Physical, Adsorptive, and Catalytic Properties of Platinum Supported on Silica Modified with Europium Oxide

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The physical, chemisorptive, and catalytic properties of platinum on a europium oxide–silica support were studied by Mössbauer spectroscopy, volumetric reduction, chemisorption, and ethane hydrogenolysis experiments. The Mössbauer spectroscopy and volumetric reduction experiments showed that 40% of the silica-supported Eu^{3+} cations could be reduced to Eu^{2+} at 773 K; and the reducibility of the europium cations was enhanced to about 50% by the addition of platinum to the europium oxide–silica support. The primary reduction process was the formation of surface hydroxyl groups. The platinum particle sizes determined by hydrogen and carbon monoxide chemisorption, and confirmed by X-ray diffraction and electron microscopy, were substantially smaller for platinum on the mixed-oxide support than for platinum on silica. There was no evidence of suppressed H_2 or CO chemisorption on platinum. The rate of ethane hydrogenolysis was an order of magnitude lower over platinum on the mixed-oxide support. This decreased activity may be explained in geometric terms; e.g., the Pt particles are smaller on the mixed-oxide support and ethane hydrogenolysis is a structure-sensitive reaction. © 1989 Academic Press, Inc.

INTRODUCTION

Knowledge of the interactions which can occur between a metal and its support can be particularly important for the preparation of catalysts with desired catalytic properties. These metal–support interactions can alter the physical, chemical, and/or catalytic properties of the metal, as recently reviewed by Stevenson *et al.* (*1*). For example, it was first reported by Tauster *et al.* (*2*) that when a Group VIII metal is supported on a reducible oxide support, such as titania, and reduced at high temperatures, the chemisorptive capacity of the metal is suppressed. The authors termed this behavior strong metal–support interactions, or SMSI. It was subsequently reported that these interactions can alter the catalytic properties of the metal; in general, these interactions favor facile reactions such as hydrogenation and dehydrogena-

tion and inhibit demanding reactions such as hydrogenolysis (*1*). It is generally believed that reduced support species partially cover the active metal surface, thereby altering the geometric and/or electronic properties of the metal and also forming new active sites at metal–support interfaces.

Although most of the studies of metal–support interactions have involved metals supported on transition metal oxides, a few studies have involved metals supported on rare earth oxides. For example, Bell and co-workers (*3–6*) found that CO chemisorption was suppressed over Pd/La_2O_3 compared to Pd/SiO_2. In addition, Pd/La_2O_3 showed higher specific activity toward both methane and methanol synthesis from CO and H_2, although the activation energy for methane synthesis was higher over the La_2O_3-supported catalyst. Temperature-programmed reduction studies indicated that the lanthana in contact with palladium was partially reduced, and the authors attributed the altered chemisorption and reaction behavior to an interaction

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in which the reduced LaO_x moieties partially cover the Pd metal but provide additional sites for CO dissociation.

In a systematic study of rare earth oxides as catalyst supports, Vannice and co-workers (7, 8) investigated chemisorption and CO hydrogenation over palladium supported on seven rare earth oxide supports: La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Gd_2O_3, and Eu_2O_3. The existence of suppressed H_2 or CO chemisorption after a high-temperature reduction could not be confirmed because chemisorption uptakes were small even after a low-temperature reduction. All of the rare earth-supported catalysts showed higher activity for both methane and methanol synthesis compared to the activity of palladium black, and the activation energy of each reaction was the same for all of the catalysts including the unsupported palladium. The authors attributed the high activity to the creation of new active sites at the metal–support interface.

Metal–support interactions have also been reported for metals supported on high-surface-area, noninteracting supports which have been promoted with rare earth oxides. For example, Rieck and Bell (9) reported a suppression of hydrogen and CO chemisorption, as measured by temperature-programmed desorption, for Pd/SiO_2 catalysts promoted with La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, or Sm_2O_3; the dispersions of the promoted and unpromoted samples, as measured by H_2–O_2 titration, were the same. This latter result was due to the reversible spreading followed by nucleation of rare earth oxides over Pd in the reducing followed by oxidizing treatments employed during H_2–O_2 titrations. Temperature-programmed reduction results indicated that the palladium aided in the reduction of the rare earth oxide promoter. The promoted catalysts showed enhanced methane synthesis activity compared to an unpromoted catalyst.

In contrast to the chemisorption behavior reported by Bell and co-workers, Ryndin *et*

al. (*10*) observed that platinum supported on a mixed-oxide containing silica and praseodymia had a higher dispersion and greater thermal stability than the unpromoted sample. The promoted catalyst showed a decreased activity for ethane hydrogenolysis, although the activation energy for the reaction was lower for the promoted catalyst than for the unpromoted sample. Again, the rare earth-promoted catalyst showed an increased activity for CO hydrogenation with a high selectivity toward methanol. Similar behavior was reported for Pd supported on ceria-promoted silica (*11*).

The aforementioned experimental studies indicate clearly that interactions occur between a noble metal and a rare earth oxide, but the exact nature of these interactions remains unclear. The present study further explores noble metal–rare earth oxide interactions by investigating a silica-supported platinum catalyst containing a europium oxide additive. In particular, the experiments in this study were designed to determine the effects of the platinum on the reducibility of the europium cations and to determine the effects of the europium on the chemisorptive and catalytic properties of the platinum.

Europium oxide was the rare earth chosen for this study primarily because the reducibility of Eu_2O_3 is qualitatively similar to that of TiO_2 and because europium is a Mössbauer element. Thus, the reducibility of supported Eu^{3+} and the effects of platinum on that reducibility could be readily determined by Mössbauer spectroscopy. In addition, volumetric reduction of the supported Eu^{3+}. The chemisorptive properties of the platinum, both with and without the europium oxide additive, were determined by hydrogen and carbon monoxide chemisorption and confirmed by X-ray diffraction and transmission electron microscopy. Ethane hydrogenolysis was used as a probe reaction to determine the effects of the europium oxide on the catalytic properties of the platinum.

