γ-Al₂O₃-Supported Re–Pt Cluster Catalyst Prepared from [Re₂Pt(CO)₁₂]: Characterization by Extended X-ray Absorption Fine Structure Spectroscopy and Catalysis of Methylcyclohexane Dehydrogenation

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Abstract: A model catalyst prepared from [Re₂Pt(CO)₁₂] supported on γ-Al₂O₃ was characterized by extended X-ray absorption fine structure (EXAFS) spectroscopy, and its stability in operation in a flow reactor was tested for the dehydrogenation of methylcyclohexane at 1 atm and 400 °C. EXAFS data characterizing the unused catalyst measured at both the Re L₃ and Pt L₃ edges at liquid nitrogen temperature with the sample in the presence of H₂ distinguish the Re–Pt from the Pt–Pt and Re–Re interactions. The EXAFS results form the basis of a simplified model of the supported bimetallic structures, consisting of Re₉Pt₉ entities, with oxophilic Re in a low positive oxidation state interacting strongly with the oxygen atoms of the γ-Al₂O₃ support and stabilizing the dispersion of the Pt atoms. The catalyst made from [Re₂Pt(CO)₁₂] was found to be more resistant to deactivation during catalytic dehydrogenation of methylcyclohexane than catalysts prepared conventionally from Re and Pt salt precursors. The catalyst prepared from [Re₂Pt(CO)₁₂] was more highly dispersed than the others, and its resistance to deactivation is attributed to the role of Re in stabilizing the dispersion of the Pt.

Introduction

The addition of Re to Al₂O₃-supported Pt catalysts improves the activity maintenance in industrial naphtha reforming, and Re–Pt/γ-Al₂O₃ is the predominant catalyst used for this process. However, notwithstanding years of research, the catalyst structure and the roles of Re remain elusive targets. In attempts to understand the role of Re better, we prepared model Re–Pt/γ-Al₂O₃ catalysts from [Re₂Pt(CO)₁₂] and have already reported the synthesis and characterization by infrared spectroscopy, X-ray photoelectron spectroscopy, and temperature-programmed reduction together with the results for a comparable catalyst prepared from salt precursors. These results demonstrate that [Re₂Pt(CO)₁₂], following deposition on γ-Al₂O₃ and treatment in H₂ at 400 °C, was converted into small bimetallic entities, with the Re present in a low positive oxidation state and largely inaccessible to the probe molecule CO.

Here, we summarize results of structural characterization of the sample by extended X-ray absorption fine structure (EXAFS) spectroscopy and hydrogen chemisorption as well as catalytic performance in methylcyclohexane dehydrogenation. Data are included to compare the performance of the model catalysts made from [Re₂Pt(CO)₁₂] with the performance of Pt/γ-Al₂O₃ and Re–Pt/γ-Al₂O₃ catalysts made conventionally from salt precursors.

EXAFS spectroscopy is among the most incisive methods for the characterization of dispersed catalysts that lack long-range order. This technique has been used to characterize the metal–metal interactions in supported bimetallic catalysts, including Re–Pt/γ-Al₂O₃ prepared from salt precursors. The data showed that, after reduction with H₂ at 500 °C, alloy-like Re–Pt particles were present, but the interpretation was limited by the overlap of the Re L₃ and Pt L₃ edge data. Furthermore, the analysis did not include any contribution from the metal–support interface, and a k³ weighting was used in the Fourier transformation (k is the wave vector), making the analysis insensitive to low atomic weight scatterers, such as the oxygen atoms of the support. Caballero et al. used in situ EXAFS spectroscopy to investigate the effect of hydrocarbon deposits on Pt/γ-Al₂O₃ and on Re–Pt/γ-Al₂O₃ catalysts, detecting a new type of Pt–C bond formation on the bimetallic catalyst under reaction conditions. In their EXAFS analysis, the authors did not attempt to distinguish between Pt–Pt and Pt–Re absorber–backscatterer pairs and did not detect any contribution from the metal–support interface, notwithstanding the small average Pt and Re–Pt cluster sizes (the first-shell metal–metal coordination numbers were 4.4 and 3.6, respectively).

Because of the high dispersion of the metal in our catalyst made from [Re₂Pt(CO)₁₂], there was negligible overlap of the Re- and Pt-edge data in the X-ray absorption spectrum. Thus, the sample presented an excellent opportunity to characterize the Re—Pt interactions without neglecting the metal—support contributions in the data analysis. The results demonstrate that Re and Pt backscatterers can be distinguished well, provided that a low- k weighting (preferably, a k⁰ weighting) is used in the analysis of the EXAFS data.

The catalytic test reaction, dehydrogenation of methylcyclohexane, was chosen because it is a structure-insensitive reaction catalyzed by the metallic function of a reforming catalyst. Because methylcyclohexane is a potential coke precursor, this reaction is appropriate to characterize the deactivation of the metal and acid functions of the catalyst.

Because methylcyclohexane is a structure-insensitive reaction catalyzed by the metallic function of a reforming catalyst, the reaction is appropriate to characterize the deactivation of the metallic function of the catalyst. The conversion of methylcyclohexane proceeds with a high selectivity for toluene formation (although methane and benzene form also), giving a simpler product distribution than other commonly used test reactions for characterization of hydrocarbon reforming, e.g., n-hexane reforming. Moreover, this reaction involves both the metal and acid functions of the catalyst.

**Results**

**EXAFS Spectroscopy.** The raw EXAFS data characterizing the sample made from [Re₂Pt(CO)₁₂] on γ-Al₂O₃ following treatment in H₂ at 400 °C are presented in Figure 1a (Re edge) and Figure 1b (Pt edge). The data represent the sample in the presence of H₂ at nearly liquid nitrogen temperature. Oscillations were completely damped at values of k > 13 Å⁻¹ beyond the Re L₃ edge. Consequently, the contribution from the Re EXAFS at the Pt L₃ edge was less than the noise, allowing the use of standard separate-element methods to analyze the Pt-edge EXAFS function without complicated deconvolution techniques.

