Journal of Catalysis **182,** 274–277 (1999)
Article ID jcat.1998.2358, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

Rh–Pt Clusters and Aggregates on MgO: Catalysts for Toluene Hydrogenation

M. Shirai, O.-B. Yang, W. A. Weber, and B. C. Gates

Department of Chemical Engineering and Materials Science, University of California, Davis, California 95616

Received August 7, 1998; revised November 19, 1998; accepted November 23, 1998

Supported metal catalysts modified by incorporation of a second metal, such as Pt/Al_2O_3 incorporating Re or Ir and used for naphtha reforming (1), may be superior to the simple monometallic catalysts for various reasons, e.g., modification of the metal surface composition by the second metal. Because it is difficult to control the size, structure, and composition of dispersed bimetallic species made conventionally from two different salts, researchers have used molecular metal clusters with preformed metal–metal bonds as precursors. Occasionally, these preparations have given highly dispersed bimetallic clusters (2), but frequently they have instead given segregated metals or bimetallics with low dispersions, and usually the structures of the metal-containing species have been far from well defined (3).

We have used $[PtRh_5(CO)_{15}]^-$ to prepare supported Pt–Rh cluster catalysts, having chosen this precursor because it can be prepared in high yield on MgO (4). Extended X-ray absorption fine structure (EXAFS) (5) and infrared (4, 5) data characterizing the structures of the catalysts and their formation from the precursor have been reported; performance of the catalysts for toluene hydrogenation and EXAFS data characterizing the used catalysts are reported here. The new data show that extremely small supported Pt–Rh clusters have been made that are active, stable catalysts; the data show that aggregated clusters are markedly more active than the clusters.

The preparation of the supported bimetallic catalysts is described elsewhere (4, 5); briefly, $[PtRh_5(CO)_{15}]^-$ was synthesized from $RhCl_3 \cdot xH_2O$ and Na_2PtCl_6 on MgO powder (surface area approximately 70 m^2/g) and treated to remove the CO ligands. The samples were characterized by ν_{co} infrared and EXAFS spectroscopies and X-ray absorption near edge spectroscopy (XANES) (5). The supported metal carbonyl precursors were decarbonylated at 1 atm in flowing He (at 125, 175, or 400°C) or in H_2 (at 125, 200, 275, or 400°C) for 2 h. The resulting bimetallic catalysts contained 1.1 wt% (Pt + Rh).

For comparison, a MgO-supported Rh catalyst containing 1.1 wt% Rh was prepared by mixing $[Rh_6(CO)_{16}]$ and MgO together in a flask with pentane for 1 day. Subsequently pentane was removed by evacuation and the resultant sample was decarbonylated, either in H_2 at 200°C to form clusters characterized by a Rh–Rh coordination of 4.9 or in He at 400°C to form aggregates characterized by a Rh–Rh coordination number of about 8.5.

Each catalyst was used for toluene hydrogenation in a once-through flow reactor; a typical catalyst sample (40 mg) was diluted with 400 mg of inert α-Al_2O_3 particles. Prior to measurements of catalyst performance, the supported metal carbonyl precursors in the reactor were treated in flowing He or H_2 to remove CO ligands and form the active catalysts. The catalytic activity was measured under the following conditions: partial pressures, $P_{H_2} = 710$, $P_{toluene} = 50$ Torr; temperature = 80, 100, or 120°C; a typical flow reactor experiment lasted 8 h. Details are as reported elsewhere (6).

Used catalyst samples for EXAFS analysis were obtained by loading the reactor with 400 mg of catalyst in the absence of α-Al_2O_3; these samples were used to catalyze toluene hydrogenation for 4 h at 100°C. The sealed reactor was transferred to a N_2-filled dry box, and the catalyst, without air contamination, was removed and stored for transfer to a synchrotron.

The EXAFS data were collected at the Rh *K*-edge and the Pt L_{III}-edge for the samples under vacuum at liquid-nitrogen temperature. Data characterizing the unused catalysts were analyzed as described elsewhere (5); data characterizing the used catalysts were analyzed in the same way. The EXAFS parameters are summarized in Table 1. The number of parameters used to fit the data characterizing each sample ranged from 8 to 20; the statistically justified number, estimated on the basis of the Nyquist theorem (7), was at least 22 for each sample.