EXPERIMENTAL

Catalyst Preparation

Three catalysts were prepared and examined in this study to determine the interactions between platinum and europium oxide on a silica support. These catalysts were Eu/SiO_2, Pt/SiO_2, and $Pt/Eu/SiO_2$; the approximate loadings of these catalysts were 6% (by weight) europium and 1% platinum.

All samples were prepared by incipient wetness impregnation using 1 cm^3 of solution to wet 1 g of silica support (Cab-O-Sil, Grade S-17, 400 m^2/g, Cabot Corp.). The Eu/SiO_2 sample was prepared by dissolving the appropriate amount of $EuCl_3 \cdot (H_2O)_6$ (Aldrich Chemical Co.) into distilled water. The Pt/SiO_2 sample was prepared in an analogous manner from $H_2PtCl_6 \cdot (H_2O)_6$ (Strem Chemicals, Inc.). The $Pt/Eu/SiO_2$ sample was prepared by the addition of the platinum solution to Eu/SiO_2 which had been calcined in flowing oxygen at 773 K for 6 h. All samples were dried overnight at 413 K before storage.

The gases used in this study for catalyst treatment, volumetric reduction, and chemisorption measurements were purified according to the following procedures. Hydrogen was purified by diffusion through a Pd–Ag membrane in a Milton-Roy Serfass hydrogen purifier. Oxygen was purified by passage through a molecular sieve trap at 195 K, and nitrogen was purified by passage through copper turnings at 470 K followed by molecular sieves at 195 K. Carbon monoxide was purified by flowthrough glass beads at 570 K, followed by copper turnings at 470 K followed by molecular sieves at 195 K.

Mössbauer Spectroscopy

Mössbauer spectra of the europium-containing samples were collected using an Austin Science Associates Model S-600 Mössbauer spectrometer synchronized with a Tracor-Northern Model TN-1705 multichannel analyzer. All spectra were taken at room temperature in the constant acceleration mode. Gamma radiation was detected with a proportional counter; the γ-ray source was 50 mCi of $^{151}SmF_3$. The velocity scale was calibrated against the peak positions of a standard composed of 0.21 g EuS and 0.17 g EuF_3, which gives peaks at -12.52 and -0.59 mm/s, respectively (12). All spectra were computer-fit using the program MFIT (13), and isomer shifts are reported relative to Eu_2O_3.

Catalysts were studied as 0.3-g pellets approximately 2 mm thick. The pellet was mounted in a stainless-steel holder and placed in a quartz cell with thin quartz windows to allow transmission of γ-rays. The cell could be removed from the spectrometer and attached to a conventional gas-handling/vacuum system for sample pretreatment.

In a typical experiment, the sample pellet was placed inside the cell and pretreated in flowing oxygen for 20 h at 773 K. After the oxygen was evacuated, the sample was reduced in flowing hydrogen for 1 h at 773 K and then cooled to room temperature in flowing hydrogen. The sample was next sealed in hydrogen, and a Mössbauer spectrum was collected. After the spectrum of the reduced sample was recorded, the sample was treated in flowing oxygen at 773 K for 0.5 h. The sample was subsequently sealed in oxygen at room temperature, and a second spectrum was collected.

Volumetric Reduction

The amounts of hydrogen consumed, $[H_2]$, and water formed, [W], during the reduction of the three catalyst samples were measured using a standard gas-handling/vacuum system in a manner similar to that of Hall and Massoth (14). Since all of the hydrogen consumed must either react with oxygen to form water or adsorb on the catalyst (e.g., in the form of hydroxyl groups), the amount of hydrogen adsorbed, $[H_{2,A}]$, was determined from the volumetric reduction experiments by the difference of the measured quantities $[H_2]$ and [W].

In a typical experiment, approximately 1

g of catalyst was placed in a quartz cell; the cell was part of a closed loop which contained an all-glass pump to recirculate the gases and a cold trap 195 K to collect the water formed during the reduction. The entire experiment was conducted at 773 K. The sample was first treated in oxygen for 20 h to remove residual water held by the silica and then evacuated for 1 h. Next, a known amount of hydrogen was expanded into the cell and loop. The water formed during this reduction was collected in the cold trap. The remainder of the recirculation loop was wrapped in heating tape and maintained at 373 K to prevent water from condensing on the glass walls. At the end of 1 h, the final hydrogen pressure, which was typically about 6.7×10^3 Pa, was measured with a Texas Instruments precision pressure gauge. The hydrogen was then pumped out of the system through the cold trap, and the sample was evacuated for 0.5 h. Next, with the sample isolated from the system, the cold trap was warmed to room temperature and the pressure of the water vapor collected during the reduction was measured.

H_2O and CO Chemisorption

Hydrogen and CO chemisorption experiments were performed on all three catalysts after three standard pretreatments:

Pretreatment A: Evacuation for 18 h at 393 K, followed by reduction in flowing hydrogen for 2 h at 493 K.

Pretreatment B: Treatment in flowing oxygen at 773 K for 20 h, followed by reduction in flowing hydrogen for 2 h at 573 K.

Pretreatment C: Treatment in flowing oxygen at 773 K for 20 h, followed by reduction in recirculating hydrogen at approximately 6.7×10^3 Pa at 773 K for 1 h.

Pretreatment A was designed to give a highly dispersed Pt/SiO_2 catalyst, as described by Dorling et al. (15). Pretreatment B was designed to determine the effect of an extended high-temperature oxygen treatment on catalyst dispersion. As previously explained, this treatment was necessary to remove water from the catalyst prior to volumetric reduction experiments. Pretreatment C was designed to determine the effect of a high-temperature reduction on the apparent catalyst dispersion. This high-temperature reduction was the same as that used in the volumetric reduction experiment.