Structural results obtained for a sample prepared from [H₃Re₃(CO)₁₂] on γ-Al₂O₃ provided a basis for analysis of metal—support interactions in the bimetallic sample. The Re L₃-edge EXAFS data characterizing the sample prepared from [Re₂Pt(CO)₁₂] were first compared with the Re L₃-edge EXAFS data characterizing the sample prepared from [H₃Re₃(CO)₁₂] by a k⁰-weighted Fourier transformation (Figure 2). As summarized in the section below entitled EXAFS Data Analysis, a k⁰-weighted Fourier transform can distinguish between Pt and Re as neighboring atoms. The Re—O and Re—Re contributions appear in similar radial regions, as indicated by the imaginary part of the Fourier transform. However, an additional contribution was found, in the range 2.4 < r < 2.8 Å. This contribution is inferred to be an indication of the presence of Pt in the neighborhood of Re, because when only a Re—O and a Re—Re contribution were included in the fit, it was not possible to fit the k⁰-weighted Fourier transform in the range 2.4 < r < 2.8 Å (where r is the absorber—backscatterer distance). Moreover, in k space the fit starts to deviate from the data at values of k > 9 Å⁻¹; the amplitude of the fit is too high, and it is clear that another scatterer has to be included, which has a different enough phase shift to diminish the amplitude of the oscillations at high values of k as a consequence of interference.

On the basis of the assumption that a bimetallic interaction can be detected from both the Re L₃ and the Pt L₃ edges, the strategy used in analyzing the EXAFS data for the Re—Pt sample is analogous to the predictor—corrector scheme in numerical analysis; the Re L₃ edge is the predictor and the Pt L₃ edge is the corrector. Because a criterion for a satisfactory analysis was that the same values for the distances (R_p—Re = R_p—Pt) and for the disorder (Δσ_p—Re = Δσ_p—Pt) had to be...
obtained from both the Re-edge and the Pt-edge data, the Re–Pt distance and the Re–Pt disorder (Δσ^2_{Re–Pt}) estimated in the analysis of the Re data were used as the first guesses for the Pt–Re distance and the Pt–Re disorder, respectively. Table 1 includes details of the Fourier transformation and analysis ranges. A three-shell fit (Re–O, Re–Re, and Re–Pt) in r space (Fourier transform range, 3.5 < k < 13 Å⁻¹) with k⁰ weighting, an r-space window of 1 < r < 3.5 Å, and 12 free parameters resulted immediately in a set of coordination parameters nearly the same as the values presented in Table 2. The Pt EXAFS data were also analyzed by using a k⁰-weighted fit in r space with the window 1 < r < 4 Å and a Fourier transform range of 3.5 < k < 8.5 Å⁻¹.

Several structural models were used to guide the fitting of the Pt-edge EXAFS data; they included the following contributions, respectively: (1) Pt–Pt + Pt–Re, (2) Pt–Pt + Pt–Pt + Pt–O, and (3) Pt–Re + Pt–O. The only structural model which led both to acceptable coordination parameters and to an acceptable goodness of fit was that including only a Pt–Re and a Pt–O coordination. Remarkably, the fit based on this model gave approximately the same values for the Pt–Re distance and the Pt–Re disorder term (Δσ^2) as were obtained from the first fit results obtained for the Re-edge data. With the optimized structural parameters obtained from the Pt EXAFS data, the coordination parameters characterizing the Pt edge were further refined until consistent results were obtained from the analysis of both sets of data. The final fits in k space for the Re and the Pt EXAFS are indicated with dotted lines in Figure 1, parts a and b, respectively.

The individual Re–Re, Re–Pt, and Re–O contributions, which constitute the total Re EXAFS signal, are plotted in Figure 3a. The Re–Pt and Re–Re EXAFS signals at values of k > 10 Å⁻¹ are opposite in phase, which explains the rapid damping of the total EXAFS signal at values of k in this range. Inclusion of a Re–Pt contribution in the Re EXAFS data analysis was therefore necessary to give a good fit in this range of k. Figure 3a also shows that the Re–O contribution is dominant at low values of k; thus this contribution cannot be ignored in the analysis.

The individual Pt–Re and Pt–O EXAFS contributions are shown in Figure 3b. The results show that the Pt–O contribution is large at low values of k, which again explains the importance of using a k⁰ weighting in the analysis. The agreement between the Fourier transforms of each individual contribution and the Fourier transforms of the corresponding difference files are shown for the Re and Pt EXAFS analyses in Figures 4 and 5, respectively.

Table 1 includes further details of the fitting procedure and the final goodness of fit values. The coordination parameters obtained in the analysis are given in Table 2. The values in brackets, determined in a statistical analysis of the data, indicate the limits of precision given in the last digit of the values of the coordination parameters. In the statistical analysis of the Pt EXAFS data, the coordination distance and disorder of the Pt–Re coordination were not allowed to vary and were kept equal to the values obtained for the same coordination analyzed from the Re EXAFS data. This method allowed the statistical analysis of the Pt EXAFS data, which were obtained over only a small range of values of k, limiting the degrees of freedom in the fitting.

**Hydrogen Chemisorption.** The hydrogen chemisorption results show that Pt/γ-Al₂O₃ dried at 120 °C in He followed by reduction in H₂ at 500 °C had a H/Pt ratio (atomic) of 0.92, whereas Pt/γ-Al₂O₃ dried in He at 500 °C followed by reduction in H₂ at 500 °C had a lower fraction of the metal atoms exposed, as indicated by a H/Pt ratio (atomic) of 0.51. The treatment conditions stated here match those used in the catalysis experiments.

