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NOTE

Supported Pt and Re–Pt on Alumina Prepared by Sol-Gel Synthesis with *in Situ* Water Formation: Role of Rhenium

Sol-gel chemistry offers flexible methods for the preparation of porous metal oxides such as the transition aluminas used as catalyst supports. The physical properties of sol-gel materials depend on the nature of the reactants, the rate of mixing, and the conditions of drying. Sol-gel chemistry has also been investigated for the preparation of supported metal catalysts such as Pt on metal oxides, including Al_2O_3 (1) and SiO_2 (2), and Sn–Pt/Al_2O_3 (3). In the synthesis of Pt/Al_2O_3, the physical properties of the porous material were controlled by the synthesis conditions, but only little control of the Pt dispersion was achieved (1). The bimetallic catalysts had high surface areas and pore volumes, but a typical Pt dispersion was not high (e.g., a H/Pt ratio of 0.3 was found for a sample containing 1 wt% Pt and 0.9 wt% Sn) (3).

Because the oxophilic metal Re in Re–Pt/Al_2O_3 catalysts evidently helps to maintain the dispersion of Pt (4, 5), we investigated the role of Re in influencing the dispersion of Pt in Re–Pt/Al_2O_3 prepared by a sol-gel synthesis. Alumina-supported samples were prepared in the initial absence of water under conditions allowing uniform reaction of the precursors. The precursors were Al(O-*s*-Bu)$_3$, Pt(acac)$_2$, and $Re_2(CO)_{10}$ in *s*-butyl alcohol. Acetic acid was included in the reactant mixture because it catalyzes the dehydration of the alcohol, leading to *in situ* formation of water uniformly in the medium and thereby to control of the rates of the hydrolysis and condensation reactions that lead to formation of a gelatinous precipitate (6). The gelatinous precipitate was transformed into porous products by calcination in air (6, 7).

The results show that in the presence of the Re precursor, the Pt particles are small (about 35 Å in average diameter), whereas in the absence of Re, the Pt particles are larger (about 110 Å in average diameter); the Re precursor plays a significant role in controlling the Pt dispersion.

The products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and surface area/pore volume measurements. Surface area/pore volume measurements were made with a Micromeritics Digisorb instrument with N_2 as the adsorbate at $-196°$C. The samples were dried and evacuated for about 4 h at 300°C prior to characterization. X-ray diffraction patterns of the dried gelatinous precipitates (powders) were measured with a Scintag Model XDS 2000 diffractometer by using CuKα radiation. In preparation for TEM, the powders were dispersed on a copper grid; the TEM instrument was a Zeiss EM 109.

The reagents used in the sample preparations included aluminum *s*-butoxide, Al(O-*s*-Bu)$_3$ (98%), *s*-butyl alcohol, *s*-BuOH (99+%), and glacial acetic acid (99.99%) (Aldrich). Pt(acac)$_2$, (98%) and $Re_2(CO)_{10}$ were supplied by Strem. In the preparation of the precursor for Re–Pt/Al_2O_3, a mixture of Al(O-*s*-Bu)$_3$, Pt(acac)$_2$, and $Re_2(CO)_{10}$ was added to *s*-BuOH so that the metal contents were 1.0 wt% Pt and 1.0 wt% Re; the concentration of Al(O-*s*-Bu)$_3$ was 1 *M*. The mixture was brought to reflux and stirred for 24 h; a yellow–gray mixture formed. In the preparation of the precursor for Pt/Al_2O_3, a mixture of Al(O-*s*-Bu)$_3$ and Pt(acac)$_2$ was added to *s*-BuOH so that the metal content was 1.0 wt% and the concentration of Al(O-*s*-Bu)$_3$ was 1 *M*. The mixture was brought to reflux and stirred for 24 h; a black mixture formed. In the preparation of Al_2O_3 without Pt and Re, Al(O-*s*-Bu)$_3$ (1 *M*) in *s*-BuOH was stirred for a few minutes and then dried at 80°C for 24 h and calcined in air at temperatures $>400°$C. Acetic acid was added to aliquots of each of the three mixtures so that the ratio [HOAc]/[Al(O-*s*-Bu)$_3$] was 1. A few minutes after addition of the acetic acid, gelatinous precipitates formed. Prior to characterization, each gelatinous precipitate was dried overnight at 80°C in air.