In addition to the above measurements, chemisorption experiments were also performed for $Pt/Eu/SiO_2$ after two additional pretreatments:

Pretreatment D: Treatment in flowing oxygen at 773 K for 20 h, followed by reduction in recirculating hydrogen for 5 h at 773 K.

Pretreatment E: Treatment in flowing oxygen at 773 K for 20 h, followed by reduction in recirculating hydrogen for 1 h at 873 K.

These pretreatments were designed to determine if the severity of the reduction affected chemisorption properties. After all pretreatments, the catalyst sample was evacuated for 1 h at 623 K (for Pretreatments A and B) or 773 K (for Pretreatments C, D, and E) and then cooled to room temperature for chemisorption.

Hydrogen chemisorption isotherms were collected at room temperature and relatively low pressures ($<1.0 \times 10^4$ Pa) to minimize adsorption on the support. Platinum dispersion was calculated from the hydrogen chemisorption uptake by assuming a stoichiometry of one surface platinum atom per hydrogen atom adsorbed (16). After the hydrogen isotherm was completed, the sample was evacuated at 623 K for 1 h and cooled to room temperature, and a CO isotherm was determined. The CO isotherm was collected at pressures up to 3.0×10^4 Pa. A correction for reversible uptake was made by evacuating the sample for 0.5 h at room temperature and measuring a second isotherm. The irreversible uptake of CO was determined by subtracting the second isotherm from the first at an equilibrium

pressure of 1.3×10^4 Pa (*17*). The stoichiometry for irreversible CO chemisorption was assumed to be 1.15 atoms of surface Pt per molecule of CO adsorbed (*16*).

X-Ray Diffraction and Electron Microscopy

X-ray diffraction line broadening experiments were performed on selected samples with a Picker X-ray diffractometer using Cu$K\alpha$ radiation. The diffraction peak at $2\theta = 39.8°$, which corresponds to the platinum (111) plane, was scanned at 0.125° (2θ)/min. The particle diameter was determined from the peak width using the Scherrer equation with Warren's correction for instrumental broadening (*18*).

The platinum particles were also measured by transmission electron microscopy. Specimens for TEM were prepared by dispersing selected catalyst samples in methanol and depositing the solution on 3-mm-diameter, 400-mesh copper grids containing "holey" carbon film. The specimens were observed on a JEOL Model 100B transmission electron microscope using bright field imaging at a magnification of 125,000×.

Ethane Hydrogenolysis

Ethane hydrogenolysis was carried out in a glass system operating at a total pressure of 1 atm, with the catalyst in a down-flow geometry. Typical reaction conditions were set at a hydrogen pressure of 2×10^4 Pa and an ethane pressure of 3×10^3 Pa, with the remainder of the gas being helium. Research purity ethane (99.99%) was obtained from Matheson and used without further purification; high-purity hydrogen was passed through a Deoxo unit and molecular sieves at 78 K prior to use; and the helium carrier gas was purified by passage through copper turnings at 470 K followed by molecular sieves at 78 K before use. Gas analysis was accomplished chromatographically (Carle Instruments Model 8700) using a Poropak Q column operated at 443 K.

In a typical experiment, 0.1 to 0.3 g of catalyst, which had been previously cal-

cined for 20 h at 773 K, was loaded into the reactor and reduced to hydrogen at 773 K for 1 h. The sample was then cooled in flowing hydrogen to the desired temperature. Ethane hydrogenolysis was subsequently carried out for 3 min, at which point the ethane flow was stopped while the hydrogen/helium flow was continued for 10 min. The ethane flow was then continued and ethane hydrogenolysis carried out for another 3 min. This procedure is very similar to that described by Sinfelt (*19*), and it was used to collect all data.

RESULTS

Mössbauer Spectroscopy

The Mössbauer spectrum of a sample of Eu/SiO$_2$ which had been treated in oxygen for 20 h at 773 K and then reduced at 773 K for 1 h is shown in Fig. 1A. The spectrum of the same sample after a subsequent treatment in oxygen at 773 K for 0.5 h is shown in Fig. 1B. Computer-fit values for the line positions, linewidths, and peak areas of these fits are given in Table 1. For the reduced sample, the peak with an isomer shift (I.S.) of -13.9 mm/s can be assigned to Eu^{2+}, since the isomer shift of divalent europium cations ranges from -12 to -15 mm/s (*12*). Similarly, the peak at 0.2 mm/s corresponds to Eu^{3+}, since the isomer shift of trivalent europium cations ranges from -1.0 to $+0.5$ mm/s (*12*). As expected, the oxygen treatment at 773 K completely oxidizes the reduced europium cations.

