Particle-size Effects of Activated Carbon-supported Rhodium Catalysts on Hydrogenation of Naphthalene in Supercritical Carbon Dioxide Solvent

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Naphthalene hydrogenation over activated carbon-supported rhodium metal particles having dispersion between 10 and 30% was studied; the turnover frequencies increased with decreasing dispersion in supercritical carbon dioxide, while were independent of the metal dispersion in *n*-heptane.

The size of metal particles directly influences the catalytic performance of a supported metal.[1] The tuning of metal particle size of supported metal catalysts is important for structure sensitive reactions in which turnover frequencies (TOFs) depend on the metal particle size and dispersion.

Catalytic hydrogenation over supported metal catalysts in supercritical carbon dioxide (scCO$_2$) has attracted considerable attention because of several advantages such as: (i) nontoxicity and nonflammability of carbon dioxide as a solvent, (ii) easy separation of products and catalysts without distillation processes, and (iii) higher reaction rates because of complete miscibility of hydrogen and carbon dioxide.[2] Further, the control of selectivity in such systems is well demonstrated by manipulating the partial pressure of carbon dioxide.[3] We have recently reported that an activated carbon-supported rhodium catalyst was very effective for naphthalene hydrogenation in scCO$_2$.[4] Ring hydrogenation of naphthalene has potential application as a hydrogen storage system[5] and at present being practiced commercially in the production of high-performance diesel fuel.[6] In this study, we observed that the metal dispersion and particle size of rhodium supported on activated carbon greatly influenced the catalyst activities for naphthalene hydrogenation in scCO$_2$, while catalyst performance was independent of the metal dispersion in *n*-heptane solvent.

Four different activated carbon-supported rhodium catalysts were prepared with a systematic variation in their particle sizes as well as metal dispersion values; 5 wt % Rh/AC and 10 wt % Rh/AC were prepared by a conventional impregnation method using rhodium(III) chloride solution, while 5 wt % Rh/AC-0.3u and 5 wt % Rh/AC-1.0u were prepared by an impregnation method using rhodium(III) chloride solution with urea (urea/rhodium = 0.3 and 1.0 for 5 wt % Rh/AC-0.3u and 5 wt % Rh/AC-1.0u, respectively) (See ESI).[11] We succeeded in preparing Rh/C catalysts having uniformly dispersed rhodium metal particles and changing particle size in a wide range by adding urea rather than changing rhodium content more than 10 wt % and reduction temperature.

The TEM images[11] of 5 wt % Rh/AC and 10 wt % Rh/AC show very small dots (<1 nm) which could not be distinguished from the activated carbon support. The XRD pattern of 5 wt % Rh/AC did not show any diffraction peaks that could be ascribed to rhodium metal; however, a very broad diffraction peak was observed for 10 wt % Rh/AC,[11] suggesting that 5 wt % Rh/AC
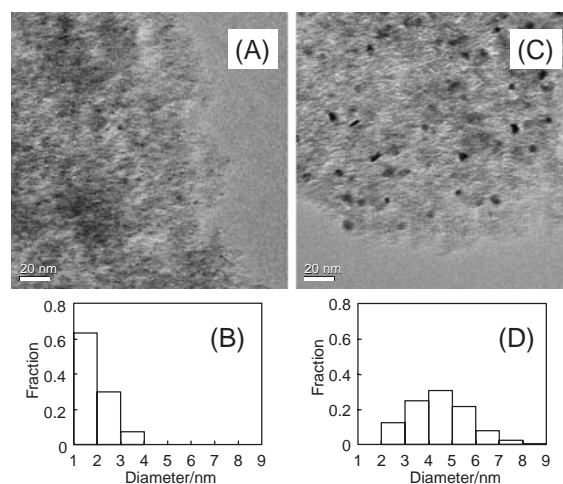
Figure 1. TEM images and particle-size distributions of 5 wt % Rh/AC-0.3u (A), (B) and 5 wt % Rh/AC-1.0u (C), (D).

and 10 wt % Rh/AC have rhodium particles even less than 1 nm. The TEM images of 5 wt % Rh/AC-0.3u (Figures 1A and 1B) and 5 wt % Rh/AC-1.0u (Figures 1C and 1D) clearly show the rhodium particles having average particle sizes of 2.3 and 5.1 nm, respectively, which were close to those calculated from the half width of the XRD peak of Rh(111) using Scherrer's equation (2 and 4 nm for 5 wt % Rh/AC-0.3u and 5 wt % Rh/AC-1.0u, respectively).[11] The number of surface rhodium atoms (metal dispersion) and particle sizes were also determined by hydrogen chemisorption[11] assuming spherical metal particles and these results are summarized in Table 1. The particle sizes of various catalysts calculated from the hydrogen adsorption method showed the following order: 5 wt % Rh/AC < 10 wt % Rh/AC < 5 wt % Rh/AC-0.3u < 5 wt % Rh/AC-1.0u, which was consistent with that obtained by TEM; however, the particle sizes determined by the hydrogen adsorption method were much

Table 1. Dispersion and particle size of activated carbon-supported rhodium catalysts

Catalyst	Dispersion[a]/%	Particle size/nm	
		TEM	H$_2$ ad.[b]
5 wt % Rh/AC	27.9	<1[c]	3.9
10 wt % Rh/AC	26.0	<1[c]	4.2
5 wt % Rh/AC-0.3u	19.7	2.3[d]	5.6
5 wt % Rh/AC-1.0u	10.1	5.1[d]	10.9