**Catalyst Performance.** The catalysis experiments were carried out to provide a comparison of the performance of the [Re₂Pt(CO)₁₂]-derived catalyst with those of conventional salt-derived catalysts; two of the latter (without Re) were prepared to have different fractional exposures of Pt by variations in the
the conditions of treatment (drying and reduction), as stated in the preceding paragraph; a third salt-derived catalyst contained both Re and Pt.

Under the conditions of these experiments, each catalyst was characterized by a high initial conversion, >90%. The results of the catalytic reaction experiments do not provide a meaningful discrimination of the catalysts on the basis of initial activities. Rather, they indicate clear distinctions with regard to catalyst stability. The conversion of methylcyclohexane observed with each catalyst decreased with time on stream in the flow reactor (Figure 6). The [Re₂Pt(CO)₁₂]-derived catalyst was the most resistant to deactivation; after 40 h on stream, it was markedly more active than the other catalysts. Of the two Pt/γ-Al₂O₃ catalysts, the one with the higher fractional exposure of Pt was the more resistant to deactivation.

The catalysts were similar to each other in their selectivities. The selectivity for dehydrogenation, measured by the yield of toluene (defined as moles of toluene formed/mole of methylcyclohexane converted) as a function of time on stream, is shown in Figure 7. Each catalyst was characterized by an induction period of about 20 h, after which the yield of toluene was about 90%.

The data are accurate enough to provide only partial information regarding the minor products. The hydrodealkylation conversion is indicated by the fraction of methane and the fraction of benzene in the product stream. The product analyses for methane were more accurate than those for benzene, and thus the former are taken as the best indication of the selectivity for toluene dealkylation. The results agree qualitatively with those reported by Jossens and Petersen with regard to the selectivities for dehydrogenation and hydrodealkylation of methylcyclohexane by γ-Al₂O₃-supported Re-Pt and Pt catalysts prepared from salt precursors.

The treatment conditions influencing Pt crystallite growth during activation of salt-derived Pt/Al₂O₃ catalysts affect the products of the reaction.

During the reduction of PtO$_2$ to give Pt at high temperatures, the rate of Pt migration and sintering is weakened. Thus an experiment was done to test for a change in the fraction of Pt exposed as a result of Pt sintering during the catalyst preparation. In one of the preparations, the He flow was switched to H$_2$ flow at high temperature during the activation of a Pt/γ-Al$_2$O$_3$ catalyst. After drying at 500 °C in He, the Pt/γ-Al$_2$O$_3$ catalyst was cooled to room temperature in He, and instead of beginning H$_2$ flow to replace He after a temperature of 500 °C had been reached, the H$_2$ flow was maintained during the entire heating process, as the temperature was ramped to 500 °C. After continued treatment in H$_2$ at 500 °C for 4 h, the catalyst was subjected to the same reaction conditions for methyclyclohexane dehydrogenation as the Pt catalyst with a lower fractional exposure of Pt, which had been dried at 120 °C in He followed by treatment in H$_2$ at 500 °C.

The rates of deactivation of these two catalysts were different (Figure 6); these results suggested that the fractional exposure of the Pt (which was influenced by the sintering) was important in determining the rate of catalyst deactivation.

**Discussion**

**Distinguishing Pt and Re Scatterers in the Presence of Low-Z Scatterers.** The results of the EXAFS data analysis show that it is possible to distinguish between Re and Pt as backscattering atoms, provided that no $k$ weighting is used in the analysis. It is immediately clear from Figure 3, parts a and b, that inclusion of Re–O and Pt–O contributions from the support is necessary to obtain a satisfactory analysis of the Re and Pt EXAFS data characterizing the sample prepared from [Re$_2$Pt(CO)$_{12}$]. Metal–support contributions can be detected only if these contributions are a large enough part of the total EXAFS spectrum, i.e., only if the metal particles or clusters are small enough. The fact that it was possible to obtain a good fit of the data by using only first-shell metal–metal and metal–oxygen contributions is also a strong indication that the bimetallic clusters in the sample consisted of only a few metal atoms.

**Structural Model of Supported Pt–Re Clusters.** The EXAFS data provide the basis for a structural model of the supported bimetallic clusters, as follows. Analysis of the Pt L$_{III}$-edge EXAFS data shows that there were only Re and O neighbors around each Pt atom, with an average Pt–Re distance of 2.74 Å and an average Pt–Re coordination number of 2.5 (any hydrogen backscatters were not detected in the EXAFS analysis). Analysis of the Re L$_{III}$-edge EXAFS data resulted in an average Re–Pt coordination number of 0.8. The average Re–Re coordination number was 2.6. The Pt–support interface is characterized by a Pt–O coordination number of 1.5 with a distance of 2.69 Å. The Re–support interface is characterized by a Re–O coordination number of 2.4 with a distance of 2.14 Å.

These data form the basis for a structural model of the supported bimetallic species, but because the coordination numbers and distances are averaged over all the different types of coordinations present, the structural model is simplified. The model is shown in Figure 8; it does not account for any hydrogen present. The coordination numbers representing the model are compared in Table 3 with the values determined in the EXAFS analysis. The agreement is good. The model implies that two Re$_2$Pt moieties originating from the [Re$_2$Pt(CO)$_{12}$] precursor were the building blocks of the average supported bimetallic cluster, which is represented as approximately Re$_4$Pt$_2$. We stress that this model represents the catalyst in the presence of H$_2$ at nearly liquid nitrogen temperature in a state prior to application.
under catalytic reaction conditions, the structure was likely modified by the reactants.

