comparable to a catalyst metal particle. The characteristic X rays emitted under electron bombardment would then be expected to show both Pt and Re if they are alloyed. Such an investigation of severely reduced catalysts failed to obtain adequate signal counts over background when the beam was focused to the particle size, which was about 1.5 nm (*23*). Increasing the beam diameter to about 100 Å gave spectra showing both Pt and Re, leading to the conclusion that an alloy had formed. However, simply having the two metals near each other without alloy formation would have given the same result.

Sulfiding

None of the above studies has addressed the role of sulfur, though the catalyst is commonly sulfided before use industrially. Subjecting a 0.6% Pt–0.6% Re : Al_2O_3 catalyst to small doses of sulfur (thiophene) after reduction at 500°C suppressed hydrocracking and coke formation, leading to better yield of aromatics (*24*). Sulfiding Pt : Al_2O_3 can bring about similar changes (*25*), perhaps by building a sulfur-walled "box" on the surface, in which only the desired reactions can take place, as suggested by the behavior of sulfided Pt single crystals (*26*). The role of the Re then could be to provide strong "footings" for the sulfur walls, through its strong bond formation in sulfides (*27*). An extensive study of sulfided Pt–Re : SiO_2 using chemisorption, ir, and XPS provides further support for such a model (*28*). Here it was convincingly established that a Pt–Re alloy was formed prior to sulfiding. Comparing the effect on reforming reactions of sulfiding with H_2S on Pt and Pt–Re showed effects similar to the ones noted above, but the Re-containing catalysts were more responsive (*19*). There thus appears to be general agreement that sulfur acts by selectively poisoning certain undesired reactions, perhaps by reducing the size of surface metal atom ensembles, if a Pt–Re alloy forms during reduction.

EXPERIMENTAL WORK

Sample preparation. We studied three commercial-type, laboratory-prepared reforming catalysts obtained in the calcined, unreduced form containing 0.3/0.3, 0.6/0.6, and 0.35/0.85 wt% Pt and Re on γ-alumina extrudates. All contained about 1 wt% Cl. After sweeping overnight in purified nitrogen at 125°C, the catalyst charge was raised to 485°C over 1 hr and held at temperature for two hours while rapid hydrogen flow was maintained. The tube containing the catalyst was then removed from the furnace hot zone and cooled with the hydrogen flowing. For sulfiding, a second batch of catalyst was subjected to the same reduction treatment, but ended by cooling to 425°C rather than room temperature. The hydrogen flow was changed to H_2 + 0.1%v H_2S and maintained for a time to provide a sulfur dose equivalent to converting half the Re in the catalyst to Re_2S_7. Flow of the purified hydrogen was restored and the catalyst cooled as before. The samples were removed and crushed under dry nitrogen in a glove box. All further preparation steps including instrument loading were carried out under dry N_2.

Electron microscopy. The work was carried out on a Vacuum Generators HB-5 dedicated STEM, having a minimum beam diameter of about 5 Å (*29*). Its ion-pumped vacuum system minimizes contamination buildup on the beam-illuminated area during the long times needed to accumulate a statistically significant number of X-ray counts from the smallest beam diameters. We examined individual particles, groups of two or three particles and areas 100 Å or so in diameter. At no point did we encounter any contamination buildup.

Ion scattering spectroscopy. ISS takes advantage of the near unity probability for a low energy (1–2 keV) noble gas ion to be neutralized at a surface so as to obtain essentially first monolayer analytical sensitivity. It is not directly sensitive to whether an element is dispersed monoatomically or as a continuous film, making it an appealing technique for highly dispersed catalysts. Moreover, the energy of the backscattered ions may be adequately interpreted in terms of single binary elastic collisions. Each atomic mass and therefore effectively each element has a unique ratio of backscattered to incident ion energy (E/E_0) for a given bombarding ion. A further consequence is that the bombarding ion must have a significantly lower mass than the elements which it seeks to detect. Important aspects of ISS have been recently reviewed (*30*).

The energy resolution of the instrument determines to what extent the presence of neighbor elements in the periodic table can be detected, since E_0 is very sharply defined by the ion gun. Unfortunately, mass resolution decreases as mass increases to an extent that our instrument cannot detect separate peaks for Pt and Re. With Ne^+ as the bombarding ion and a 137° laboratory scattering angle, the peak width estimated (*30*) for either element alone is 0.030 E/E_0 units. Equal amounts of both in the first monolayer are expected to give a single peak 0.041 E/E_0 units wide under the same conditions. Inherent mass resolution would be improved somewhat by bombarding with Ar^+, but the energy of the backscattered ions would have been shifted to a range where the decreased energy resolution due to the angular acceptance of the analyzer would have offset the benefit obtained. The samples were mounted by pressing into indium.

