

Effects of Co Ion Dispersion upon Selective Catalytic Reduction of NO on CoO/Al₂O₃ Catalysts

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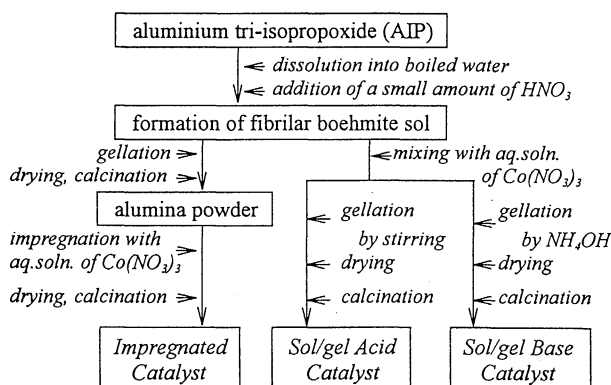
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(Received May 21, 1997; CL-970381)

In alumina-supported cobalt oxide catalyst prepared by sol-gel method, cobalt ions were highly dispersed so as to react with alumina at 773 K to form cobalt aluminate, which enhanced the activity for SCR-NO reaction by propene. While in the catalyst by impregnation cobalt aluminate was not formed at 773 K, which resulted in the poor activity for SCR-NO reaction.

Although the catalyst compositions are the same, the catalytic activity and selectivity happen to depend upon the catalyst preparation routes.¹ This is ascribed to the difference in the dispersion state of active species or in the physical properties of the support used. Interaction between active species and support is also one of the factors to control the catalyst performance. Accordingly, specification of the most effective factor for better catalyst is important for the development of catalyst preparation techniques. In the present study alumina-supported cobalt oxide catalysts were prepared by three different methods, and applied to the selective catalytic reduction (SCR) of NO by propene in order to specify the most effective factor for the reaction.

Catalysts used here were 2 wt% CoO supported on alumina, prepared by three different methods according to the procedures given in Scheme 1. Aluminium tri-isopropoxide (AIP) was used as a starting material for alumina because of its less impurities. One is the conventional impregnation; immersing alumina powder with an aqueous solution of cobalt nitrate. Others are sol-gel methods using, or not using, ammonium hydroxide for gelation, and are designated "sol-gel base" or "sol-gel acid" method, respectively.



Scheme 1. Preparation procedure of CoO/Al₂O₃ catalysts.

All the catalysts were dried and calcined at 773 or 1073 K for 3 h before submitting to the SCR reaction. In Table 1 are given the physical parameters of these catalysts, indicating that those of the

Table 1. Physical properties of the catalysts prepared

catalyst	calcination temp (K)	surface area (m ² /g)	mean pore radius (nm)	pore volume (ml/g)
impregn.	773	190	2.0	0.21
	1073	137	3.2	0.27
sol/gel acid	773	180	2.1	0.21
	1073	119	3.3	0.25
sol/gel base	773	200	4.0	0.42
	1073	148	4.7	0.42

impregnated catalyst calcined at 773 K were similar to those of the sol-gel acid catalyst calcined at 773 K, but were different from those of the sol-gel base catalyst calcined at 773 K. Depth profiles of Co ions in these catalysts were measured by AES, using Ar⁺ ion sputtering method. Auger signals assigned to Co and Al were observed at 650-800 and around 1400 eV, respectively, and peak intensity ratio of Co/Al was calculated on the several points of the catalyst surface after every sputtering. The results obtained for the catalysts calcined at 773 K are shown in Figure 1, indicating that most of the Co ions were deposited on the surface of the impregnated catalyst, while those were highly dispersed in alumina supports of both sol-gel catalysts. Thus, the dispersion states of Co ions in the sol-gel catalysts were much different from those in the impregnated catalyst.

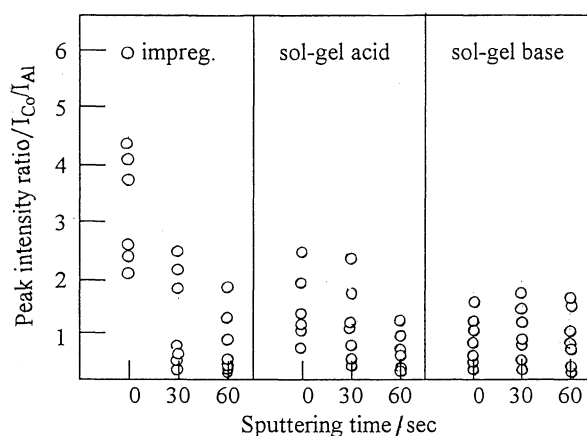


Figure 1. Depth profiles of Co ions in the CoO/Al₂O₃ catalysts.

These three kinds of the catalysts were submitted to the SCR reaction using gases consisting 1000 ppm NO, 300 ppm propene, 10 % oxygen and He as a diluent with W/F being 0.2 g s cm⁻³,² in order to see which is a more effective factor, physical parameters

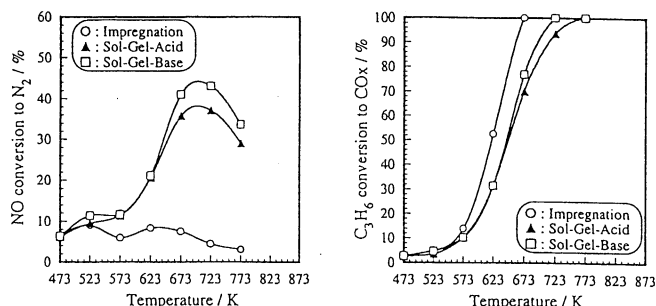


Figure 2. Conversions of NO (left) and propene (right) on three kinds of $\text{CoO}/\text{Al}_2\text{O}_3$ catalysts calcined at 773 K.

or dispersion states. The reaction temperature was varied from 473 to 873 K, and the conversions of both NO and propene were observed at the steady-state of reaction at various temperatures. In Figure 2 are depicted the results obtained for these catalysts. Catalytic performance of the impregnated catalyst was significantly different from those of both sol-gel catalysts. Catalytic activities of the sol-gel catalysts calcined at 773 K for NO reduction were higher than that observed on the impregnated catalyst calcined at 773 K, while the catalytic activities for propene combustion on the sol-gel catalysts were, inversely, lower than that on the impregnated catalyst.