The Re–O and Pt–O coordination numbers are crucial parameters for the structural model. The average Pt–O and Re–O coordination numbers \( N \) obtained from the EXAFS data analysis \((N_{\text{Pt–O}} = 1.5, N_{\text{Re–O}} = 2.4)\) can be explained only by a model in which the Re–Pt cluster has a [111] epitaxy in registry with the [111] surface planes of the \( \gamma \)-Al\(_2\)O\(_3\) support. This arrangement corresponds to a layer of Re atoms that are all in contact with the support, with each Re atom positioned in a 3-fold hollow site, corresponding to an average Re–O coordination number of 3. Within the expected limits of accuracy of the experimental Re–O coordination number determined in the EXAFS analysis, this value (2.4) is indistinguishable from the value of 3 corresponding to the model. The average Pt–O coordination number of 1.5 is accounted for if one Pt atom is placed in a 3-fold hollow site, thus having three oxygen neighbors of the support, and if the second Pt atom is coordinated only to Re atoms and is positioned on top of the layer of Re atoms (Figure 8).

The suggestion that the clusters reside on the [111] surface of \( \gamma \)-Al\(_2\)O\(_3\) is consistent with the surface chemistry of \( \gamma \)-Al\(_2\)O\(_3\) powder. The [111] surface plane of \( \gamma \)-Al\(_2\)O\(_3\) is not the only plane exposed by powder \( \gamma \)-Al\(_2\)O\(_3\), but it is stable and has been suggested on the basis of electron diffraction and electron microscopy21–23 to be the predominant surface. Consistent with the structural hypothesis, the metal–support interface structures of Rh/\( \gamma \)-Al\(_2\)O\(_3\)24 and Ir/\( \gamma \)-Al\(_2\)O\(_3\)25 determined from EXAFS data are consistent with the assumption that the metal particles are preferentially positioned on the [111] surface planes of the support. Additional EXAFS evidence of a [111] epitaxy has been obtained for Pt/\( \gamma \)-Al\(_2\)O\(_3\), for which the formation of the metal–support interface was followed as a function of the reduction temperature.26

Characterization of the sample made from \([\text{Re}_2\text{Pt(CO)}_{12}]\) by X-ray photoelectron spectroscopy and threshold resonance experiments2 indicated the presence of Re in a low positive oxidation state. This low-valent form has an average Re–Re distance of 2.61 Å, determined by the EXAFS data, which is 0.13 Å less than the value for bulk Re metal. A short Re–Re distance of 2.67 Å was also determined by EXAFS analysis for \( \gamma \)-Al\(_2\)O\(_3\)-supported clusters formed from \([\text{H}_3\text{Re}_3\text{(CO)}_{12}]\) after treatment in \( \text{H}_2 \).13 X-ray photoelectron spectroscopy also indicated a low, non-zero oxidation state of Re in this sample,2 which was modeled as trirhenium rafts on the surface of \( \gamma \)-Al\(_2\)O\(_3\).13

Metal–metal distances in small supported clusters of noble metals are contracted relative to those of the bulk metal.27–29 Theoretical calculations30 show that a contraction of the metal–metal distance with decreasing cluster size is a consequence of a decrease in the delocalization energy, which leads to a higher charge density between the metal atoms. This leads to a better screening of the nuclei, resulting in a shortened metal–metal distance. However, the EXAFS experiments described in this paper were carried out with samples in the presence of chemisorbed hydrogen. Chemisorption of hydrogen leads to withdrawal of electron density from the metal atoms25 and therefore tends to cancel the effect of decreasing the delocalization energy; in the presence of chemisorbed hydrogen30,31 the metal–metal distance relaxes back to values nearly equal to those observed for bulk noble metals. Thus, the short Re–Re distance of 2.61 Å observed here for the Re–Pt clusters in the presence of chemisorbed hydrogen can only be explained by the positive oxidation state of the oxophilic Re, consistent with the X-ray photoelectron spectra.

The 2.14-Å Re–O distance is in close agreement with the metal–oxygen distances characterizing the metal–support interface in reduced \( \gamma \)-Al\(_2\)O\(_3\)- and KLTG zeolite-supported Pt catalysts after reduction at high temperatures \((\geq 450 \degree \text{C})\)3,8 and is regarded as a bonding distance characteristic of oxygen ions interacting with cations in low oxidation states.32 In contrast, the 2.69-Å Pt–O distance is typical of the metal–oxygen distances observed in noble metal–metal oxide support interfaces in which atomic (chemisorbed) hydrogen is present3,20,24 and which have been reduced at temperatures in the range of 300 to 450 °C. Reduction at high temperatures \((\geq 450 \degree \text{C})\)3,8 or evacuation at 350 °C after low-temperature (300 °C) reduction33 leads to the disappearance of this long metal–oxygen

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**Table 3.** Comparison of Coordination Numbers \( N \) Characterizing EXAFS Data Analysis and Structural Model

<table>
<thead>
<tr>
<th>coordination</th>
<th>EXAFS</th>
<th>model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re–Re</td>
<td>2.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Re–Pt</td>
<td>0.8</td>
<td>1.25</td>
</tr>
<tr>
<td>Re–O</td>
<td>2.4</td>
<td>3.0</td>
</tr>
<tr>
<td>Pt–Re</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Pt–O</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

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distances and results in a direct contact of the interfacial metal atoms with the support oxygen ions at a distance of about 2.1 or 2.2 Å, which is a metal ion–oxygen bonding distance. Readsorption of hydrogen at room temperature after evacuation at low temperatures restores the metal–oxygen distance of about 2.7 Å. The differences between the Re–O and the Pt–O distances observed after reduction at 400 °C with the sample measured in the presence of H₂ are inferred to result from the oxophilic nature of Re, favoring its coordination with oxygen, while atomic hydrogen could still be present between the Pt and its oxygen neighbors of the support.

The structural model of Figure 8 is consistent with all the available characterization data. For example, infrared spectra indicated the lack of adsorption of NO or CO on Re in the bimetallic sample made from [Re₂Pt(CO)₁₂]. The absence of these adsorbates on the Re led to the suggestion that nearby Pt blocked adsorption on Re. This suggestion is consistent with the structural model, whereby one Pt atom lies atop the Re monolayer, covering the Re atoms, and the other Pt atom is in direct contact with the support and also directly accessible for adsorption.

