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Research Note

A TEM study on the localization of metal particles in cogelled xerogel catalysts

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Abstract

The localization of metal and alloy particles in monometallic Pd/SiO$_2$ and bimetallic Pd–Ag/SiO$_2$ sol–gel catalysts prepared by cogelation was examined by rotating transmission electron microscopy. The analysis of the resulting micrograph series provides a direct proof that the 2-to 3-nm active metal nanoparticles in those catalysts are located inside microporous silica particles or aggregates. Such localization has long been suspected but with, up to now, no direct evidence.

Keywords: Cogelled catalysts; Metal particles localization; Rotating transmission electron microscopy

1. Introduction

An attractive method of preparing nanometer-sized uniform metal or alloy particles dispersed in the porosity of a silica matrix by sol–gel processing of metal complexes has been used for about 15 years [1–6]. This method involves using an alkoxysilane-functionalized ligand of the type (RO)$_3$Si–X–L in which the ligand, L, able of forming a complex, –L$_n$M^{m+}, with a metallic cation, M^{m+} (e.g., Pd^{2+}, Ag$^+$, Cu^{2+}), is connected to the alkoxide moiety, (RO)$_3$Si–, via an inert and hydrolytically stable tethering organic group, X. The concomitant hydrolysis and condensation of such molecules with a network-forming reagent such as Si(OC$_2$H$_5$)$_4$ (TEOS) (i.e., their *cogelation*) results in materials in which the catalytic metal is anchored to the SiO$_2$ matrix [1,7,8]. This method enables the preparation of efficient monometallic and bimetallic catalysts [4,6].

Our previous studies suggest that after drying, calcination, and reduction, these materials contain a majority of metal or alloy nanoparticles of around 2–3 nm, which, because of a nucleation effect induced by the alkoxysilane-functionalized metal complexes, are located inside microporous silica particles while remaining completely accessible for a fluid phase, as established from CO chemisorption results and catalytic tests. Such accessibility would result from the presence of micropores of around 0.8 nm in silica particles that contain metal particles [4,9–11].

The localization of small metal particles inside silica particles is suggested by transmission electron microscopy (TEM). However, TEM does not provide indisputable proof of such a localization, because only projections of the objects are analyzed. The aim of the present study was to use a rotating TEM technique [12] to confirm the localization of small metal and alloy particles inside the silica xerogel support in cogelled catalysts.

2. Experimental

Two cogelled xerogel catalysts were examined: a monometallic Pd/SiO$_2$ (sample X0 [4]) and a bimetallic Pd–Ag/SiO$_2$ (sample X67 [4] and sample Pd–Ag(33-67) [13]). Details of the preparation have been given previously [4]. The actual Pd and Ag contents in the catalysts were determined by ICP-AES as follows: monometallic sample, 3.3 wt% Pd/SiO$_2$; bimetallic sample, 1.9 wt% Pd–3.7 wt% Ag/SiO$_2$. The actual contents are higher than nominal contents calculated from synthesis vari-

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ables (1.5 wt% Pd/SiO_2 and 1.5 wt% Pd–3.0 wt% Ag/SiO_2) due to loss of unreacted TEOS during gel drying [13].

Both catalysts have been characterized in previous studies by N_2 adsorption–desorption, Hg porosimetry, He pycnometry, X-ray diffraction, CO chemisorption, and static electron microscopy (SEM, TEM, and STEM-EDX) [4,13].

In this study, the two samples were characterized by rotating TEM, a TEM analysis technique involving rotation of the sample in situ to provide views at various angles. The images were obtained with a Tecnai 20F electron microscope operating at 200 kV and equipped with a field-emission gun. After the specimen is positioned at the eucentric height within the microscope, it can be rotated without significantly displacing the image. A special sample holder was used that allows rotation of the specimen by about 70°. Specimens were prepared by grinding and subsequent ultrasonic treatment. A drop of the resulting suspension was placed onto a holey carbon grid.