After addition of acetic acid to the mixture containing no Re or Pt, a white gelatinous precipitate of Al_2O_3 formed within minutes. During the first step of the preparation with the mixture of Al(O-*s*-Bu)$_3$ and Pt(acac)$_2$, after it had been brought to reflux and stirred for 24 h, it changed from clear light yellow to black. Addition of acetic acid, after cooling of the black mixture, led to formation of the gelatinous precipitate. (In contrast, when the resultant mixture was allowed to cool and stand for few hours prior to addition of acetic acid, a black deposit formed, and the preparation was unsuccessful.) In contrast to the observations for the sample prepared without Re, no color change was observed after the mixture of Al(O-*s*-Bu)$_3$, Pt(acac)$_2$, and $Re_2(CO)_{10}$ had been brought to reflux and stirred for 24 h. After cooling of this mixture, acetic acid was added, leading to the formation of a gelatinous precipitate. (However, when this mixture was cooled and allowed to stand for a few hours

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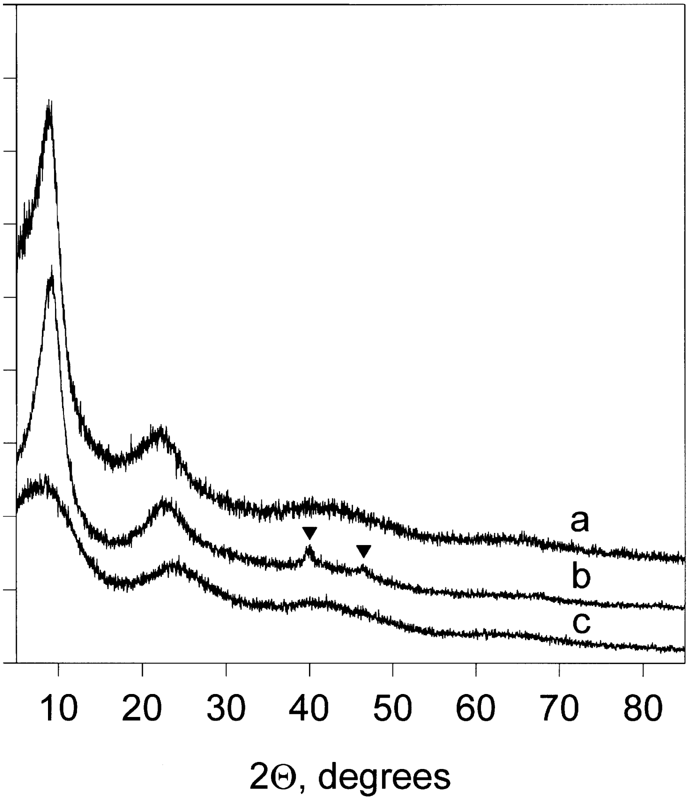

FIG. 1. X-ray diffraction patterns of gelatinous precipitates after drying at 80°C: a, Al_2O_3; b, Pt/Al_2O_3; and c, $Re–Pt/Al_2O_3$.