The intimacy of Pt and Re in this novel structure presumably makes the reduction of Re more facile than that in a sample prepared from the separate precursors [H₃Re₃(CO)₁₂] and [Me₂Pt(COD)]; the latter demonstrated no difference in its reducibility of Re by H₂ relative to that of a monometallic Re sample. We conclude that the Pt and Re in the latter sample were not in intimate contact.

Thus, in the catalyst made from [Re₂Pt(CO)₁₂], Re exists at the interface between Pt and the Al₂O₃ surface, and its oxophilicity may promote a strong bonding of the clusters to the Al₂O₃ surface. Electron-deficient Re is expected to be more strongly bonded to the support than metallic Re. Since Pt is stably bonded to Re in the bimetallic structure, we suggest that low-valent Re cations are better ligands for Pt than the available alternatives. The small cluster size also allows the exposure of Re and Pt to O₂ during passivation in a temperature-programmed oxidation, resulting in the oxidation of metallic Pt to Pt²⁺ and of low-valent Re to Re⁶⁺ or Re⁷⁺, as was observed. The low temperature for the maximum rate of reduction of the passivated cluster-derived Pt–Re sample also confirms the relative intimacy of Re and Pt.

The structural model of Figure 8 does not closely resemble any known molecular analogue, but it makes good chemical sense in that the oxophilic Re is coordinated to as many oxygen atoms of the support as possible (assuming the [111] face of the γ-Al₂O₃), and the Pt atoms are as highly coordinated as possible given the arrangement of Re atoms indicated by the EXAFS data. We suggest that structures similar to those of the model formed on the support surface as a result of decarboxylation of the precursor formed from [Re₂Pt(CO)₁₂] by treatment in H₂ at 400 °C and that these surface species are quite stable. Because the model is based on EXAFS data determined near liquid nitrogen temperature, it is not known how closely the structures present during catalysis or chemisorption resemble the model.

In summary, we conclude that the proposed structural model representing the sample prepared from [Re₂Pt(CO)₁₂] on γ-Al₂O₃ is consistent with the results of all the physical characterization data. We emphasize, however, that because EXAFS spectroscopy gives only average structural information, the bimetallic cluster proposed in Figure 8 is not expected to be unique. It seems likely that other small bimetallic clusters having similar structural characteristics but containing fewer or more Re and Pt atoms exist in a mixture of surface species.
the appropriate variables (shown elsewhere) is a function of dispersion for a given metal loading. The slope of the plot of rate constant. Surface areas of exposed metal and of active sites for coke formation are summarized in Table 4.

The data were linearly regressed from on stream time 15 to 50 h, initial high conversions the reaction came close to equilibrium. The ratio of the Pt surface areas estimated from the catalysis data plotted as suggested by eq 4 for these two supported Pt catalysts (that dried at 120 °C and that dried at 500 °C) was determined to be 1.8, and their metal dispersion ratio was found by hydrogen chemisorption to be 1.6. Within the limit of accuracy of the chemisorption and reaction experiments, the ratio of the ordinate intercepts is in good agreement with the ratio of exposed metal areas. This agreement suggests the appropriateness of the assumptions underlying the simple model presented here.

The value of \( k_0A_1\tau \) characteristic of the \([\text{Re}_2\text{Pt(CO)}_{12}]\)-derived catalyst is greater than the corresponding values characteristic of the other catalysts. This result implies that the \([\text{Re}_2\text{Pt(CO)}_{12}]\)-derived catalyst had the maximum number of exposed and catalytically active metal atoms. This inference is in agreement with a structural model in which Pt is located on top of the Re monolayer with 100% dispersion. The Re−Pt salt-derived catalyst is characterized by a smaller value of \( k_0A_1\tau \) than the \([\text{Re}_2\text{Pt(CO)}_{12}]\)-derived catalyst (Table 4). Thus, consistent with the above interpretation, we infer that the former had fewer catalytically active metal atoms exposed than the latter.

To examine whether the intercept of the linear plot suggested by eq 4 is a function of the exposed metal surface area, \( A_1 \), the fractional exposure of Pt of the two \( \gamma\)-Al\(_2\)O\(_3\)-supported catalysts from the same batch after the activation procedures was measured by \( \text{H}_2 \) chemisorption. The \( \text{H}/\text{M} \) value of each Pt catalyst was converted to metal dispersion by the correlation determined by Kip et al., which is based on the assumption that the metal clusters were hemispherical. The two \( \gamma\)-Al\(_2\)O\(_3\)-supported Pt catalysts with the same Pt loading have fractional Pt exposures of 0.85 (\( \text{H}/\text{M} = 0.92 \)) and 0.54 (\( \text{H}/\text{M} = 0.51 \)).

<table>
<thead>
<tr>
<th>catalyst</th>
<th>( k_0A_1\tau )</th>
<th>( k_0A_2 ), h(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/( \gamma)-Al(_2)O(_3), salt derived(^a)</td>
<td>1.95</td>
<td>0.019</td>
</tr>
<tr>
<td>Pt/( \gamma)-Al(_2)O(_3), salt derived(^b)</td>
<td>1.08</td>
<td>0.021</td>
</tr>
<tr>
<td>Re−Pt/( \gamma)-Al(_2)O(_3), salt derived</td>
<td>1.24</td>
<td>0.020</td>
</tr>
<tr>
<td>Re−Pt/( \gamma)-Al(_2)O(_3)</td>
<td>2.56</td>
<td>0.011</td>
</tr>
<tr>
<td>([\text{Re}<em>2\text{Pt(CO)}</em>{12}]) derived</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Sample dried at 120 °C and then reduced; see text. \(^b\) Sample treated at 500 °C in He for 1 h followed by reduction in \( \text{H}_2 \) at 500 °C; see text.