The percentage of Eu^{3+} which is reduced to Eu^{2+} after treatment in hydrogen can be determined from the Mössbauer spectra by assuming that the recoil-free fraction of Eu^{2+} is the same as that of Eu^{3+}. The resulting percentage reduction of Eu/SiO$_2$ after the 1-h hydrogen treatment at 773 K is 39%. The assumption of equal recoil-free fractions for Eu^{2+} and Eu^{3+} was made in a previous study of supported europium by Ross and Delgass (*20*), because these two cations are known to have the same recoil-free fraction in bulk Eu$_3$O$_4$ (*21*).
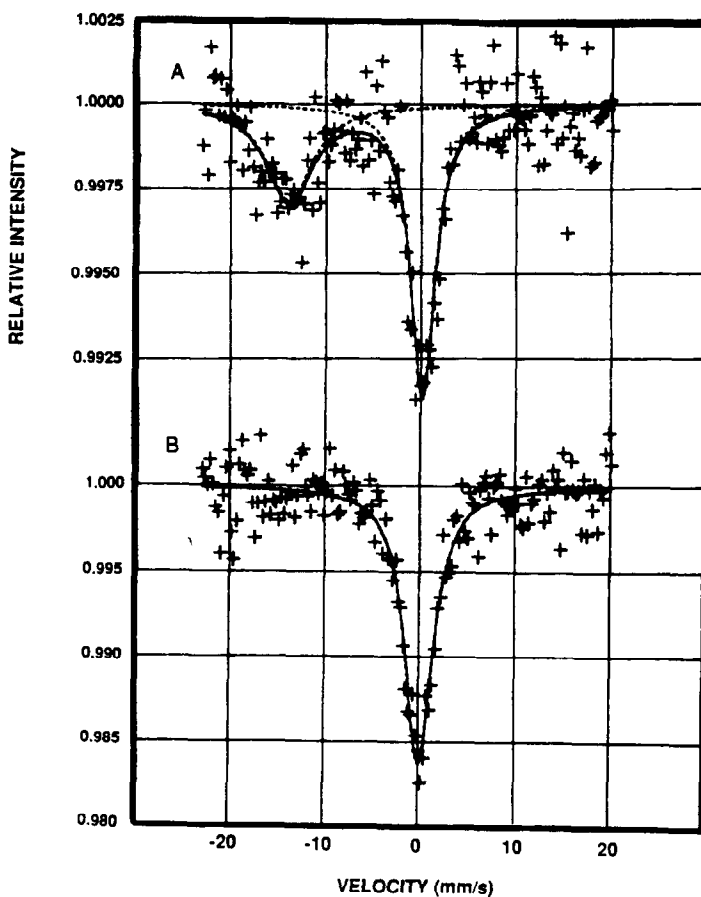
Fig. 1. Mössbauer spectra of Eu/SiO_2. (A) After reduction at 773 K; (B) after oxidation at 773 K.

TABLE 1

Mössbauer Spectroscopy Parameters for 6% Eu/SiO_2 and 1% $Pt/6\%$ Eu/SiO_2

Treatment	I.S. (mm/s)	Eu^{2+} peak width (mm/s)	Area (% mm/s)	I.S. (mm/s)	Eu^{3+} peak width (mm/s)	Area (% mm/s)
			6% Eu/SiO_2 sample			
1 h H_2, 773 K	−13.9 ± 0.5	5.8 ± 1.4	2.7 ± 0.5	0.17 ± 0.16	3.1 ± 0.4	4.2 ± 0.4
0.5 h O_2, 773 K	—	—	—	0.04 ± 0.08	3.6 ± 0.2	9.2 ± 0.4
			1% $Pt/6\%$ Eu/SiO_2 Sample			
1 h H_2, 773 K	−14 ± 0.6	6.8 ± 1.7	2.0 ± 0.4	0.06 ± 0.24	3.3 ± 0.7	1.9 ± 0.3
0.5 h O_2, 773 K	—	—	—	−0.32 ± 0.15	3.4 ± 0.4	4.9 ± 0.4

The spectrum of a sample of Pt/Eu/SiO$_2$ which had been treated in oxygen for 20 h at 773 K and then reduced at 773 K for 1 h is shown in Fig. 2A. The spectrum of the same sample after treatment in oxygen at 773 K for 0.5 h is shown in Fig. 2B. The computer-fit parameters for these spectra are given in Table 1. As for the sample without platinum, the reduced Pt/Eu/SiO$_2$ sample shows two peaks corresponding to Eu^{2+} and Eu^{3+}. The corresponding percentage reduction of the Pt/Eu/SiO$_2$ is 51%. The oxygen-treated sample shows a peak at -0.3 mm/s, which corresponds to Eu^{3+}. The isomer shifts and peak widths of both Eu^{2+} and Eu^{3+} are similar for the samples with and without platinum.

Volumetric Reduction

The amounts of hydrogen consumed, water formed, and hydrogen adsorbed during the reduction of Eu/SiO$_2$, Pt/SiO$_2$, and Pt/Eu/SiO$_2$ are given in Table 2. The silica support did not consume a measurable amount of hydrogen at 773 K. Each volumetric reduction experiment was repeated on a fresh sample.

Approximately 70–80% of the total hydrogen consumed during the reduction of Eu/SiO$_2$ is adsorbed on the catalyst surface. If all of the hydrogen consumed is considered to contribute to the reduction of the europium, then

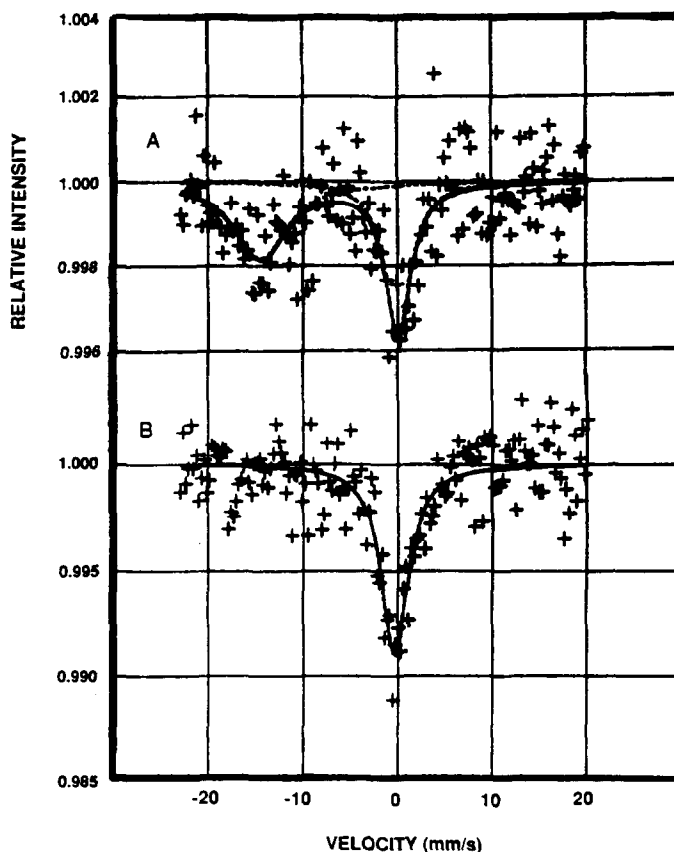$$\% \text{ reduction} = 2[\text{H}_2]/[\text{Eu}] \times 100,$$

FIG. 2. Mössbauer spectra of Pt/Eu/SiO$_2$. (A) After reduction at 773 K; (B) after oxidation at 773 K.