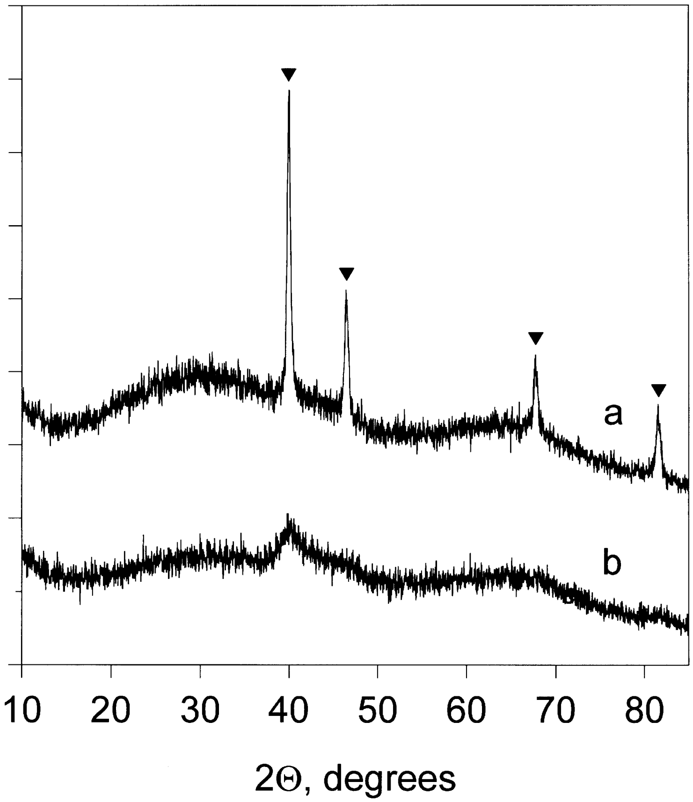

FIG. 2. X-ray diffraction patterns of gelatinous precipitates after calcination at 450°C: a, Pt/Al_2O_3; b, $Re–Pt/Al_2O_3$.

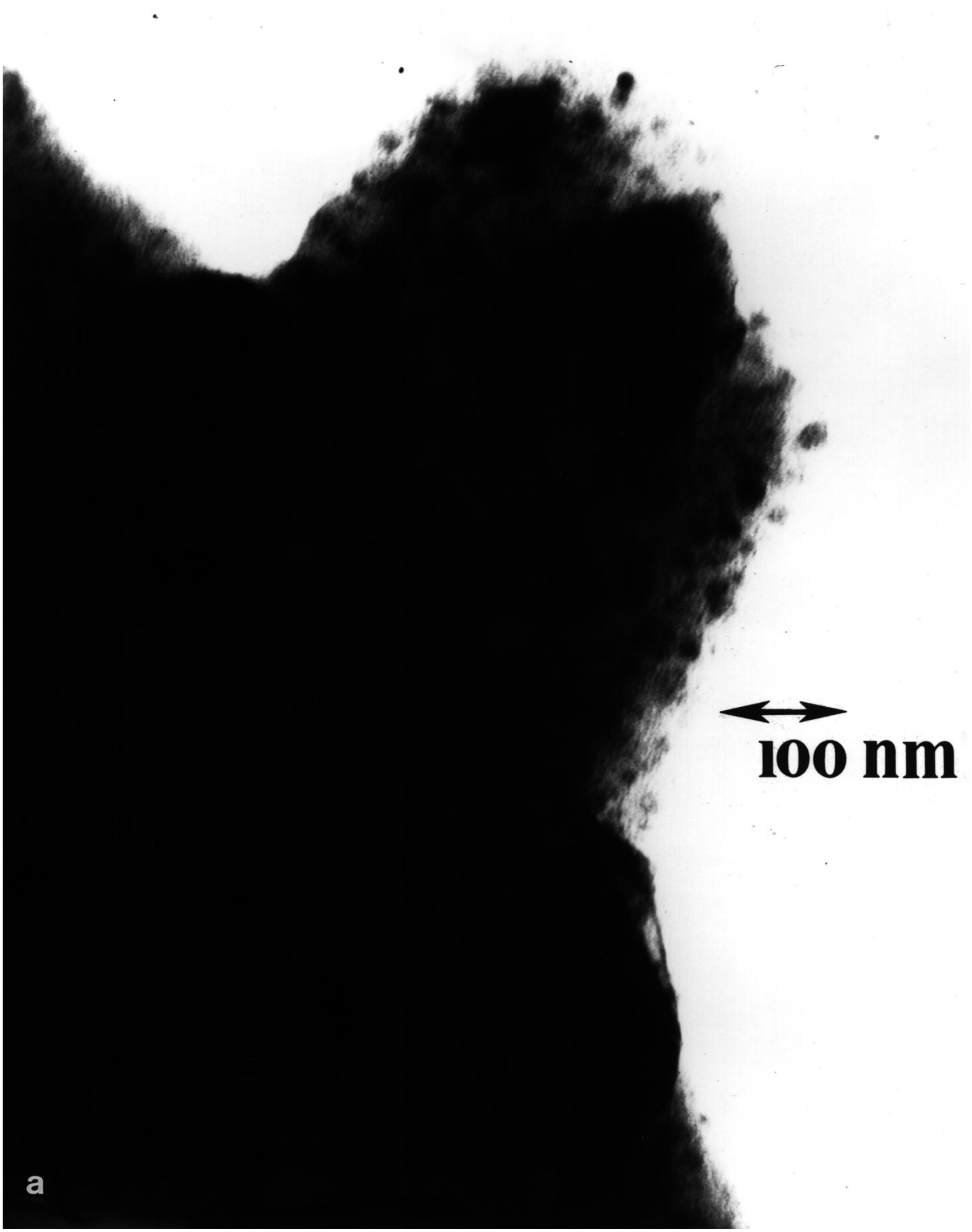

FIG. 3. Transmission electron micrographs of gelatinous precipitates after calcination at 400°C: a, Pt/Al_2O_3; b, $Re–Pt/Al_2O_3$.