Where a is the activity factor related to coke formation, \( P_m \) is the partial pressure of methylcyclohexane in the reactant stream, \( t \) is the contact time, \( \tau \) is the on stream time, \( k_0 \) is the rate constant for the dehydrogenation reaction, and \( k_d \) is the decay rate constant. Surface areas of exposed metal and of active sites for coke formation are assumed to be independent of the \( \text{H}_2 \) partial pressure and first order in methylcyclohexane. Furthermore, for simplicity, the exponent of \( a \) is assumed to be one.

Integrating eq 2 from on stream time 0 to \( t \) leads to the following expression for the activity factor \( a \):

\[
\ln \left( \frac{P_m}{P_m^0} \right) = \ln \left( k_0A_1\tau \right) - \left( k_0A_2 \right)t
\]

Substitution of eq 3 into eq 1 followed by integration gives an expression in terms of the inlet partial pressure, \( P_m^0 \), and outlet partial pressure, \( P_m \), of methylcyclohexane. Data that are consistent with the model are expected to fall near a linear plot indicated by the following equation:

\[
\ln \left( \frac{P_m}{P_m^0} \right) = \ln \left( k_0A_1\tau \right) - \left( k_0A_2 \right)t
\]
Thus, on the basis of its performance for methylcyclohexane dehydrogenation, the catalyst prepared from [Re2Pt(CO)12] is regarded as a prototype supported bimetallic cluster catalyst with a maximized Pt dispersion and a maximized resistance to deactivation. Furthermore, the EXAFS data demonstrate that the supported bimetallic clusters have such simple structures that they can be regarded as nearly molecular in character, being modeled as Re2Pt2. Like commercial naphtha-reforming catalysts, the catalyst derived from [Re2Pt(CO)12] consists of an oxophilic metal and a noble metal, with the oxophilic metal contributing to the stability of the noble metal.

Experimental Methods

Catalyst Preparation. Catalysts were prepared by adsorption of [Re2Pt(CO)12] on γ-Al2O3 followed by thermal treatment to remove the carbonyl ligands. Salt-derived γ-Al2O3-supported Pt (0.36 wt % Pt) and Re–Pt catalysts (0.32 wt % Pt and 0.59 wt % Re) were prepared from aqueous solutions of the precursors [Pt(NH3)4](NO3)2 and NH4-ReO4 by the incipient wetness technique. The catalyst preparations are described in detail elsewhere.2

Catalyst Testing. The catalysts were tested in a fixed-bed flow reactor with an inside diameter of 1.3 cm. Conversion of methylcyclohexane was measured as a function of time on stream with reactants flowing at a constant rate. Methylcyclohexane (Baker, 99%) was degassed, dried with activated 4A zeolite, and stored under dry N2 before use. It was introduced into the reactor stream at a constant flow rate with a syringe pump. The flowing liquid was vaporized and mixed with a flowing preheated mixture of H2 (Matheson, 99.999%) and He (Matheson, 99.999%). Each of these feed gases was purified by flow through traps containing particles of Cu and activated 4A zeolite to remove traces of O2 and moisture, respectively. The catalyst powder (50 mg) was mixed with inert particles (Fisher “RR” Alundum, 90 mesh) in the volume ratio of 1 to 10 to minimize bypassing in the reactor.

In the catalysis experiments, the temperature was 400 °C, the pressure atmospheric, and the weight hourly space velocity (WHSV) of methylcyclohexane 9.3 g of methylcyclohexane/(g of catalyst h). The total gas flow rate was 45 mL (NTP)/min, with a methylcyclohexane/H2/He volumetric ratio of 1/11/10.

The product vapors were analyzed with an on-line gas chromatograph equipped with flame ionization detectors. Aliphatic hydrocarbons (C1–C3) were separated at 65 °C in a 4.6-m × 3.2-mm column packed with 23% SP-1700/Chromosorb P AW. Benzene, methylcyclohexane, and toluene were separated in a 3.1-m × 3.2-mm column packed with 10% TCEP/Chromosorb P AW in series with a 1.5-m × 3.2-mm column packed with 5% Apiezon L on Chromosorb W AW.

In a blank test performed with the reactor packed with inert alundum particles pretreated with flowing H2 at 500 °C for 4 h, no conversion of methylcyclohexane and H2 was observed. Catalysts prepared by adsorption of [Re2Pt(CO)12] (0.33 wt % Pt, 0.59 wt % Re) on γ-Al2O3 were loaded into the tubular reactor in a N2-filled drybox and brought on stream without air exposure. They were treated in flowing H2 at 400 °C for 4 h [flow rate = 100 mL (NTP)/min] with a heating rate of 5 °C/min. Salt-derived catalysts were dried at 120 °C for 1 h in flowing He followed by heating in flowing H2 from 120 to 500 °C [flow rate 100 mL (NTP)/min] with a heating rate of 10 °C/min. The reduction was completed by treatment of the sample in flowing H2 at 500 °C for 4 h. Another γ-Al2O3-supported Pt catalyst prepared from a salt precursor was dried at 500 °C for 1 h in flowing He followed by introduction of flowing H2 at 500 °C; this temperature was held for 4 h to give a different Pt dispersion from that of the similarly prepared sample. After reduction of the catalyst, the reactor was cooled in flowing H2 to 400 °C before the flow of reactants was started.

Hydrogen Chemisorption. Hydrogen chemisorption experiments were carried out with a Micromeritics Chemisorb 2800 instrument to determine H/Pt ratios as a measure of the fraction of the Pt exposed in the supported Pt catalysts. Such experiments were not attempted for the Re–Pt catalysts because of the uncertainty in the H/metal stoichiometry that would be needed to estimate the fraction of metal exposed.