As shown in Table 1, the physical parameters of the impregnated catalyst calcined at 773 K were similar to those of the sol-gel acid catalyst calcined at 773 K. However, Figure 1 suggests that the dispersion states of Co ions in the impregnated catalyst were different from those in both sol-gel catalysts calcined at 773 K. Considering the results given in Figure 2, it can be concluded that, for the SCR-NO reaction on $\text{CoO}/\text{Al}_2\text{O}_3$ catalyst, the dispersion states of Co ions is more effective factor than the physical parameters of the catalyst.

We have a new problem how Co ion dispersions attributed to the SCR reaction. In order to discuss the problem, the SCR reaction was carried out on these three kinds of catalysts calcined at 1073 K under the same conditions as mentioned above. The results are shown in Figure 3. It was found that the catalytic activity of the impregnated catalyst for SCR-NO reaction was extremely enhanced by the calcination at 1073 K, though its activity for the propene combustion decreased. Thus, the catalytic activities for NO reduction and for propene combustion on these three kinds of catalysts became the same after the calcination at 1073 K for 3 h, which may cause the structural changes of Co ions in the catalysts. In order to confirm the structural changes by calcination at 1073 K, EXAFS techniques were applied to the

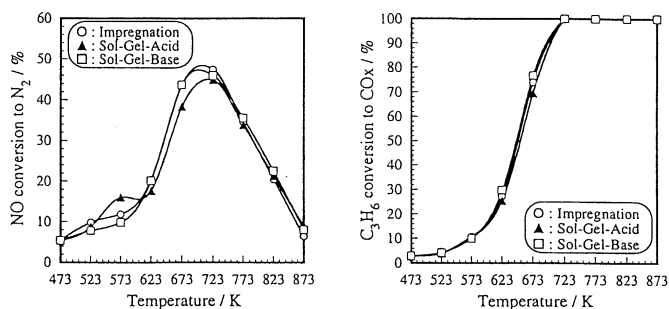


Figure 3. Conversions of NO (left) and propene (right) on three kinds of $\text{CoO}/\text{Al}_2\text{O}_3$ catalysts calcined at 1073 K.

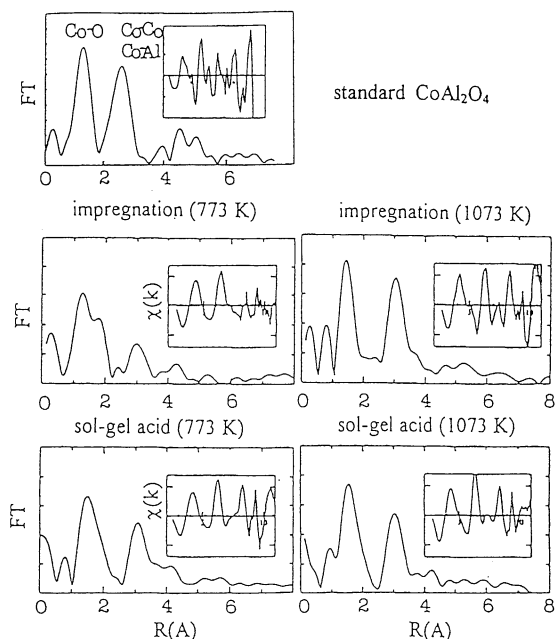


Figure 4. EXAFS Fourier patterns of the standard CoAl_2O_4 (upper), impregnated (middle) and sol-gel acid (lower) catalysts calcined at 773 and 1073 K.

catalysts calcined at 773 and 1073 K, respectively. EXAFS Fourier patterns of the impregnated and the sol-gel acid catalysts are shown in Figure 4 (those of the sol-gel base catalyst are not given here, because they are almost the same to those of the sol-gel acid one).

EXAFS Fourier pattern of the impregnated catalyst calcined at 1073 K was similar to that of the standard CoAl_2O_4 , indicating that the cobalt oxides reacted with the alumina support to form CoAl_2O_4 at 1073 K, and that the active species in $\text{CoO}/\text{Al}_2\text{O}_3$ catalysts for SCR-NO were, probably, finely-divided CoAl_2O_4 ,³ since bulk CoAl_2O_4 did not work well for the reaction. It was also proved that CoAl_2O_4 was formed in the sol-gel catalysts calcined even at 773 K, but most of cobalt ions in the impregnated catalyst were not in the lattice of CoAl_2O_4 . In the impregnated catalyst, most of Co ions might belong to Co_3O_4 crystallites, since Co_3O_4 has been reported^{3,4} to exhibit a significantly high activity for propene combustion (see Figure 2). Now, we conclude that highly dispersed Co ions in the sol-gel catalysts were ready to react with alumina to form CoAl_2O_4 by calcination at 773 K, and exhibited a high activity for SCR-NO. In the impregnated catalyst CoAl_2O_4 crystallites were not formed by calcination at 773 K, because of the poor dispersion of Co ions in the catalyst. The most important factor for the preparation of $\text{CoO}/\text{Al}_2\text{O}_3$ catalyst to be employed for SCR-NO is in the dispersion states of Co ions.

References and Notes

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