To obtain information about layers below the first, we subjected all samples to additional ion bombardment to sputter off part of the first monolayer. The sputtering procedure consisted of taking a spectrum, bombarding, and taking another spectrum. For each spectrum, we redetermined the positions of the element peaks to compensate for shifts arising from surface charge variations.

RESULTS

Electron Microscopy

Figure 1 shows an energy-dispersive X-ray spectrum obtained from a 50-Å-diameter area on reduced-sulfided 0.6/0.6 catalyst; it is typical of most of the others. Note the absence of peaks at the locations expected for Re. Using other beam diameters and locations on the 0.6/0.6 material in both the reduced and reduced-sulfided material showed Re in less than one-fifth of the spectra. When seen, Re showed no constant ratio to Pt. Both Pt and Re were localized when detected; S, Cl, and Al were everywhere. Cu which appears in Fig. 1 was present in the specimen support grid and the specimen chamber. Fe was a contaminant introduced to the catalyst during electron microscope specimen preparation. Individual particles gave no counts over background. This result is expected, since we estimate the minimum detectable mass for Re in this system to be about 50 Re atoms using procedures described elsewhere (*31*). Nonetheless, the absence of Re from groups of Pt-containing particles is significant evidence against alloy formation.

Ion Scattering Spectroscopy

Figure 2 shows the spectrum obtained by scattering He^+ from reduced-sulfided 0.3/0.3. We used He^+ as the bombarding ion because it is the only ion that gives signals for all the elements in our catalysts. The problem with mass resolution for the heavy metals (Re, Pt) separated three columns and the modifiers (S, Cl) adjacent in the periodic table is evident. The appearance of a peak for fluorine was unanticipated and we traced it to exposure prior to reduction to room atmosphere in a laboratory where HF was in use. Fluorine was not detected in other materials. For reduced only 0.3/0.3, the modifier peak was narrower and the heavy metal peak broader. The same features were observed for the two other loadings.

Figure 3 shows the variation of intensity with ion dose for several peaks of interest: a sputter profile. Sputtering is a quite complex radiation damage process (*32*) and cannot be interpreted as simply "peeling off" layers from the surface. Some notion of the amount of material removed can be obtained from the ion doses in the figure by knowing that there are about 10^{15} atoms/cm^2 of surface and that typical sputter yields (atoms out per ion in) are in the range 1–4. The significant features are that the rise in the heavy metal peak is strongly associated with the fall of the modifier peak,

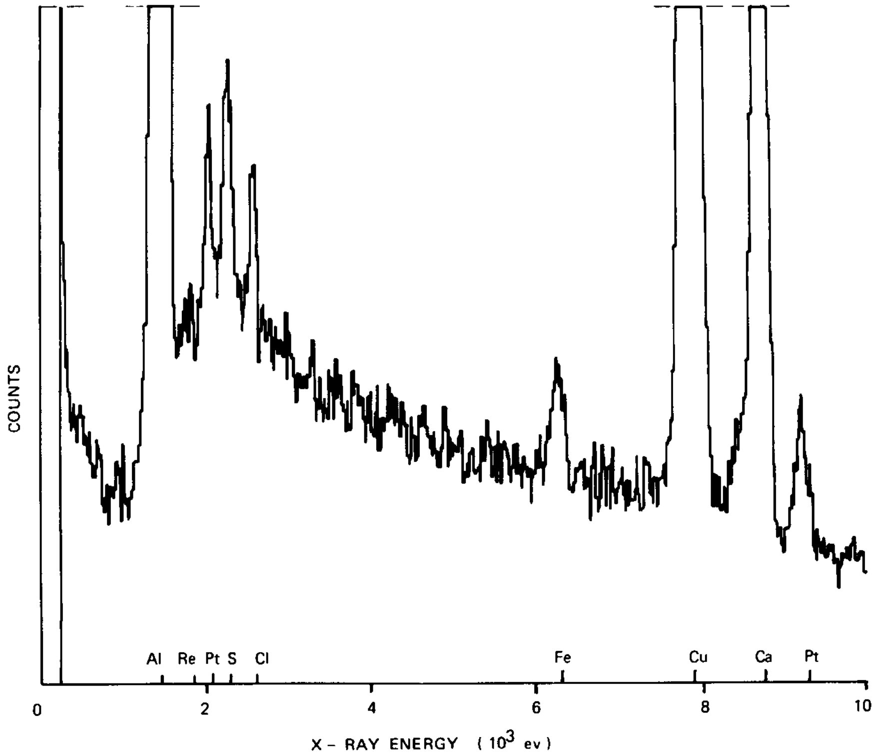

FIG. 1. Energy-dispersive X-ray spectrum from reduced and sulfided 0.6% Pt–0.6% Re : Al_2O_3. X-Ray emission energies for the catalyst constituent elements are as indicated.