EXAFS Data Collection. EXAFS data were collected at Station C-2 of the Cornell High Energy Synchrotron Source (20–40 mA, 5 GeV), which was equipped with a detunable channel-cut Si(111) monochromator. Data were also collected at beamline X-11A of the National Synchrotron Light Source at Brookhaven National Laboratory (2.5 GeV, 60–145 mA) with a Si(111) monochromator, and at the wiggler station 9.2 at the Synchrotron Radiation Source of the Daresbury Laboratory, Warrington, UK (1.9 GeV, 100–200 mA) with a Si(220) monochromator. All experiments were performed in transmission with optimized ion chambers. Each monochromator was detuned at 50% to minimize contamination arising from higher harmonics. The internal consistency of the data collected at the different stations was always checked with EXAFS data obtained with a standard 3.5-mm Pt foil. Differences in amplitude were no more than 10% from one data set to another. Precautions were taken to optimize all the EXAFS spectrometers and data collecting procedures to maximize the signal-to-noise ratio. Measurements of the samples were done at the Re LIII (10534 eV) and Pt LIII (11564 eV) edges.

Each sample was pressed to give a self-supporting wafer in a sample holder, with the amount calculated to yield optimal absorption measurements (μx = 2.5) at the Re LIII and Pt LIII edges. The sample holder was mounted in a heatable and evacuable EXAFS cell equipped with thin Be windows. Sample treatments at high temperature and transmission measurements at liquid nitrogen temperature were performed with the sample in the same cell, protected from exposure to air.

The samples were treated in H2 (99.999% purity, 100 mL/min, with a heating rate of 5 °C/min) at 400 °C for 4 h and cooled in flowing H2 to room temperature. Data were collected with samples under static H2 at approximately liquid nitrogen temperature.

EXAFS data were also obtained at liquid nitrogen temperature for a series of compounds used as references in data analysis. Re powder (average particle size, 3–4 μm, 99.999% purity, Goodfellow) was mixed with γ-Al2O3 and pressed into a self-supporting wafer. The sample in the EXAFS cell was reduced in H2 at 400 °C for 1 h and cooled in flowing H2. The other reference compounds were Pt foil (Goodfellow, 3.5 mm), Na2Pt(OH)4, NH4ReO4 (Alfa), K2ReCl6 (Alfa), and Na2PtCl6 (Strem). They were used as supplied, and the powder samples were mixed with γ-Al2O3 to achieve an optimal absorption of μx = 2.5 with Δμx = 1.

EXAFS Data Analysis

Data Reduction and Analysis Methods. Standard procedures were used to extract the EXAFS data from the measured absorption spectra. Normalization was done by dividing the absorption intensities by the height of the absorption edge and subtracting the background by using cubic spline routines.24

The spectra were analyzed by using an improved version of the Utrecht/Eindhoven EXAFS data analysis software (XDAP), including statistical analysis. The statistical analysis is based upon the methods described elsewhere.41 The parameters extracted from the measurements are the previously defined N, R, Δσ0, and ΔE0 (each of the latter with respect to the appropriate reference compound) for the various coordination shells. In this investigation, a k4 weighting was used for the primary fit. The program allowed simultaneous monitoring of the k4-weighted fits in k space and in r space as well as the sum of the squares of the residuals between the fit and the data for the k4-weighted function and for both the magnitude and the imaginary parts of the Fourier transform.

The difference file technique was applied together with phase-corrected Fourier transforms to identify the different contributions in the EXAFS data.5 Control of the difference files with application of both k2 and k4 weighting is required for good fitting as the dependence of k on the backscattering amplitude of low-Z elements (such as O) is different from that on the backscattering amplitude of high-Z elements (such as Re and Pt); the backscattering amplitude of a low-Z element becomes very small at k < 7 Å−1, whereas that of a high-Z scatterer is still significant at higher values of k.5 Optimization of both the k2- and k4-weighted fits also results in a better decoupling of the EXAFS

Although [Re₂Pt(CO)₁₂] would at first appear to be an appropriate
to difficulty in analyzing the bimetallic contribution in the EXAFS data.

Re carbonyl contribution, Re L III edge hinders the correct identification and extraction of the RePt
···
and the Re contribution by inverse transformation (the Re -
the Fourier transformation of the raw EXAFS function. 42
0.5) Å

Reference Data. EXAFS data obtained for reference compounds
were analyzed first to obtain in pure form the contribution of each
absorber-backscatterer pair. Table 5 summarizes the Fourier transform range (k_min and k_max) and the crystallographic data characterizing
the first coordination shell of each reference compound. The
valid range in k space for use of the reference compounds in modeling
each absorber−backscatterer pair is between (k_min + 0.5 Å⁻¹ and (k_max
− 0.5) Å⁻¹. This practice minimizes the truncation errors caused by the Fourier transformation of the raw EXAFS function. 43

Re−Pt and Pt−Re Absorber−Backscatterer Pair. The absence
of a suitable reference compound for the Re−Pt and Pt−Re pairs leads to
difficulty in analyzing the bimetallic contribution in the EXAFS data.
Although [Re₆Pt(CO)₁₂] would at first appear to be an appropriate reference for the Re−Pt pairs, the overlap of the Re−Pt peak with the
Re carbonyl contribution, Re...O*, in the Fourier transform of the Re L III edge hinders the correct identification and extraction of the RePt
contribution by inverse transformation (the Re−Pt distance is 2.83 Å,
and the Re...O* distance is 3.12 Å). 44 Moreover, if one attempts to
derive the Re−Pt contribution by first subtracting the Re carbonyl contribution from the experimental EXAFS function, the presence of
only one Pt neighbor about each Re atom may lead to a large uncertainty
in deriving the normalized amplitude function. The same problem arises
in obtaining a Pt−Re interaction from data for [Re₆Pt(CO)₁₂].
Therefore, the Re−Pt and Pt−Re phase shift functions and backscattering amplitudes were composed by using other reference compounds.

The normalized backscattering amplitude [F*(k)] (defined by
Vaarkamp et al. 45) has been found to be a function of the backscattering
atom. 46 The function F*(k) is generally the same for the absorber−
backscatterer pairs A–B and A′–B, where A and A′ are different absorbers. 47 Therefore, F*(k) for the Re−Re pair can be used for the
Pt−Re pair, and vice versa for the Pt−Pt and Re−Pt pairs.