TABLE 2

Volumetric Reduction Results

Sample	Reduction conditions	[H$_2$]	[W] (μmol/g)	[H$_{2,A}$]
Eu/SiO$_2$	1 h H$_2$, 773 K	33	10	23
Eu/SiO$_2$	1 h H$_2$, 773 K	34	7	27
Eu/SiO$_2$	1 h H$_2$, 773 K	53	15	38
Pt/SiO$_2$	1 h H$_2$, 773 K	17	11	6
Pt/SiO$_2$	1 h H$_2$, 773 K	10	3	7
Pt/Eu/SiO$_2$	1 h H$_2$, 773 K	125	27	98
Pt/Eu/SiO$_2$	1 h H$_2$, 773 K	126	35	91
Pt/Eu/SiO$_2$	1 h H$_2$, 773 K	140	28	112
Pt/Eu/SiO$_2$	5 h H$_2$, 773 K	130	31	99
Pt/Eu/SiO$_2$	5 h H$_2$, 773 K	158	53	105

where [Eu] is the total amount of europium in the sample. For the Eu/SiO$_2$ samples listed in Table 2, the percentage reduction based on total hydrogen consumption ranges from 18 to 26%. Alternatively, if percentage reduction is defined as the formation of an oxygen vacancy (which corresponds to the formation of water during reduction), then

$$\% \text{ reduction} = 2[W]/[Eu] \times 100$$

and only 4–8% of the Eu^{3+} cations can be considered to be reduced.

The Pt/SiO$_2$ samples consumed a small but measurable amount of hydrogen corresponding to 0.2–0.3 mol H$_2$/mol Pt. This hydrogen consumption by Pt/SiO$_2$ may be due to the chemisorption of hydrogen by exposed platinum atoms. In addition, highly dispersed platinum oxide particles which remain after the oxygen pretreatment at 773 K may also be responsible for the hydrogen consumption (22). Thus, it is possible that the amount of hydrogen consumed by the Pt/SiO$_2$ samples is dependent on the dispersion of the platinum, but the exact relationship is not known.

The Pt/Eu/SiO$_2$ samples consume significantly more hydrogen during reduction than would be expected based on a linear combination of the Eu/SiO$_2$ and Pt/SiO$_2$

samples. However, as will be shown later, the platinum of the Eu/SiO$_2$ support has a higher dispersion than the platinum on the silica support. Therefore, it is not possible from these experiments to determine the amount of hydrogen which is associated with platinum and the amount which contributes to the reduction of europium. The reduction of Pt/Eu/SiO$_2$ at 773 K appears to be complete after 1 h, since essentially no additional hydrogen is consumed in 5 h.

Chemisorption

The uptakes of hydrogen and carbon monoxide on 6% Eu/SiO$_2$ after the three standard pretreatments are given in Table 3. Essentially no hydrogen is chemisorbed by the Eu/SiO$_2$ samples after the low- or high-temperature reductions. Similarly, after the low-temperature reductions (Pretreatments A and B), the irreversible CO uptake is zero. In contrast, after reduction at 773 K (Pretreatment C), 2.4 μmol of CO are irreversibly held by the sample. This CO can be removed by evacuation at 353 K for 0.5 h.

Representative dispersions determined by H$_2$ and CO chemisorption for Pt/SiO$_2$ after the three pretreatments are given in Table 4. Each H$_2$ chemisorption experiment was repeated on a fresh sample, and the difference in uptakes was always less than 10%. After the low-temperature reduction

TABLE 3

Chemisorption Results for 6% Eu/SiO$_2$

Sample pretreatment	H$_2$ uptake (μmol/g)	CO uptake (μmol/g)
A: 2 h H$_2$, 493 K[a]	0	0
B: 20 h O$_2$, 773 K 2 h H$_2$, 573 K[a]	0	0
C: 20 h O$_2$, 773 K 1 h H$_2$, 773 K[b]	0	2.4

[a] Sample was evacuated for 1 h at 623 K prior to chemisorption.
[b] Sample was evacuated for 1 h at 773 K prior to chemisorption.

TABLE 4

Chemisorption Results for 1% Pt/SiO$_2$ and
1% Pt/6% Eu/SiO$_2$

Sample pretreatment	Dispersion	
	H$_2$	CO
1% Pt/SiO$_2$ sample		
A: 2 h H$_2$, 493 K[a]	0.36	—
B: 2 h O$_2$, 773 K		
2 h H$_2$, 573 K[a]	0.26	0.25
C: 20 h O$_2$, 773 K		
1 h H$_2$, 773 K[b]	0.19	0.18
1% Pt/6% Eu/SiO$_2$ sample		
A: 2 h H$_2$, 493 K[a]	0.59	0.60
B: 20 h O$_2$, 773 K		
2 h H$_2$, 573 K[a]	1.10	0.85
C: 20 h O$_2$, 773 K		
1 h H$_2$, 773 K[b]	0.75	0.65
D: 20 h O$_2$, 773 K		
5 h H$_2$, 773 K[b]	0.71	0.69
E: 20 h O$_2$, 773 K		
1 h H$_2$, 873 K[b]	0.17	0.20

[a] Sample was evacuated for 1 h at 623 K
prior to chemisorption.