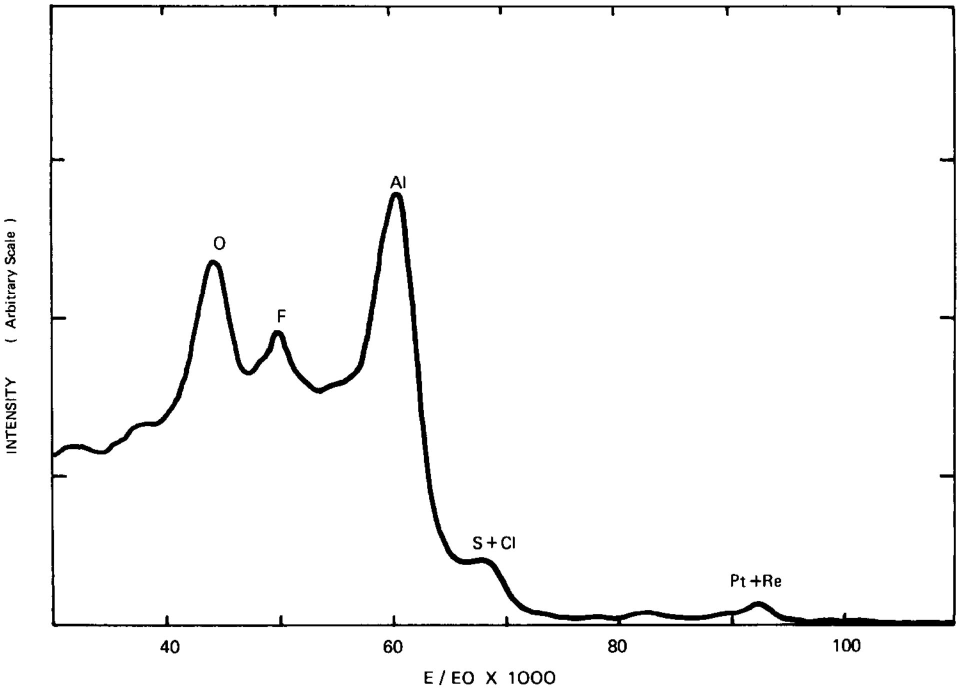

FIG. 2. Helium-4 ion scattering from reduced and sulfided 0.3% Pt–0.3% Re : Al_2O_3.

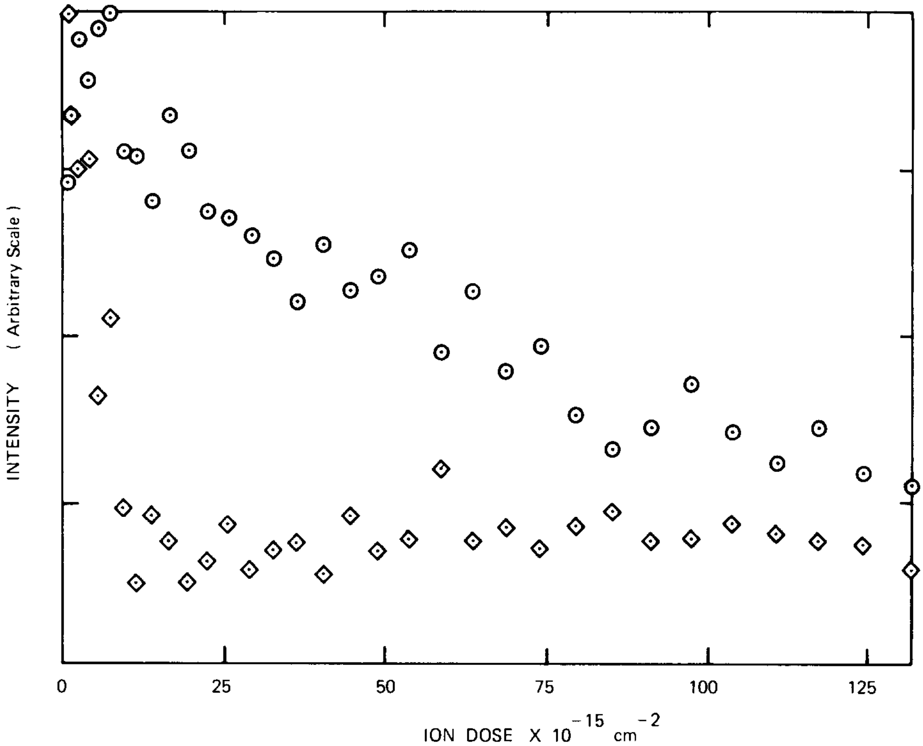

FIG. 3. Sputter profile of the catalyst in Fig. 2, showing the Pt + Re (○) and S + Cl (◇) peaks.