The property of the additivity and the transferability of the phase
shift function is 48 used to compose the Re−Pt and Pt−Re contributions.
According to theory, 49 the phase shift function of the absorber (A)−
backscatterer (B) pair X−Y consists of a linear combination of qₐ(X),
due to the absorbing atom X, and qₐ(Y), due to the backscattering atom
parameters (N and ΔE₀; R and ΔE₀). 5 In some cases the EXAFS
coordination numbers N, obtained in the data analysis had to be
corrected for the difference in distance between the absorber−
backscatterer pair of the reference shell and that of the shell to be
analyzed. This correction is required because the factor exp(−2R/kλ)
in the EXAFS formula is not always negligible. 3 The correct
coordination number N is therefore N = |exp(−2(R−R₀)/kλ)| with λ
taken to be equal to 6 Å, which is a good approximation for values of
k > 3 Å⁻¹. 5

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only one Pt neighbor about each Re atom may lead to a large uncertainty
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F*(Re−Re)(k) = F*(Pt−Re)(k)
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The property of the additivity and the transferability of the phase
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According to theory, 49 the phase shift function of the absorber (A)−
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due to the absorbing atom X, and qₐ(Y), due to the backscattering atom

Figure 9. (a) Model Pt−Re EXAFS function (solid line) (calculated
with Pt−Re reference with input parameters given in Table 6) and fit
(with Pt−Pt as reference, fit of results given in Table 5). (b) Model
Pt−Re EXAFS (see part a) (solid line) and fit (with Re−Re as reference,
fit of results given in Table 6).

B, in the L₄₄ absorption edge.

This implies that Re−Pt and Pt−Re phase shift functions can be
determined by using a combination of phase shift functions derived
from other reference compounds such as Pt foil, Re powder, K₂ReCl₆,
and Na₂PtCl₆. Sinfelt et al. 46 used this approach to analyze data for a
supported Ru−Cu catalyst with theoretical phase shift functions. The
Re−Pt and Pt−Re phase shift functions reported here are composed from the following combination of experimental phase shift functions:

q(Re−Pt) = q(Pt−Cl) + q(Re−Re) − q(Pt−Cl)
q(Re−Pt) = q(Pt−Cl) + q(Re−Pt) − q(Pt−Cl)

As a result, the relative energy (inner potential correction) (ΔE₀)
obtained in the EXAFS data analysis for the Re−Pt and Pt−Re pairs is only an adjustable parameter and does not reflect any physical
significance in the relative difference of the chemical environment
between the sample and the reference.

Distinguishing Re and Pt Backscatterers in EXAFS Data
Analysis. Re and Pt are only five positions apart from each other in
the periodic table, and it has normally been assumed that it is not
possible to distinguish between neighboring Re and Pt atoms in the

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EXAFS data analysis. To investigate this issue, a model Pt–Re EXAFS function was calculated by using the Pt–Re reference function described above. As input parameters for the calculation, the following were used: \( N \) (coordination number) = 12; \( R \) (coordination distance) = 2.77 Å; \( \Delta \sigma^2 \) (disorder term) = 0; and \( \Delta E_0 \) (inner potential correction) = 0. The model function is displayed in Figure 9a (solid line). Fitting this model function with a Pt–Pt reference function by using a \( k^0 \)-weighted fit in \( k \) space (Figure 9a, dotted line) resulted in the coordination parameters given in Table 5. The variance of the fit is only 12.4, and it can be seen in Figure 9a that the fit (using a Pt–Pt reference) at low values of \( k \) strongly deviates (both in phase and amplitude) for \( 4 < k < 6 \) Å from the model EXAFS function (calculated with a Pt–Re reference). Thus it can be concluded that \( \varphi_{a}(Pt) \neq \varphi_{a}(Re) \) and \( F^a_{Pt-Re} \neq F^a_{Pt-Pt} \).

Analyzing the Pt–Re model function with a Re–Re reference leads to the results presented in Table 6. Figure 9b shows a good agreement between the Pt–Re model function (calculated with the Pt–Re reference) (Figure 9b, solid line) and the fit (using a Re–Re reference) (Figure 9b, dotted line). The variance of the fit was found to be 0.18, from which it can be concluded that, in principle, a Re–Re reference can be used to analyze Pt–Re data. It can also be concluded from these results that the Pt absorber phase \( \varphi_{a}(Pt) \) and the Re absorber phase \( \varphi_{a}(Re) \) are not detectably different from each other, since the high quality of the fit shows that \( \varphi(Pt-Re) \) and \( \varphi(Re-Re) \) are essentially the same. On the basis of these results, it is also obvious that the backscattering amplitude \( F^a_{Pt-Re} \) is indistinguishable from \( F^a_{Re-Re} \).

In earlier work, \( k^3 \) weighting has normally been used in the data analysis. Figure 10a displays a \( k^0 \)-weighted Fourier transform of the EXAFS data presented in Figure 9a. The differences between the solid line (calculated with a Pt–Re reference) and the dotted line (the result of fitting with a Pt–Pt reference) are clear. In contrast, with the \( k^3 \)-weighted Fourier transform (Figure 10b) the differences between the dotted line and the solid line are hardly visible. Figure 10 makes clear that a \( k^3 \) weighting almost completely minimizes the differences between a Pt and Re backscatterer.

One of the most important conclusions from this model study is that a Pt and a Re neighboring atom can be distinguished. This can only be done if a \( k^0 \) weighting is used in the EXAFS data analysis. Moreover, a Pt–Pt (or Re–Re) reference cannot be used to analyze a Pt–Re (or Re–Pt) reference.

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Supporting Information Available: Details of the performance of alumina-supported cluster-derived Re–Pt catalyst (23 pages). See any current masthead for ordering and Internet access instructions.

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