Catalytic Activities of $CoAl_2O_4$ for Key Reactions Related to Selective Reduction of Nitrogen Monoxide with Ethene in Excess Oxygen

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The synthesis of Co_3O_4-free $CoAl_2O_4$ was successfully achieved, and it was revealed that this oxide ($CoAl_2O_4$) was more active than Al_2O_3 for $NO+O_2$ reaction, the initiation step of the selective reduction of NO over cobalt-loaded aluminas, but was less active than Co_3O_4-containing $CoAl_2O_4$ for $C_2H_4+O_2$ reaction, a side reaction.

Recently, cobalt-added alumina (Co/Al_2O_3) is attracting great attention as a catalyst for selective reduction of NO by hydrocarbons.[1-5] In Co/Al_2O_3 calcined in air, cobalt usually exists as Co_3O_4 and $CoAl_2O_4$.[1-5] Of the two cobalt species, Co_3O_4 can act as an oxidation catalyst, but the catalytic role of $CoAl_2O_4$ is still controversial.[5] Most bulk $CoAl_2O_4$ samples involve small amount of Co_3O_4. In order to characterize the surface $CoAl_2O_4$ of Co/Al_2O_3, XPS studies have been often conducted.[1, 2, 4, 5] In interpreting the spectra, the XPS data of a reference $CoAl_2O_4$ are necessary, but they are not available, since although several XPS spectra of bulk $CoAl_2O_4$ samples have been reported,[6-10] they are not the same; for example the binding energy value of $Co2p_{3/2}$ has dispersed in the range of 780.6[6] ~ 782.2 eV.[10] One of the main reasons causing such a difference is probably that the purities of $CoAl_2O_4$ samples are not the same. However, no reliable method for preparing Co_3O_4-free $CoAl_2O_4$ has been proposed so far.

In the present study, therefore, we attempted to prepare a special $CoAl_2O_4$ which is free from Co_3O_4 not only in the bulk but in the surface, then characterized it by XRD and XPS, and finally evaluated its catalytic activities for $NO+O_2$ and $C_2H_4+O_2$ reactions, the key-reactions of the selective reduction of NO.

$CoAl_2O_4$ was prepared as follows. Stoichiometric amounts of Co and Al metals in the form of powder were dissolved in a nitric acid solution (0.5 M) at 60 °C, then urea was added as a precipitant, heated at 95 °C to form precipitate, then filtered, washed with deionized water, filtered again, dried at 120 °C for 24 h, calcined at 500 °C for 4 h, and finally calcined at 800 °C-1200 °C for 4 h. The selective removal of Co_3O_4 from a $CoAl_2O_4$ sample was carried out as follows. The sample was first reduced with hydrogen in order to convert Co_3O_4 to metallic cobalt and then immersed in a nitric acid solution at 60 °C to dissolve out the metallic cobalt (metallization-dissolution (MD) treatment).[5] A $CoAl_2O_4$ sample was denoted as follows: $CoAl_2O_4$(calcination temp./°C) or $CoAl_2O_4$(calcination temp./°C, MD). X-Ray powder diffraction patterns were taken with a Rigaku-Electronic diffractometer RINT-1200 using monochromatic CuKα radiation. The surface area of samples was determined by the BET method using liquid N_2. X-Ray photoelectron spectroscopy (XPS) analysis was performed with a Rigaku XPS-7000 spectrometer using a AlKα X-ray source operated at 10 kV and 30 mA. The binding energies were corrected by using the value of 285.0 eV for the C 1s level resulting from the contaminated carbon. The reproducibilities of the values thus obtained were within ± 0.2 eV. The $NO+O_2$ and $C_2H_4+O_2$ reactions were performed using a fixed-bed flow tubular reactor at a W/F of 0.18 $g{\cdot}s{\cdot}cm^{-3}$ (catalyst, 0.4 g; total flow rate, 130 $cm^3{\cdot}min^{-1}$). All the catalysts were further calcined at 800 °C or 1000 °C for 4 h in air before use.

Table 1 and Figure 1 show the results of XRD studies of $CoAl_2O_4$ samples prepared by heating at different temperatures. The results listed in Table 1 suggest that in $CoAl_2O_4$(800), small amount of Co_3O_4 exists together with $CoAl_2O_4$, while in both $CoAl_2O_4$(1000) and $CoAl_2O_4$(1200), no Co_3O_4 exists.