prior to addition of acetic acid, a cloudy brownish–gray deposit was observed, and the synthesis was unsuccessful.)

After drying at 80°C for 24 h, the Al_2O_3 was a white powder, the $Pt–Re/Al_2O_3$ was a white powder, and the Pt/Al_2O_3 was a light gray powder. When the latter two samples were calcined in air at temperatures $>400°C$, they became gray and almost indistinguishable from each other. The $Re–Pt/Al_2O_3$ had a lower surface area and a lower pore volume than Pt/Al_2O_3, which had a lower surface area and a lower pore volume than Al_2O_3 (Table 1).

The XRD data characterizing the dried gelatinous precipitates of Al_2O_3 and of $Re–Pt/Al_2O_3$ indicate amorphous materials (Figs. 1a, 1c). The diffractogram representing the dried Pt/Al_2O_3 (Fig. 1b) includes two small

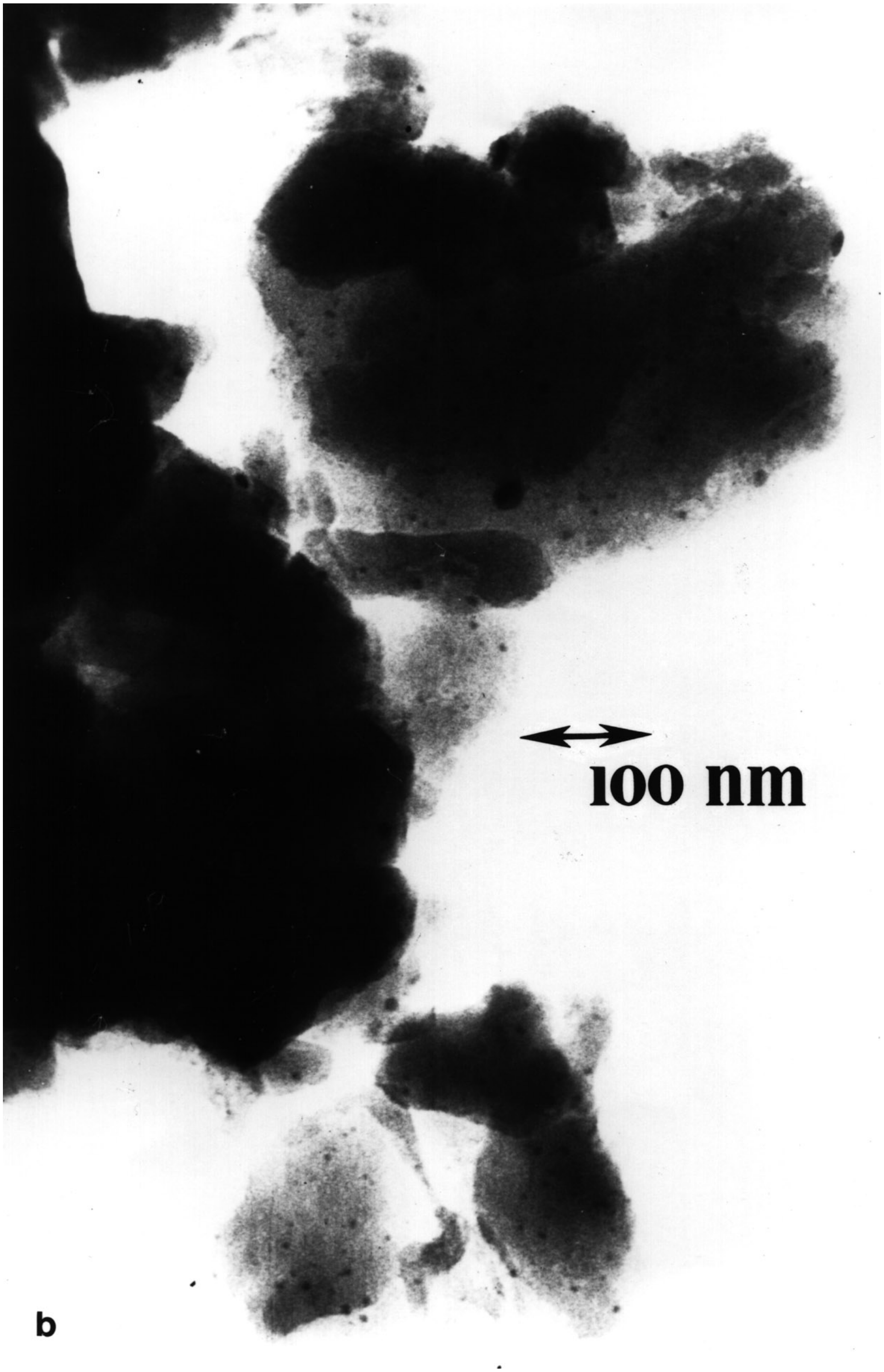

FIG. 3—*Continued*

peaks attributed to crystalline Pt. The diffractogram of the Pt/Al_2O_3 following calcination at 450°C indicates highly crystalline Pt (Fig. 2a). In contrast, the diffractogram of Re–Pt/Al_2O_3 following calcination at 450°C (Fig. 2b) is indicative of less highly crystalline material than the Pt/Al_2O_3; the Re–Pt/Al_2O_3 contained little if any crystalline Pt. After calcination in air at 900°C, both the Pt/Al_2O_3 and the Re–Pt/Al_2O_3 samples gave XRD patterns indicating the presence of crystalline Pt. Evidently this high-temperature calcination led to substantial aggregation of the Pt.

The TEM images of Pt/Al_2O_3 indicate scattering centers attributed to Pt particles. The average Pt particle size is

TABLE 1

Surface Areas and Pore Volumes of Al_2O_3, Pt/Al_2O_3, and $Re–Pt/Al_2O_3$ after Calcination at 400°C

Sample:	Al_2O_3	Pt/Al_2O_3	$Re–Pt/Al_2O_3$
Surface area (m^2/g):	240	180	150
Pore volume (mL/g):	0.19	0.16	0.15