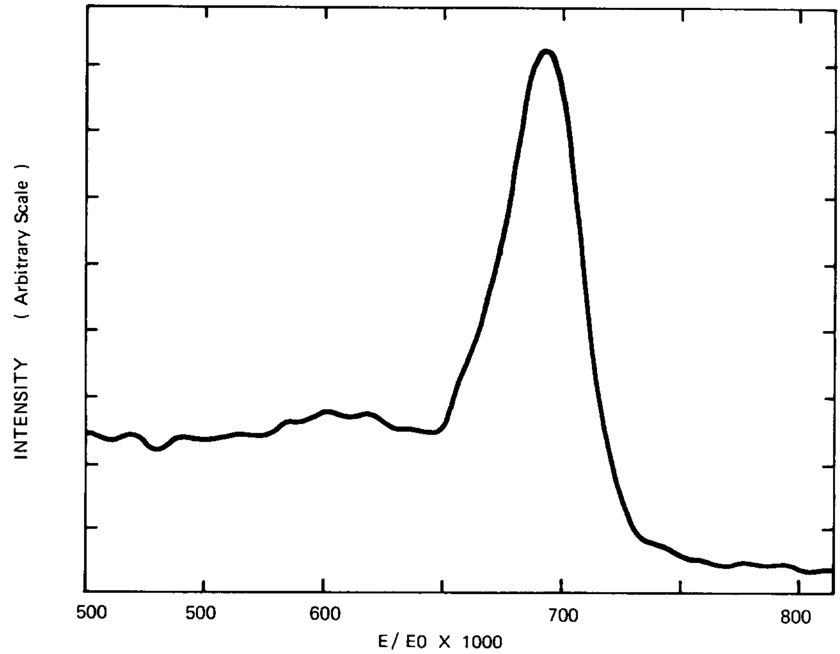

FIG. 4. Neon scattering from reduced-only 0.35% Pt–0.85% Re : Al_2O_3.

and the fall of the fluorine peak is strongly associated with the rise of the aluminum peak as well as the modifier peak. Further, the width of the heavy metal peak increased from about 0.030 to about 0.040 E/E_0 units as the modifier peak fell. This suggests that the modifiers were most strongly associated with one of the metals.

Figure 4 shows a peak obtained by Ne^+ scattering from reduced-only 0.35/0.85 catalyst; note the increased relative sensitivity for the heavy metals. Comparing reduced-only specimens from all three catalysts, the E/E_0 values for the heavy metal peak are 0.695, 0.696, and 0.692, and the peak heights are in the ratio 1, 1.73, and 2.00 for the 0.30/0.30, 0.60/0.60, and 0.35/0.85 catalysts, respectively. The peak shift to lower E/E_0 for the higher Re material could indicate more Re on the surface, but a shift of this magnitude could also come about through small changes in the surface charge neutralization.

Accurate sensitivity factors are not known for highly dispersed supported metals such as ours, so that we cannot assign atom concentrations to the peak heights. Moreover, the peaks did not have identical shapes so that caution is needed even to compare then without seeking absolute values. Nonetheless a few general observations are justified. Doubling the metal loading from 0.30/0.30 to 0.60/0.60 nearly doubled the metal peak height, which is a measure of the metal area. This implies more particles of about the same size rather than increased particle size, consistent with our electron microscope observation that the metal particle size was essentially the same for all catalysts.

The metal peak increase when the Pt/Re ratio was changed at constant loading is surprising. Re's atomic mass is lower than Pt so that there is more metal on the 0.35/0.85 catalyst on an atomic basis, but this can account for only 2% of the difference. Possibly the sensitivity factor for Re is greater than that for Pt so that the total number of ions scattered into the metal peak was greater for the Re-rich catalyst. If 0.60/0.60 and 0.35/0.85 catalyst have the same number of particles of the same size, an Re sensitivity factor 1.9 times that for Pt would account for the difference. Such a difference is not unreasonable. This would not, however, account for the difference vs the 0.30/0.30 catalyst. Still another possibility is that some Re is more "exposed" than the Pt and therefore contributes differently as loading is changed. Such a state might be dispersed more or less uniformly on the support so that the local concentration would rarely be high enough to be detected by STEM/EDS. The uniform distribution of the sulfur, which is associated most strongly with the Re, provides indirect evidence for such a view. Careful chemisorption studies coupled with more extensive electron microscopy and surface analysis are needed to accurately and firmly establish the relationships among particle size, surface, area, and surface composition.

CONCLUSIONS

Though much more work remains to be done, we conclude that, under our conditions, Pt and Re are not significantly alloyed, sulfiding specifically affects Re, and that the Re distribution most consistent with our findings is uniformly upon the support at low concentration.

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