Figure 2 shows the XPS spectra of several $CoAl_2O_4$ samples. The $Co2p_{3/2}$ binding energy of $CoAl_2O_4$(800) was 781.1 eV, while those of $CoAl_2O_4$(800, MD) and $CoAl_2O_4$(1000), and $CoAl_2O_4$ (1200) were 781.3 eV. The results of computer fitting (dotted line) indicate that $CoAl_2O_4$(800) contained $CoAl_2O_4$ as well as Co_3O_4(very little), but the others comprised only $CoAl_2O_4$. In fact, it was only $CoAl_2O_4$(800) that released Co^{2+} ions during the MD treatment, indicating that $CoAl_2O_4$(800) clearly contained Co_3O_4.

Table 1. XRD data of $CoAl_2O_4$ calcined at various temperatures

800 °C		1000 °C		1200 °C		Co_3O_4[a]		$CoAl_2O_4$[b]	
d/Å	Int.	d/Å	Int.	d/Å	Int.	d/Å	Int.	d/Å	Int.
4.672	5	4.706	2	4.702	2	4.667	16	4.679	8
2.866	51	2.869	57	2.868	60	**2.858**	33	2.865	65
2.443	100	2.447	100	2.447	100	2.437	100	2.444	100
2.023	23	2.028	16	2.028	15	**2.021**	20	2.026	14
1.859	3	1.862	4	1.861	5	1.855	<1	1.860	4
1.652	14	1.655	16	1.655	17	1.650	9	1.654	13
1.556	31	1.561	35	1.561	40	**1.556**	32	1.560	27
1.432	42	1.434	45	1.434	48	1.429	38	1.433	33

[a]JCPDS 43-1003. [b]JCPDS 44-160.

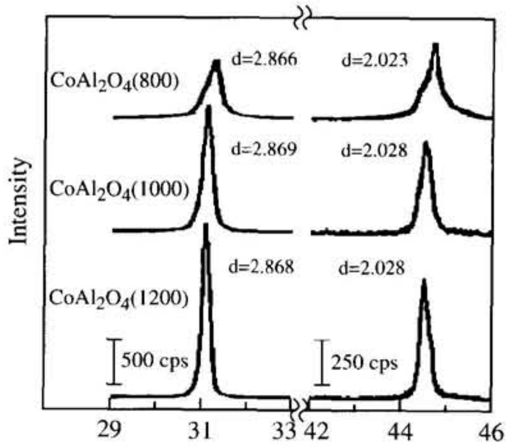

Figure 1. XRD patterns of $CoAl_2O_4$ calcined at various temperatures.

Figure 3 illustrates the activity of the $CoAl_2O_4$ catalysts for $NO+O_2$. Clearly, the activity of $CoAl_2O_4$(1000), Co_3O_4-free

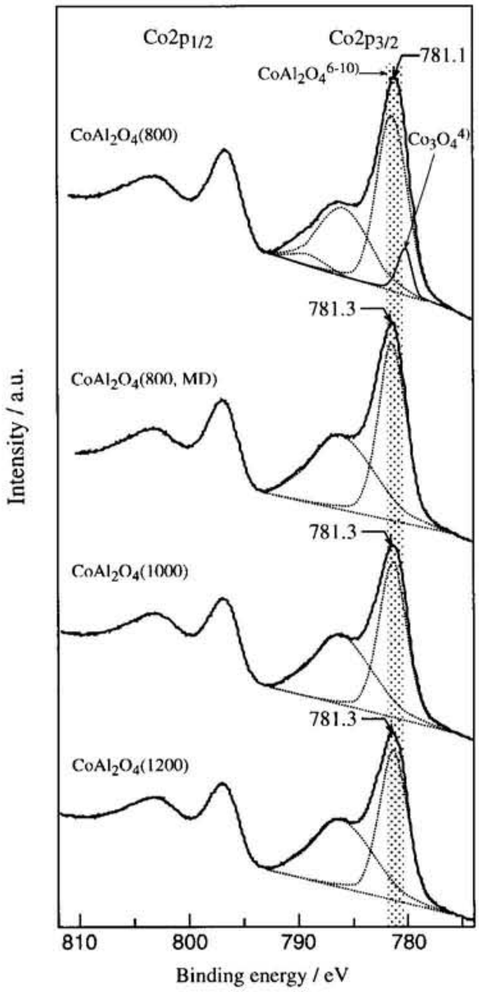

Figure 2. XPS spectra of $CoAl_2O_4$ calcined at various temperatures.