3. Results and discussion

Figs. 1 and 2 show TEM images of both samples tilted over a sequence of angles with respect to the electron beam. Fig. 1 gives a series of images of the Pd/SiO_2 sample in which the tilt axis ranges from 0° to 30° at 10° intervals, and Fig. 2 gives a series relative to the Pd–Ag/SiO_2 sample with a tilt axis ranging from −40° to +40° at 20° intervals. The dark spots appearing in all of the micrographs correspond to small (2–3 nm) Pd (Fig. 1) or Pd–Ag (Fig. 2) particles [4,13]. TEM images obtained over an angular tilt range help identify whether the metallic nanoparticles are located inside the core of silica or at its external surface. To answer this question, the relative position of metallic particles in relation to the edge of the silica matrix must be closely examined on the micrographs at the various angles. In Fig. 1, whichever the rotating angle, no metallic particles are observed on the edge of the two-dimensional projection of the silica support. Moreover, it is clearly observed with several particles that their distance in relation to the edge of silica is almost constant when the sample is tilted. The same type of observations can be made with Fig. 2, in particular the absence of Pd–Ag alloy nanoparticles at the periphery of the silica matrix. On the other hand, Fig. 3 relative to the Pd–Ag/SiO_2 sample clearly shows a large metal particle at the periphery of silica. As explained previously, such a large particle in the bimetallic catalyst is composed of pure silver [4].

The localization of small Pd or Pd–Ag particles inside the particulate silica xerogel support suggested by static TEM [4] is confirmed by rotating TEM. Indeed, as is the case for large particles, if small particles were located outside silica, their appearance at the periphery of the two-dimensional projection of the silica support should be observed at some of the angles as shown in Fig. 3, which is not the case. Moreover, the fact that the distance between metal particles and the edge of silica does not change strongly with the tilt angle supports a localization of the metal near the middle of the silica structures constituting the support. This finding is in agreement with a recent study of Pd/SiO_2 cogelled catalysts by electron tomography combined

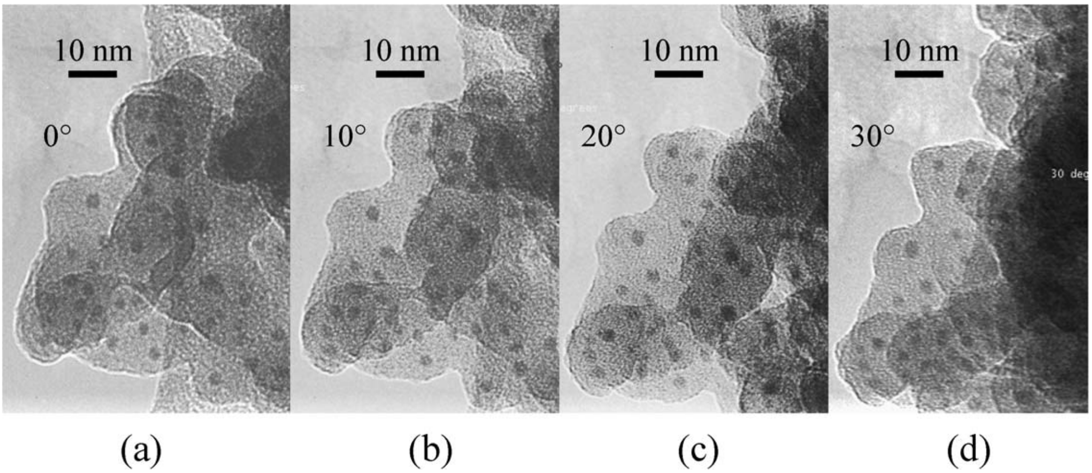

Fig. 1. Rotating TEM, Pd/SiO_2 sample: series of micrographs over an angular tilt range from 0° to 30°.

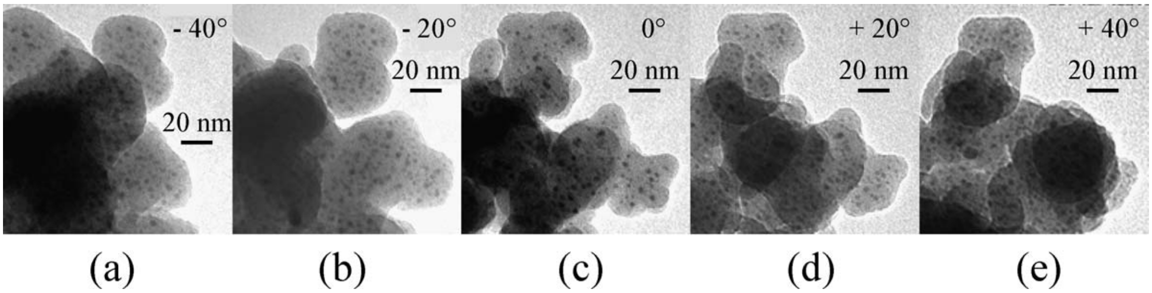

Fig. 2. Rotating TEM, Pd–Ag/SiO_2 sample: series of micrographs over an angular tilt range from −40° to +40°.

