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The Effect of Li on Structure of Supported Rh Particles in Zeolite

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We prepared Rh ion exchanged Y-type zeolite (RhY) and Li-doped RhY (Li/RhY) catalysts and studied the structure transformation of Rh intercalated species during CO adsorption and CO_2 hydrogenation by EXAFS and TEM. We found that Rh particles in RhY initially supported inside the zeolite cage as 1.3 nm spherical or hemispherical particles. CO exposure of the fresh RhY caused formation of atomically dispersed Rh species. After CO_2 hydrogenation and following reduction, the Rh particles aggregated to form 3.3 nm particles on the outer surface. Meanwhile, Rh particles in Li/RhY were embedded in the zeolite cages, which were narrowed by Li deposition on the wall. The size of the Rh particles was 0.8 nm in diameter. The Rh particles in Li/RhY were stable under reduction, CO adsorption, and CO_2 hydrogenation conditions. We concluded Li additive changed the stability of Rh particles in the supercage by modifying surface hydroxyl group concentration.

Keywords: Rh ion exchanged zeolite; Li additive; EXAFS; Rh particles

INTRODUCTION

Microporous oxides like zeolite have been reported to work as efficient supports of metal particles in catalytic reactions. The size and structure of metal particles inside the pore can be regulated by its shape and size as well as its

chemical properties like acidity. Thus the catalytic behavior of the embedded metal particles vary with the nature of the pore of microporous oxides. In our previous works, we found that Rh ion-exchanged Y-type zeolite catalysts (RhY) showed extraordinarily high activity for CO_2 hydrogenation reaction and produced exclusively methane[1]. By addition of Li to RhY, the catalysis drastically changed and the main product became CO, accompanied by the formation of alcohols[2]. In order to clarify the mechanism of Li additive effect, we studied the structures of Rh particles in RhY and Li/RhY and their structural transformation by TEM and EXAFS.

EXPERIMENTAL

A zeolite supported Rh catalyst (RhY) was prepared by ion-exchanged method as explained elsewhere [1]. NaY-type zeolite (Nishio SK-40) was suspended in aqueous solution $RhCl_3 \cdot 3H_2O$ at 363 K for 24 h. After the catalyst was filtered, washed and dried, it was calcined under the flow of dry air at 673 K for 6 h. A Li-doped catalyst (Li/RhY) was prepared by conventional impregnation method, using $LiNO_3$ as a source of Li and RhY as a substrate. After impregnation, the catalyst was calcined at 673 K for 6 h under dry air. The loading of Rh was set at 5 wt % and an atomic ratio of Li/Rh was 10.

CO_2 hydrogenation reaction was conducted by a fixed bed high pressure flow reactor at 523 K under CO_2+H_2 ($H_2/CO_2 = 3$, total pressure = 3 MPa). Prior to the reaction, the catalyst was reduced in H_2 at 673 K for 0.5 h.

The structure of supported Rh metal particles was observed by TEM and EXAFS. TEM observation was conducted by JEOL JEM-4000FXII operated at an accelerating voltage of 400 kV. Rh K-edge EXAFS was measured at BL10B in Photon Factory (PF) of Institute of Materials Structure Science

(IMSS), High Energy Accelerator Research Organization (KEK). Curve-fitting analyses of EXAFS oscillations were conducted by an EXAFS analysis program Rex (Rigaku Co.). Model parameters for curve-fitting analysis (back scattering amplitude and phase shift) were extracted from an EXAFS oscillation observed for Rh foil.

RESULTS AND DISCUSSION

Figure 1 shows Fourier transforms of EXAFS oscillations ($k^3\chi(k)$) observed for the reduced fresh (not yet used for the reaction) RhY and Li/RhY, where k represents the wave number of a scattered photoelectron, and χ is a normalized EXAFS oscillation. It clearly shows 4 peaks at 0.24, 0.38, 0.44, and 0.51 nm, and curve-fitting analysis revealed that these peaks were attributed to Rh-Rh bonding for a 1st, 2nd 3rd, and 4th coordination sphere, respectively. The coordination numbers derived from curve-fitting analysis for catalysts under various conditions are shown in Figures 2 and 3. We calculated the coordination numbers (CN) for several models (Figure 4) and compared them with observed ones. For the fresh RhY, a spherical or hemispherical model of 1.3 nm (55 atoms or 37 atoms) fits with the observed values as shown in Figures 2 (a) and 4. The average particle size obtained by TEM (1.3 nm) is consistent with this result.

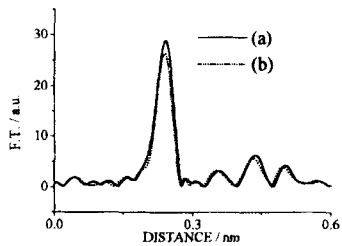

FIGURE 1 Fourier transforms of EXAFS oscillations ($k^3\chi(k)$) observed for the fresh (a) RhY and (b) Li/RhY.