[b] Sample was evacuated for 1 h at 773 K
prior to chemisorption.

of Pretreatment A, the platinum dispersion as measured by hydrogen chemisorption is 0.36. As expected, treatment of the sample in oxygen at 773 K for 20 h prior to the low-temperature reduction (Pretreatment B) causes a decrease in platinum dispersion; the dispersion after Pretreatment B calculated from the H$_2$ uptake is 0.26. Pretreatment C, involving a high-temperature reduction at 773 K, causes a further decrease in sample dispersion to 0.19. The dispersions calculated from CO uptakes are similar to those obtained from the hydrogen uptakes.

The Pt dispersions of the Pt/Eu/SiO$_2$ samples are given in Table 4. In contrast to the rapid equilibration of hydrogen with the Pt/SiO$_2$ samples, equilibration with the Pt/Eu/SiO$_2$ samples required 6–12 h. Each H$_2$ chemisorption experiment was repeated on a fresh sample, and the difference in up-

takes was less than 15%. After all of the standard pretreatments, the dispersions of the Pt/Eu/SiO$_2$ samples are higher than the dispersions of the samples without europium. After the low-temperature reduction of Pretreatment A, the platinum dispersion as measured by both H$_2$ and CO chemisorption is approximately 0.60. Treatment in oxygen prior to the low-temperature-reduction (Pretreatment B) causes an increase in dispersion. After Pretreatment B, the catalyst has a dispersion of 1.1 as measured by H$_2$ chemisorption or 0.85 as measured by CO chemisorption. The large H$_2$ uptake, and corresponding high platinum dispersion, is probably due to hydrogen spillover onto the Eu/SiO$_2$ support. Reduction of the Pt/Eu/SiO$_2$ sample at 773 K (Pretreatment C) results in a small decrease in both the H$_2$ and CO uptakes. The platinum dispersion after Pretreatment C is 0.75 when calculated from the H$_2$ uptake, or 0.65 when calculated from the CO uptake. There is essentially no change in H$_2$ or CO uptakes after treatment in hydrogen for 5 h at 773 K (Pretreatment D) compared to treatment in hydrogen for 1 h (Pretreatment C). However, after reduction for 1 h at 873 K (Pretreatment E), the platinum dispersion as measured by H$_2$ and CO chemisorption decreases to approximately 0.20.

The platinum dispersion, D, was converted to particle diameter by assuming spherical particles and a platinum surface density of 8×10^{-20} m^2/atom (23). The corresponding platinum particle diameter in nanometers is given by $d = 1.13/D$. The particle diameters determined from the chemisorption experiments are given in Table 5.

X-Ray Diffraction and Electron Microscopy

Platinum particle sizes calculated from X-ray diffraction line broadening experiments are given in Table 5. No platinum peaks were detected for the Pt/Eu/SiO$_2$ samples after reduction at 573 or 773 K, which indicates that the platinum particles

TABLE 5

Platinum Particle Size (nm) Determinations

Pretreatment[a]	Pt/SiO$_2$				Pt/Eu/SiO$_2$			
	H$_2$	CO	XRD	TEM	H$_2$	CO	XRD	TEM
A	3.1	—	—	—	1.9	1.9	—	—
B	4.3	4.5	9.7	—	1.1	1.3	<5.0	—
C	6.0	6.3	9.1	3–15	1.5	1.7	<5.0	3–8
D					1.6	1.7	—	—
E					6.6	5.7	5.4	3–8

[a] See Table 4 for a description of the pretreatment.

in these samples are less than 5 nm in diameter. No diffraction peaks corresponding to Eu$_2$O$_3$ were observed.

The range of particle sizes observed by transmission electron microscopy for selected sample is also included in Table 5. The platinum particles were generally spherical in shape. Since only a small number of particles (<35) were observed for each sample, a quantitative analysis of average particle size cannot be made.

Ethane Hydrogenolysis

The rate of ethane hydrogenolysis over Pt/SiO$_2$ at 673 K with a hydrogen pressure of 2 × 10^4 Pa and an ethane pressure of 3 × 10^3 Pa was 0.15 mol/h/g Pt. This corresponds to a turnover frequency of 0.045 s^{-1} (since the Pt dispersion is 0.18). The activation energy for the reaction was measured to be 190 ± 20 kJ/mol, and the hydrogen and ethane reaction orders at 673 K were found to be −1.3 ± 0.4 and 1.1 ± 0.2, respectively. These results are summarized in Table 6.

The rate of ethane hydrogenolysis over the Pt/Eu/SiO$_2$ sample was considerably lower than that over the Pt/SiO$_2$ catalyst. Under the same reaction conditions noted above, the rate was 0.02 mol/h/g Pt. Since the Pt dispersion for this sample was rather high (0.65), the corresponding turnover frequency was 0.0017 s^{-1}, a value approximately 25 times lower than that over Pt/SiO$_2$. Due to the low activity of this sample, the temperatures used for kinetic parameter

measurements were higher than those used to study Pt/SiO$_2$, as listed in Table 6. The activation energy was found to be 130 ± 20 kJ/mol, and the hydrogen and ethane reaction orders were determined to be −0.9 ± 0.2 and 1.3 ± 0.3, respectively. These values are summarized in Table 6. It should be noted that a sample of Eu/SiO$_2$ showed no activity for ethane hydrogenolysis under the experimental conditions of this study.