The samples formed from $[PtRh_5(CO)_{15}]^-$ on MgO were found by infrared spectroscopy to be fully decarbonylated when treated in He at temperatures >125°C or in H_2 at temperatures >200°C (5). The Rh *K*-edge EXAFS data representing these decarbonylated catalysts were used to

0021-9517/99 $30.00

TABLE 1

EXAFS Results Characterizing the Rh–Rh and Pt–Rh Contributions in MgO-Supported Catalysts[a]

Sample no.	Treatment conditions		Absorber	Backscatterer	Unused or used catalyst	N	R (Å)	$\Delta\sigma^2$ (Å^2)	ΔE_0 (eV)
	Gas	Temp. (°C)							
1[b]	He	125	Rh	Rh	Unused	4.5	2.68	0.00231	12.5
					Used	5.0	2.68	0.00420	12.0
2	He	175	Rh	Rh	Unused	6.0	2.68	0.00256	19.7
					Used	5.3	2.67	0.00338	17.2
3	He	400	Rh	Rh	Unused	10.0	2.66	0.00235	4.2
					Used	9.9	2.66	0.00281	4.4
4[b]	H_2	125	Rh	Rh	Unused	5.2	2.71	0.00436	13.0
					Used	5.2	2.70	0.00401	12.2
5	H_2	200	Rh	Rh	Unused	6.0	2.66	0.00461	16.2
					Used	5.6	2.69	0.00464	11.4
6	H_2	275	Rh	Rh	Unused	9.1	2.67	0.00315	7.7
					Used	8.7	2.69	0.00282	2.3
7	H_2	400	Rh	Rh	Unused	8.7	2.67	0.00201	2.4
					Used	9.9	2.68	0.00259	5.5
1	He	125	Pt	Rh	Unused	3.5	2.73	0.00203	20.0
					Used	—	—	—	—
2	He	175	Pt	Rh	Unused	3.1	2.76	0.00138	7.90
					Used	3.6	2.74	0.00105	9.45
3	He	400	Pt	Rh	Unused	4.7	2.76	−0.00219	−10.9
					Used	4.7	2.75	−0.00028	−3.25
4	H_2	125	Pt	Rh	Unused	3.9	2.82	0.00090	1.7
					Used	—	—	—	—
5	H_2	200	Pt	Rh	Unused	3.8	2.80	0.00200	2.8
					Used	—	—	—	—
6	H_2	275	Pt	Rh	Unused	5.0	2.74	0.00000	2.7
					Used	4.5	2.76	0.00011	−2.6
7	H_2	400	Pt	Rh	Unused	5.0	2.76	0.00000	−4.0
					Used	5.0	2.76	0.00043	−2.9
8	H_2	200	Rh	Rh[c]	Unused	4.9	2.68	0.00283	10.4
					Used	4.0	2.69	0.00283	8.4

[a] Notation: N, first-shell coordination number of absorber–backscatterer pair; R, distance; $\Delta\sigma^2$, Debye–Waller factor; ΔE_0, inner potential correction.

[b] Sample was only partially decarbonylated.

[c] Supported rhodium catalyst with no Pt; others contained both Rh and Pt.

determine the fits shown elsewhere (5, 6), and the parameters accounting for the Rh–Rh contributions are summarized in Table 1 for both the unused and used catalysts. The data show that the decarbonylated noble metal species in the unused and used samples of each catalyst were indistinguishable from each other, within the experimental error (approximately ±15–20% in the coordination numbers). Furthermore, the shape and magnitude of the Fourier transform characterizing each used catalyst agree well with those characterizing the corresponding unused catalyst. These comparisons show that there was negligible aggregation or fragmentation of the supported metals during catalysis.

The samples formed by treatment of $[PtRh_5(CO)_{15}]^-$ on MgO in He at 125 or 175°C (Samples 1 and 2) or in H_2 at 125 or 200°C (Samples 4 and 5) were found by EXAFS spectroscopy to have Rh–Rh coordination numbers ≤ 6, indicating metal entities consisting of about 20 atoms or less, on average (8); these are referred to as clusters.