about 110 Å in the image representing the Pt/Al_2O_3 formed after calcination at 400°C (Fig. 3a). The TEM image of the $Re–Pt/Al_2O_3$ sample (Fig. 3b) indicates metal particles that are only about 35 Å in average diameter.

The XRD pattern of the gelatinous precipitate of Pt/Al_2O_3 dried at 80°C shows the presence of crystalline Pt (Fig. 1b). This result suggests that even during the first step of the preparation, giving a black deposit, the $Pt(acac)_2$ was reduced to metallic Pt. We infer that $Pt(acac)_2$ was reduced by the alcohol.

Because no peaks for crystalline Pt were observed in the XRD pattern of the dried $Re–Pt/Al_2O_3$ (Fig. 1c), in contrast to the results for Pt/Al_2O_3, it is evident that Re affected the formation of crystalline Pt. We infer that the reduction of the Pt by the alcohol was hindered by the $Re_2(CO)_{10}$ or that the metallic Pt formed in the presence of Re was highly enough dispersed to give a diffractogram characteristic of an amorphous material. Thus the data suggest that the $Pt(acac)_2$ reacted with $Re_2(CO)_{10}$ to form a complex that was resistant to reduction and/or that the reduction of Pt occurred and the Re hindered its aggregation.

In summary, $Pt(acac)_2$ was evidently reduced to Pt metal in all the preparations, and $Re_2(CO)_{10}$ or species derived from it minimized the degree of reduction of the Pt and/or hindered the aggregation of the Pt into larger particles. There is extensive evidence of strong interactions between Re and Pt in supported Re–Pt catalysts, as determined, for example, by EXAFS spectroscopy (8–10). Some authors have attributed the high dispersions of Pt in $Re–Pt/Al_2O_3$ catalysts to the anchoring of small Pt clusters to the Al_2O_3 surface by layers of cationic Re (10). Our results suggest that in the sol-gel synthesis, complexes of oxophilic Re interact with Pt even at an early stage of the preparation.

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