[a]Dispersion determined by a hydrogen adsorption method. [b]Calculated using the dispersion value on the assumption that particles were spherical. [c]Under detection limit. [d]Average particle sizes were calculated using $\Sigma(n_i d_i^3)/\Sigma(n_i d_i^2)$. Here, n_i and d_i denotes number and diameter of particles, respectively.
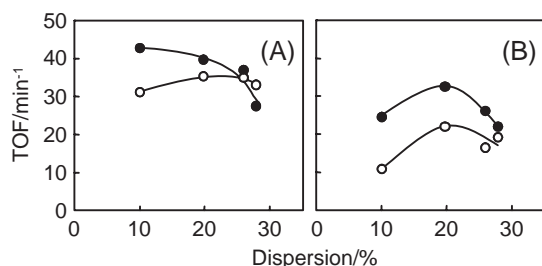
Figure 2. TOF as a function of the metal dispersion of activated carbon-supported rhodium catalysts for the hydrogenation of naphthalene (A) and tetralin (B) in 15 MPa of carbon dioxide (●) and in 20 cm^3 of n-heptane (○). Partial pressure of hydrogen: 3 MPa; reaction temperature: 313 K; reactor capacity: 50 cm^3; initial substrate: 2.34 mmol; catalyst weight; 0.003 g.

larger than those from TEM and XRD results. This difference could be explained by i) the location of rhodium particles within the pores of activated carbon support, and the surface of rhodium particles being covered with carbon, and/or ii) residual chloride ions derived from the precursor, which inhibit the adsorption of hydrogen atoms.[7] The number of adsorbed hydrogen atoms is considered to be the number of surface metal atoms which could act as active sites.

The influence of metal dispersion and particle size on naphthalene hydrogenation was examined by the initial consumption rate of naphthalene in both scCO$_2$ and n-heptane.[11] The amount of naphthalene decreased linearly from the beginning of the reaction in both the solvents, and mainly tetralin (91–95% of selectivity depend on catalysts and solvents), small amounts of cis- and $trans$-decalin (3–7% and 0.3–0.8%, respectively) and octahydronaphthalene (0.8–1.5%) were formed. Figure 2A shows TOF as a function of the metal dispersion for the hydrogenation of naphthalene in both scCO$_2$ and n-heptane at 313 K. The TOF values for naphthalene hydrogenation in scCO$_2$ decreased from 43 to 26 min^{-1} with an increase in the metal dispersion from 10 to 28%, while TOF values remained almost constant in the range between 31 and 35 min^{-1} in the same dispersion range for naphthalene hydrogenation in n-heptane, indicating a strong influence of metal dispersion on the catalyst activity of naphthalene hydrogenation in scCO$_2$.

We also studied the hydrogenation of tetralin in scCO$_2$ and in n-heptane. The amount of tetralin decreased linearly from the beginning of the reaction, and mainly cis-decalin (77–81% of selectivity), small amounts of $trans$-decalin (11–13%) and octahydronaphthalene (8–11%) were the products formed in both the solvents. Figure 2B shows the TOF values as a function of metal dispersion for the hydrogenation of tetralin in both scCO$_2$ and n-heptane at 313 K. The 5 wt % Rh/AC-0.3u catalyst having a dispersion value of 20%, which corresponded to 2.3 nm particle size determined by TEM, showed maximum TOF among the supported catalysts used in both the solvents. The different tendencies were observed between the hydrogenation of naphthalene and tetralin, though both reactants were completely dissolved in scCO$_2$ under the reaction conditions, which was confirmed by direct observation. It is reported that silica-supported rhodium metal particles between 1.4 and 2.0 nm showed a maximum TOF value in the hydrogenation of benzene because the most appropriate ensembles of rhodium atoms were formed.[8] It should be noted that, although the TOF values of

tetralin hydrogenation over all the supported catalysts used were higher in scCO$_2$ than in n-heptane, the TOF values decreased steeply from a maximum over the catalysts having 26 and 28% of dispersion in scCO$_2$ compared with n-heptane.

It has been reported that carbon monoxide is formed on supported noble metal catalysts during hydrogenations in scCO$_2$ by reverse water–gas shift reaction,[2d,9] and that dissociation of carbon dioxide proceeds over stepped surfaces of rhodium metal.[10] Selective poisoning of stepped or kinked sites on a supported platinum catalyst by carbon monoxide was also observed for the hydrogenation of chloronitrobenzene in scCO$_2$.[2d] Hence, one probable explanation for the decrease of the TOF value over the rhodium catalysts having higher dispersion values in scCO$_2$ is the catalyst poisoning by carbon monoxide formed during the hydrogenation in scCO$_2$ on low coordination rhodium sites, whose proportion is larger in higher rhodium dispersion. However, we cannot show any direct evidence for the formation of carbon monoxide during the hydrogenation in scCO$_2$ at this stage. Another possible explanation is that the effect of particle size on the electronic states of rhodium particles could be different in the two solvents and further research is needed in this regard.

Higher reaction rates were observed in scCO$_2$ than those in organic solvents for several hydrogenation reactions over supported metal catalysts;[2,3,4a,4b] however, exceptions were also reported.[4c] One of the reasons behind this contradiction would be the particle-size effect in scCO$_2$ demonstrated in this study. The present results also suggest that the tuning of metal particle size and metal dispersion is very important for heterogeneous catalytic reactions in scCO$_2$.

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11 Supporting Information is available ellectoronically on the CSJ-Journal web site; http://www.csj.jp/journals/chem-lett/.