The bimetallic samples decarbonylated at higher temperatures (Samples 3, 6, and 7) were found by EXAFS spectroscopy to incorporate metal entities with Rh–Rh coordination numbers >6, indicating metal entities consisting of more than 20 atoms each, on average; these are referred to as aggregates to distinguish them from the smaller clusters.

The Pt L_{III}-edge EXAFS data characterizing the samples decarbonylated in He (at 125, 175, or 400°C) (Samples 1–3) or in H_2 (at 125, 200, 275, or 400°C) (Samples 4–7) are of lower quality than the Rh K-edge data because of the low Pt loading and nonuniformities in thickness and density of the sample wafers; the Pt-edge data are sufficient only to provide trends in the Pt–Rh coordination numbers and evidence of the existence of Pt interactions with low-*Z* scatterers (5). The structural parameters used to fit the Pt–Rh contributions are summarized in Table 1.

The Rh *K*-edge and Pt L_{III}-edge XANES characterizing the supported metal clusters and aggregates suggest that the samples decarbonylated at lower temperatures in He and in H_2 are more electron deficient than those treated at higher temperatures, as shown by their higher white-line intensities (6); however, because the white line is affected by properties other than the electron density, this suggestion is only tentative.

Toluene hydrogenation catalysis to give methylcyclohexane was observed when the reactor was packed with the supported metal samples, but in blank experiments when the reactor was packed with only α-Al_2O_3, the conversion of toluene + H_2 at 100°C and 1 atm was negligible. Each of the only partially decarbonylated catalysts formed by treatment at 125°C in He or in H_2 (Samples 1 and 4, respectively) underwent a slow break-in as the activity increased by 20% over 10 h on stream while operated at 120°C, indicating that decarbonylation was occurring. In contrast, the initially decarbonylated catalysts, after an initial induction period of about 1 h, underwent slow, steady deactivation, presumably as a result of formation of carbonaceous deposits. After 10 h on stream each catalyst typically had lost about 20% of its activity.

A typical run consisted of operating the catalyst after pretreatment, first at 120°C for 3 h, then at 100°C for 3 h, and then at 80°C for 3 h. The conversions were approximately 5–10%. As data obtained for similar catalysts (7) demonstrate that these conversions were nearly differential, we assume that the conversions observed in this work were also differential, providing the basis for determining rates, represented in units of {moles of toluene converted $[\text{g of } (\text{Pt} + \text{Rh}) \cdot \text{s}]^{-1}$} (Samples 1, 2, 4, and 5). Each rate was determined as the average of several observed rates. The error in the measured activity of a catalyst is estimated to be about ±25%, with the uncertainty determined in part by the catalyst deactivation. The apparent activation energies, E_a, determined from the temperature dependences of the rates, were found to be roughly 6 kcal/mol for each of the Pt–Rh catalysts formed by decarbonylation in He or in H_2—the E_a values are indistinguishable from each other within the experimental error (Table 2).

The Rh–Rh coordination numbers of the fully decarbonylated bimetallic clusters formed at the lowest temperatures (Samples 2 and 5) were about 6, indicating cluster sizes of about 15–20 atoms, on average. Thus, these data and those representing the partially decarbonylated clusters (Samples 1 and 4) show that there was some aggregation of the metal during decarbonylation, but that small clusters were formed.

TABLE 2

Toluene Hydrogenation Catalyzed by MgO-Supported Clusters and Aggregates

Sample no.[a]	$N_{\text{Rh–Rh}}$[b]	Reaction temp. (°C)	$10^5 \cdot$ activity (mol/(s · g of Rh + Pt))	E_a (kcal/mol)[c]
1[d]	4.5	80	5.5	6
		100	9.7	
		120	12.7	
2	6.0	80	12.7	7
		100	22.6	
		120	34.5	
3	10	80	101	6
		100	180	
		120	240	
4[d]	5.2	80	6.2	5
		100	10.6	
		120	12.9	
5	6.0	80	23.6	7
		100	43.9	
		120	68.9	
6	9.1	80	127	5
		100	182	
		120	245	
7	8.7	80	106	6
		100	187	
		120	251	
8	4.9	100	6.0	

[a] See Table 1.