Since the size of the zeolite cage is 1.3 nm, the Rh particles in the fresh RhY were 1.3 nm in size and existed

in the cage as spherical or hemispherical particles. When CO was introduced to the fresh RhY, the coordination numbers greatly decreased. If we simply evaluated the particle size based on the CN of the first shell, it would be 0.5 nm (6 atoms), which should not have third neighbored Rh atoms. However, we observed the higher (3rd and 4th) coordination shells (Figure 2). Therefore, the decrease in coordination number was due to the partial formation of atomically dispersed Rh carbonyl species. The size of remaining particles was probably around 1 nm, judging from the ratio of CN between the 1st and 3rd shells. For the reduced used (already used for the CO_2 hydrogenation reaction) RhY, we observed notable increase in CN's. Compared with CN's calculated for models, it is concluded that the size of the particle was about 3 nm (1055 atoms), which agrees with TEM observation (average particles size = 3.3 nm). Thus the Rh particles in RhY varied their form according to the conditions.

On the other hand, for the fresh Li/RhY, if we evaluated the particle size from CN of the 1st shell, it would be 1.0 nm (28 atoms) as shown in Figures 3 (a) and 4. But, Figure 3 (a) and 4 do not agree well at higher coordination shells. Moreover, the average particle size detected by TEM was 3.0 nm. This conflict was settled by a model which consisted of a mixture of 0.8 nm particles (13 atoms) and

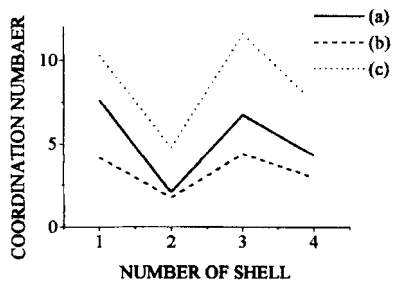

FIGURE 2 Coordination numbers determined by curve-fitting analysis. (a) fresh RhY, (b) CO adsorbed on (a), (c) used RhY.

3.0 nm ones (1055 atoms). In fact, when the ratio of 0.8 nm: 3.0 nm was 9:1, the calculated coordination numbers was fitted to the observed ones (Figures 3 (a) and 4). TEM detected only larger particles. We concluded that most of the Rh particles in Li/RhY were 0.8 nm in size and were embedded in the cage surrounded by Li additive. When CO was adsorbed on Li/RhY, the coordination numbers changed slightly as shown in Figure 3 (b). A small increase in CN was observed after the reaction (Figure 3 (c)), which was due to increase of the portion of larger particles (3.0 nm). However, the majority of the Rh species were still small particles of 0.8 nm, which were embedded in the Li deposited zeolite cages. We conclude that the Rh particles in Li/RhY are relatively stable against H_2, CO and CO_2+H_2.

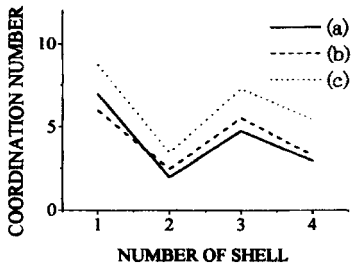

FIGURE 3 Coordination numbers determined by curve-fitting analysis. (a) fresh Li/RhY, (b) CO adsorbed on (a), (c) used Li/RhY.

The different behavior of Rh particles may arise from the different reactivity of the pore surfaces. In RhY, the surface of the pore is covered with OH groups after the reduction treatments. The OH groups can react with Rh particles under the presence of CO in a following reaction scheme.[3]

$$\{Rh\}_n + 2CO + 2OH \rightarrow Rh(CO)_2(O-)_2 + \{Rh\}_{n-1}$$

The CO produced during the reaction also induces the disruption of Rh-Rh

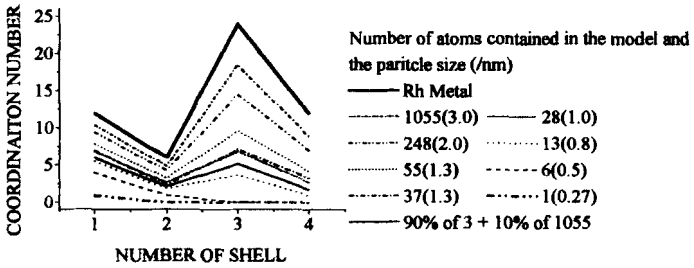

FIGURE 4 Calculated coordination numbers for model particles. Spherical models were used except for 37 atoms (hemispherical). A fine solid line indicates a mixture model (90% 13 atoms +10% 1055 atoms).

bond, creating atomically dispersed Rh species. The monoatomical species can migrate through the pore channel and may be irreversibly caught by large Rh particles present in external surfaces. On the other hand, by addition of Li, OH group is replaced by OLi. The degradation of Rh particles is impossible in the Li/RhY and Rh particles are maintained in the pore. It is suggested that such different behavior of Rh particles under reaction conditions causes different catalyses in CO_2 hydrogenation reactions.

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