DISCUSSION

Reducibility of Supported Eu^{3+}

The primary objectives of both the Mössbauer spectroscopy and the volumetric reduction experiments were to determine the reducibility of supported europium cations and to investigate the effect of platinum on that reducibility. Although bulk Eu$_2$O$_3$ cannot be reduced to Eu$_3$O$_4$ or EuO at temperatures below 1473 K, it was shown by Ross and Delgass (20) that supported Eu^{3+} can be reduced at lower temperatures. These researchers used Mössbauer spectroscopy to show that after hydrogen treatment at 773 K for 6 h, the percentage of Eu^{3+} cations reduced to Eu^{2+} in 10.5% Eu/SiO$_2$ was 43%. The reduced Eu/SiO$_2$ sample was completely oxidized by exposure to air at room temperature. As can be seen in Table

TABLE 6

Ethane Hydrogenolysis Kinetic Parameters for Pt/SiO$_2$ and Pt/Eu/SiO$_2$

Kinetic parameters[a]	Pt/SiO$_2$	Pt/Eu/SiO$_2$
TOF (s^{-1})[b]	0.045	0.0017
E_A (kJ/mol)	190 ± 20[c]	130 ± 20[d]
m	−1.3 ± 0.4[e]	−0.9 ± 0.2[f]
n	1.1 ± 0.2[e]	1.3 ± 0.3[f]

[a] Turnover frequency (TOF) = A exp($-E_A/RT$)$P_{H_2}^m P_{C_2H_6}^n$.

[b] Turnover frequency at 673 K for P_{H_2} = 2 × 10^4 Pa, $P_{C_2H_6}$ = 3 × 10^3 Pa.

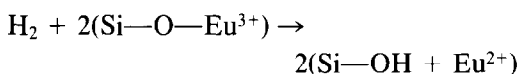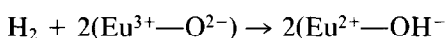[c] Measured in the temperature range 670–715 K.

[d] Measured in the temperature range 695–735 K.

[e] Measured at 673 K.

[f] Measured at 693 K.

1, the Mössbauer spectroscopy results from this study confirm that supported Eu^{3+} can be reduced to Eu^{2+} at 773 K and can be reoxidized by exposure to oxygen. The percentage reduction of 6% Eu/SiO_2 after treatment in hydrogen for 1 h is 39%, which is in good agreement with the results of Ross and Delgass.

The results of the volumetric reduction experiments also show that supported europium oxide can be reduced in hydrogen at 773 K. The average amount of hydrogen consumed by the Eu/SiO_2 samples corresponds to a maximum percentage reduction of Eu^{3+} of 18–26%, while the amount of water formed during reduction corresponds to a percentage reduction of only 4–8%. This latter value is much smaller than the extent of reduction determined by Mössbauer spectroscopy; therefore, it must be concluded that adsorbed hydrogen leads to reduction of Eu^{3+} to Eu^{2+}. This would correspond to the formation of surface hydroxyl groups via the possible reactions

$$H_2 + 2(Eu^{3+}\!\!-\!\!O^{2-}) \rightarrow 2(Eu^{2+}\!\!-\!\!OH^-$$

$$H_2 + 2(Si\!\!-\!\!O\!\!-\!\!Eu^{3+}) \rightarrow$$
$$2(Si\!\!-\!\!OH + Eu^{2+})$$

A possible explanation for the slightly lower percentage reduction determined by the hydrogen consumed in the volumetric measurements, compared to the Mössbauer spectroscopy results, is that the sample for Mössbauer spectroscopy was pretreated in flowing hydrogen at 1×10^5 Pa, whereas the sample reduced volumetrically was treated in 6.6×10^3 Pa of hydrogen. Thus, the higher hydrogen pressure used during Mössbauer spectroscopy could increase the number of surface hydroxyl groups and consequently increase the percentage of Eu^{3+} cations reduced to Eu^{2+}.

The addition of 1% platinum to Eu/SiO_2 results in an increase in the percentage of Eu^{2+} cations that are detected by Mössbauer spectroscopy after reduction. The percentage reduction for $Pt/Eu/SiO_2$ is 51% after hydrogen treatment at 773 K. Presum-

ably, as in the Pt/TiO_2 system (24), the platinum aids in the reduction of Eu^{3+} by dissociating hydrogen molecules; the atomic hydrogen can then spill over to the support and reduce Eu^{3+} to Eu^{2+}. The assumption that hydrogen can spill over to the europium cations is supported by the hydrogen chemisorption data, which show evidence of slow hydrogen uptake. The increase in percentage reduction for $Pt/Eu/SiO_2$ is not large, perhaps because not all of the europium is in the immediate vicinity of a platinum particle and because the mobility of hydrogen atoms on the mixed-oxide support is limited.

As previously explained, the percentage reduction of Eu^{3+} in $Pt/Eu/SiO_2$ is difficult to determine quantitatively from the volumetric reduction experiments because of the consumption of hydrogen by platinum. However, the results of these measurements are consistent with the Mössbauer spectroscopy results in that the hydrogen consumption by $Pt/Eu/SiO_2$ is larger than the combined uptakes of the Pt/SiO_2 and the Eu/SiO_2 samples.

Effect of Europium Oxide on Platinum Dispersion

As can be seen from Table 5, there is good agreement between the average particle sizes of Pt/SiO_2 determined by H_2 and CO chemisorption; however, the particle sizes determined by X-ray diffraction are significantly larger, mainly because this technique gives a volumed-averaged size and it cannot detect particles less than 5 nm in diameter. Thus, although the chemisorption results show that the average platinum particle on Pt/SiO_2 after the high-temperature reduction is 6 nm, the electron microscopy results indicate that the particle size distribution for these samples is quite broad and that a number of particles are larger than 10 nm.

There is no evidence for suppressed chemisorption over $Pt/Eu/SiO_2$. In fact, the most striking feature of Table 5 is that the platinum particles on the mixed-oxide sup-

port are significantly smaller than the particles on the silica support after comparable pretreatments, as measured by both chemisorption and physical methods. For instance, after a low-temperature reduction (Pretreatment A), the platinum particle size on the silica support is 3 nm as determined by chemisorption, whereas on the mixed-oxide support it is only 2 nm; treatment in oxygen followed by a low-temperature reduction (Pretreatment B) causes the platinum on the silica support to grow to approximately 4.4 nm, while this treatment causes a decrease in the particle size on the mixed oxide to approximately 1.2 nm.