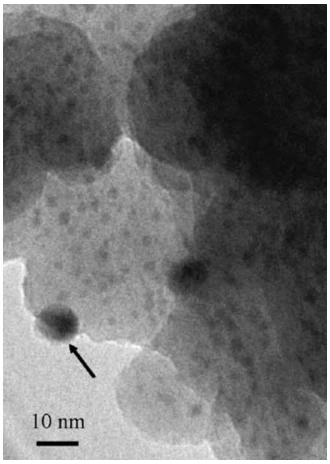

Fig. 3. Pd–Ag/SiO_2 sample: TEM micrograph showing a large metal particle at the periphery of silica (arrow).

with image analysis [14] showing that palladium particles are localized deep inside the silica skeleton and that the distance between the palladium particles and the silica surface is approximately half of the diameter of the silica skeleton.

4. Conclusion

Rotating TEM provides evidence of what had been suggested, but not proven, for a long time—namely, that small active metal particles in cogelled catalysts are located inside the particulate silica xerogel support. Therefore, it appears that the cogelation method enables the building of a real cage around those metal particles to protect them from sintering by a migration and coalescence mechanism [15]. Indeed, cogelled catalysts like the Pd/SiO_2 and Pd–Ag/SiO_2 samples contain small (2–3 nm) metal particles located inside microporous silica particles containing micropores of around 0.8 nm [4]. Thus, because they are larger than the micropores of the silica particles in which they are located, the highly dispersed metal crystallites in cogelled catalysts are caged while remaining completely accessible. Therefore, these crystallites are sinter-proof during high temperature activation and reaction. This is a remarkable property of cogelled catalysts, because sintering of supported metals is a main cause of catalyst deactivation [16,17].

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References

[1] B. Breitscheidel, J. Zieder, U. Schubert, Chem. Mater. 3 (1991) 559.
[2] U. Schubert, New J. Chem. 18 (1994) 1049.
[3] A. Kaiser, A. Görsmann, U. Schubert, J. Sol-Gel Sci. Technol. 8 (1997) 795.
[4] B. Heinrichs, P. Delhez, J.-P. Schoebrechts, J.-P. Pirard, J. Catal. 172 (1997) 322.
[5] G. Trimmel, U. Schubert, J. Non-Cryst. Solids 296 (2001) 188.
[6] S. Lambert, C. Cellier, P. Grange, J.-P. Pirard, B. Heinrichs, J. Catal. 221 (2004) 335.
[7] U. Deschler, P. Kleinschmit, P. Panster, Angew. Chem. Int. Ed. Engl. 25 (1986) 236.
[8] S.P. Watton, C.M. Taylor, G.M. Kloster, S.C. Bowman, in: K.D. Karlin (Ed.), Progress in Inorganic Chemistry, vol. 51, Wiley, New York, 2003, p. 333.
[9] S. Lambert, J.-F. Polard, J.-P. Pirard, B. Heinrichs, Appl. Catal. B 50 (2004) 127.
[10] S. Lambert, C. Alié, J.-P. Pirard, B. Heinrichs, J. Non-Cryst. Solids 342 (2004) 70.
[11] S. Lambert, C.J. Gommes, C. Alié, N. Tcherkassova, J.-P. Pirard, B. Heinrichs, J. Non-Cryst. Solids 351 (2005) 3839.
[12] F. Winter, G.L. Bezemer, C. van der Spek, J.D. Meeldijk, A.J. van Dillen, J.W. Geus, K.P. de Jong, Carbon 43 (2005) 327.
[13] B. Heinrichs, F. Noville, J.-P. Schoebrechts, J.-P. Pirard, J. Catal. 192 (2000) 108.
[14] C.J. Gommes, K. de Jong, J.-P. Pirard, S. Blacher, Langmuir 21 (2005) 12378.
[15] E. Ruckenstein, in: S.A. Stevenson, J.A. Dumesic, R.T.K. Baker, E. Ruckenstein (Eds.), Metal–Support Interactions in Catalysis, Sintering, and Redispersion, Van Nostrand Reinhold, New York, 1987, p. 139.
[16] G.F. Froment, K.B. Bischoff, Chemical Reactor Analysis and Design, Wiley, New York, 1990.
[17] D.L. Trimm, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 3, Wiley–VCH, Weinheim, 1997, p. 1263.