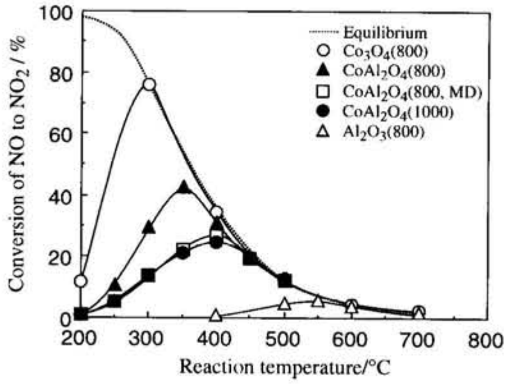

Figure 3. Temperature dependence of the activity of various catalysts for $NO+O_2$. NO = 1000 ppm, O_2 = 2.0%, He = balance.

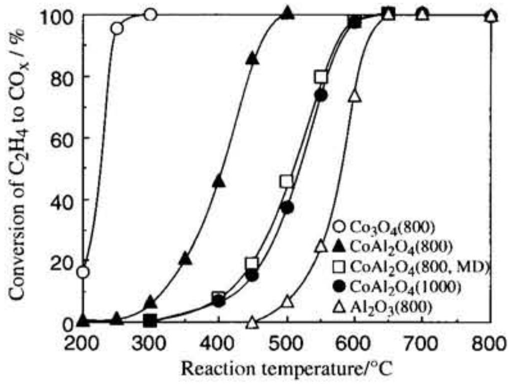

Figure 4. Temperature dependence of the activity of various catalysts for $C_2H_4+O_2$. C_2H_4 = 500 ppm, O_2 = 2.0%, He = balance.

$CoAl_2O_4$, was lower than that of $CoAl_2O_4$(800), Co_3O_4-containing $CoAl_2O_4$, but sufficiently higher than Al_2O_3. As can be seen in Figure 4, $CoAl_2O_4$(1000) was less active than $CoAl_2O_4$(800) for $C_2H_4+O_2$ too. $CoAl_2O_4$(800)'s superiority in the activities over $CoAl_2O_4$(1000) can be due to the specific surface area, and really their specific surface areas were considerably different, 52 and 20 $m^2 \cdot g^{-1}$, respectively. However, the specific surface area was not a critical factor for determining the oxidation activities of the $CoAl_2O_4$ catalysts, because $CoAl_2O_4$(800, MD) showed lower activities than $CoAl_2O_4$(800), although the former's specific surface area (74 $m^2 \cdot g^{-1}$) was higher than the latter's. Therefore, the lower oxidation activities of $CoAl_2O_4$(1000) is due to the absence of Co_3O_4.

Over Co/Al_2O_3 catalysts, $NO+C_2H_4+O_2$ is considered to occur via the following reaction mechanism.[5]

$$NO + O_2 \rightarrow NO_2 \quad (1)$$
$$NO_2 + C_2H_4 \rightarrow (C_xH_yO_z) \rightarrow N_2 + CO_x + H_2O \quad (2)$$
$$C_2H_4 + O_2 \rightarrow CO_x + H_2O \quad (3)$$

Over Co/Al_2O_3 step (1) and step (2) are reported to be catalyzed by Co species and Al_2O_3, respectively.[2] Thus, an ideal Co/Al_2O_3 catalyst for $NO+C_2H_4+O_2$ should be more active than Al_2O_3 for step (1) and be as poorly active as possible for step (3), a side reaction. Figures 3 and 4 suggest that such requirements can be fulfilled by using Co_3O_4-free $CoAl_2O_4$ as the Co species. Such a catalyst will be prepared so as to reduce its Co_3O_4 content, by calcining at 800 °C[4] or by removing residual Co_3O_4 selectively.[5]

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