It is clear that the platinum dispersion on $Pt/Eu/SiO_2$ is very high when calculated from either H_2 or CO chemisorption. Additional insight into the chemisorptive behavior of $Pt/Eu/SiO_2$ can be obtained by comparing the H_2 and CO uptakes given in Table 4. For example, after Pretreatment B the $Pt/Eu/SiO_2$ sample consumes more than one hydrogen atom per platinum atom, and as already mentioned, hydrogen equilibration takes much longer for the europium-containing sample than for Pt/SiO_2. It should be noted that bulk Eu_2O_3 does not chemisorb hydrogen at room temperature (7), and neither does silica-supported europium oxide (Table 3). Therefore, the excess, slow hydrogen uptake can be attributed to the spillover of hydrogen atoms from the platinum onto the europium oxide support. The phenomenon of hydrogen spillover has been previously proposed for Pt/TiO_2 by Beck and White (25) and Jiang et al. (26). Because of spillover, platinum dispersions determined by hydrogen chemisorption may be artificially high, and carbon monoxide chemisorption may be a more reliable indicator of metal dispersion. It should be recalled, however, that after reduction at 773 K, partially reduced Eu/SiO_2 can irreversibly chemisorb a small amount of CO at 298 K (Table 3), as can bulk Eu_2O_3 (7).

Although it has been shown that both hydrogen and carbon monoxide chemisorption on $Pt/Eu/SiO_2$ may overestimate metal dispersions (and thus predict artificially small particle sizes), the X-ray diffraction and electron microscopy results confirm that the platinum particles on the mixed-oxide support are indeed significantly smaller than the particles on the silica support at reduction temperatures up to 873 K. The ability of a rare earth promoter to increase metal dispersion and thermal stability has also been noted for Pd/SiO_2 promoted with ceria (11) and Pt/SiO_2 promoted with praseodymia (10). In addition, Regalbuto et al. (27) have recently reported that the tungsten oxide increases the dispersion of platinum on silica.

Ethane Hydrogenolysis

The ethane hydrogenolysis results show clearly that Pt on Eu/SiO_2 is approximately an order of magnitude less active than Pt supported on SiO_2. This is consistent with the behavior typically observed for ethane hydrogenolysis over titania-supported metals (1, 28–37). It is instructive to discuss briefly these results with respect to possible electronic and geometric modifications of Pt caused by the Eu/SiO_2 support.

The observation that the apparent activation energy for ethane hydrogenolysis over $Pt/Eu/SiO_2$ is lower than that over Pt/SiO_2 may at first be attributed to electronic effects of the Eu/SiO_2 support. However, this is probably not the case. In work reported elsewhere (38), we have conducted kinetic modeling studies of ethane hydrogenolysis over Group VIII metals. The fundamental parameters of this modeling are the strengths with which hydrogen and carbonaceous species are bonded to the surface. For the case of Pt, we have estimated these bond strengths from calorimetric studies of hydrogen and carbon monoxide adsorption, combined with bond-order-conservation calculations (39). In short, we find that the lower activation energy for ethane hydrogenolysis over $Pt/Eu/SiO_2$ maybe due primarily to the fact that this sample was studied at a higher temperature than Pt/SiO_2.

Furthermore, we find calorimetrically that the differential heat of hydrogen adsorption on $Pt/Eu/SiO_2$ is the same as that over Pt/SiO_2 (38). This is in agreement with the work of Chou and Vannice (40, 41) who found that the support had no effect on the heats of hydrogen and carbon monoxide adsorption on Pd. We thus conclude that the lower activity of $Pt/Eu/SiO_2$ for ethane hydrogenolysis may be due primarily to a geometric effect.

The origin of the geometric effect of the Eu/SiO_2 support on Pt remains uncertain at present. We suggest, however, that the effect may be related simply to the ability of Eu/SiO_2 to stabilize small Pt particles, as discussed above. Since ethane hydrogenolysis is a structure-sensitive reaction (42, 43), small Pt particles may be less active than larger particles, and this may be the origin of the lower activity of the $Pt/Eu/SiO_2$ sample. We cannot eliminate the possibility that reduced europium oxide species migrate onto the Pt surface. However, europium oxide may be bonded strongly to the silica surface, as evidenced by the fact that no X-ray diffraction peaks are observed for bulk europium oxide phases and that the reducibility of europium is not characteristic of bulk europium oxides. Accordingly, it is possible that europium oxide species remain bonded to the silica support and serve as anchoring sites for Pt particles. This would explain the increase in Pt dispersion upon oxygen treatment of the $Pt/Eu/SiO_2$ sample; i.e., Pt oxide species migrate over the support and become trapped at Eu oxide centers during oxidation. In the absence of these Eu oxide centers, platinum on silica sinters during oxygen treatments.

SUMMARY

The primary objective of this study was to investigate the interactions between supported platinum and a europium oxide additive. It was determined by Mössbauer spectroscopy that supported Eu^{3+} can be reduced at 773 K and that the reducibility of the supported europium cations is enhanced by the platinum metal. A large extent of this reduction is due to the adsorption of hydrogen with the formation of surface hydroxyl groups. There is no evidence from this study of $Pt/Eu/SiO_2$ for the existence of suppressed H_2 or CO chemisorption on platinum. However, an interaction between the platinum and the europium oxide which is responsible for stabilizing Pt in a high state of dispersion takes place. The low activity for ethane hydrogenolysis of Pt supported on Eu/SiO_2 may be due to the smaller metal particle size on this support than in the case of Pt supported on silica.

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