[b] Rh–Rh first-shell coordination number from EXAFS spectroscopy.

[c] Apparent activation energy; see text.

[d] Sample only partially decarbonylated; relatively low activity is inferred to indicate some effect of poisoning by CO.

A comparison of the activities of the supported Pt–Rh cluster catalysts (Samples 2 and 5) with the activity of supported Rh clusters of nearly the same size measured under the same conditions (Sample 8) suggests that the bimetallic clusters were the more active. The data suggest that the Pt in the clusters led to a small increase in activity. This result is in agreement with reports indicating that Pt has a higher activity than Rh for hydrogenation of arenes (9), but the suggestion is not very strongly demonstrated because the average cluster sizes in the several samples were not quite the same.

The clearer result in the activity data is that showing that the activities of the catalysts incorporating the supported metal aggregates (Samples 3, 6, and 7) are greater (by nearly an order of magnitude) than those of the catalysts incorporating supported metal clusters (Samples 2 and 5). The apparent activation energies were about the same for as the supported catalysts (Table 2). The difference in activities between the clusters and aggregates may be related to differences in the surface compositions and structures of these different catalysts, but in view of the EXAFS results indicating that the metal surfaces were enriched in

Pt in these samples (5), we suggest that the data are an indication of a cluster/particle size effect. This result parallels the results obtained for the same reaction catalyzed by supported Ir clusters and particles; the smaller clusters are the less active (10). The explanation(s) for this size dependence remain to be developed, but it has been suggested (10) that the electron deficiency of the clusters relative to the larger aggregates may be partly responsible for the differences in catalytic activity; this explanation is consistent with the XANES data and may extend to the bimetallic samples.

ACKNOWLEDGMENTS

We thank the following for support: the Korea Science and Engineering Foundation (for a fellowship to support O.-B.Y.); the Petroleum Research Fund, administered by the American Chemical Society; the Stanford Synchrotron Radiation Laboratory; and the Department of Energy, Division of Materials Sciences (Contract DE-FG05-89ER45384), for its role in the operation and development of beam line X-11A at the National Synchrotron Light Source, supported by the Department of Energy, Division of Materials Sciences and Division of Chemical Sciences (Contract DE-AC02-76CH00016). X-ray absorption data were analyzed with the XDAP software (11).

REFERENCES

1. Sinfelt, J. H., “Bimetallic Catalysts: Discoveries, Concepts, and Applications.” Wiley, New York, 1983.
2. Fung, A. S., Kelley, M. J., Koningsberger, D. C., and Gates, B. C., *J. Am. Chem. Soc.* **119**, 5877 (1997).
3. Braunstein, P., and Rose, J., *in* “Catalysis by Di- and Polynuclear Metal Cluster Complexes” (R. D. Adams and F. A. Cotton, Eds.), p. 443. Wiley–VCH, New York, 1998.
4. Xu, Z., Kawi, S., Rheingold, A. L., and Gates, B. C., *Inorg. Chem.* **33**, 4415 (1994).
5. Yang, O.-B., Shirai, M., Weber, W. A., and Gates, B. C., *J. Phys. Chem. B* **102**, 877 (1997).
6. Weber, W. A., Ph.D. dissertation, University of California, Davis, 1998.
7. Koningsberger, D. C., and Prins, R., Eds., “X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES.” Wiley, New York, 1988.
8. Kip, B. J., Duivenvoorden, F. B. M., Koningsberger, D. C., and Prins, R., *J. Catal.* **105**, 26 (1987).
9. Koussathana, M., Vamvouka, D., Economou, H., and Verykios, X., *Appl. Catal.* **77**, 283 (1991).
10. Xu, Z., Xiao, F.-S., Purnell, S. K., Alexeev, O., Kawi, S., Deutsch, S. E., and Gates, B. C., *Nature* **372**, 346 (1994).
11. Vaarkamp, M., Linders, J. C., and Koningsberger, D. C., *Physica B* **209**, 159 (1995).