Synergy of $CoAl_2O_4$ and Al_2O_3 in $CoAl_2O_4$-Al_2O_3 Catalysts for Selective Reduction of Nitrogen Monoxide with Ethene in Excess Oxygen

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A well-mixed $CoAl_2O_4$-Al_2O_3 catalyst calcined at 800 °C showed higher activity for the title reaction than that calcined at 500 °C as well as a roughly-mixed $CoAl_2O_4$-Al_2O_3 catalyst. The results of characterization suggested that in a $CoAl_2O_4$-Al_2O_3 catalyst the synergy of $CoAl_2O_4$ and Al_2O_3 particles at their interfaces is a critical factor causing its high activity.

The selective catalytic reduction of NO with hydrocarbons(HC) in the presence of excess oxygen ($NO+HC+O_2$) was reported to be catalyzed by zeolites as well as metal oxides, with or without transition metal.[1, 2] Among metal oxides, alumina has been represented so far.[2] Alumina is often used together with transition metals.[2] Cobalt-loaded alumina, Co/Al_2O_3, has been examined extensively as one of such metal-promoted alumina catalysts in order to clarify its catalytic action. Over both Al_2O_3 and Co/Al_2O_3, $NO+HC+O_2$ proceeds via the following reaction pathway: $NO + O_2 \rightarrow NO_2$, $NO_2 + HC \rightarrow N_2$.[3, 4] In Co/Al_2O_3 catalysts the Co species and Al_2O_3 are believed to catalyze the first step and the second step, respectively.[5] Generally, the Co species exist as $CoAl_2O_4$ and Co_3O_4. For highly active Co/Al_2O_3 catalysts, $CoAl_2O_4$ is inevitable Co species[3, 5, 6] and Co_3O_4 is required to be highly dispersed.[6] Recently, it is proved that $CoAl_2O_4$ itself sufficiently catalyzes the first step, and favorably it is not so active for a side reaction such as $HC+O_2$[7] Thus, the roles of $CoAl_2O_4$ and Al_2O_3 of Co/Al_2O_3 catalysts have been revealed more and more. It should be noted here that $CoAl_2O_4$ can catalyze $NO_2 \rightarrow NO + O_2$ too, because it is active for its reverse reaction, the first step. If NO_2, which was produced from NO and O_2 over $CoAl_2O_4$, does not move immediately to the surface of Al_2O_3 but stays for a little while on $CoAl_2O_4$, NO_2 will readily convert to NO, and as a result the second step will be hindered. So in active Co/Al_2O_3 catalysts, $CoAl_2O_4$ and Al_2O_3 would come closer together. However, the structure of the active surfaces has never been investigated. Therefore, we describe the activities of $CoAl_2O_4$-Al_2O_3 catalysts for $NO+C_2H_4+O_2$, in which $CoAl_2O_4$ and Al_2O_3 were mixed in three different ways.

$CoAl_2O_4$ and Al_2O_3 were prepared by the same method as described elsewhere[7] except for the calcination temperatures; in this experiment each catalyst was calcined at 1000 °C and 800 °C, respectively (denoted as $CoAl_2O_4(1000)$ and $Al_2O_3(800)$). A well-mixed $CoAl_2O_4$-Al_2O_3 catalyst was prepared as follows: a mixture of $CoAl_2O_4(1000)$ and $Al_2O_3(800)$ with the Co content of 5 wt% was ground for 10 min with a FRITSCH planetary micro mill pulverisette 10 using agate pot and balls, followed by pelletizing, crushing, sieving(30-42 mesh), and finally calcining at 500 °C or 800 °C for 4 h in air. This type of $CoAl_2O_4$-Al_2O_3 catalyst is denoted as WMC-temperature of calcination/ °C; WMC is the acronym of "well-mixed and calcined". For comparison, a roughly-mixed $CoAl_2O_4$-Al_2O_3 catalyst (its Co content is the same as that of WMC-500), which just consists of the components in the form of pellets(30-42 mesh), was also prepared and used as a catalyst without further calcination. This type of $CoAl_2O_4$-Al_2O_3 catalyst is denoted as RM; RM is the acronym of "roughly-mixed". $CoAl_2O_4(1000)$, $Al_2O_3(800)$, and Co_3O_4-free $Co(5\ wt\%)/Al_2O_3$ calcined at 800 °C (denoted as $Co(5)/Al_2O_3(800, MD)$)[4] were also used in the form of pellets(30-42 mesh size). The reaction of $NO+C_2H_4+O_2$ was carried out in a fixed bed flow reactor at W/F of 0.18 $g{\cdot}s{\cdot}cm^{-3}$ at temperatures ranging from 200 °C to 800 °C. All the catalysts were packed with quartz wool plugs in a U-shaped quartz tube reactor (inner diameter, 6 mm) and then heated *in situ* at 300 °C. A reactant gas (NO,1000 ppm; O_2, 2.0%; C_2H_4, 500 ppm; He, balance) was passed at a total flow rate of 130 $cm^3{\cdot}min^{-1}$ through a catalyst bed (0.40 g). The outflow gas was analyzed by gas chromatography using a Molecular Sieve 5A column (3 m; N_2, O_2, CO, and NO were separated) and Porapak Q column (3 m; CO_2, C_2H_4, and N_2O were separated). Sampling was carried out twice at every temperature to check the reproducibility of the activity. In $NO+C_2H_4+O_2$, N_2O formation was negligible under the present reaction conditions. X-Ray powder diffraction patterns were taken with a Rigaku-Electronic diffractometer RINT-1200 using monochromatic Cu$K\alpha$ radiation; 50 mg of silicon powder was mixed as an internal standard with 1.0 g of a sample powder. The surface area of the samples was determined by the BET method using liquid N_2; the reproducibilities of the values were within ±1%. X-Ray photoelectron spectroscopy (XPS) analysis was performed with a Rigaku XPS-7000 spectrometer using a Al$K\alpha$ 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.

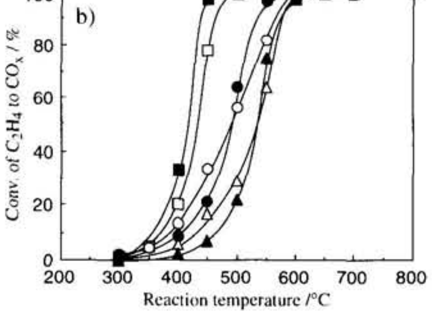

Figure 1. Temperature dependence of the catalytic activity of various catalysts for $NO+C_2H_4+O_2$.

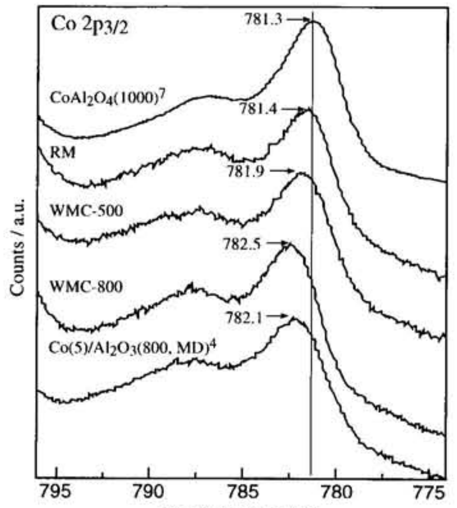

Figure 2. XPS spectra of various catalysts.

Figure 1 shows the activities of three types of $CoAl_2O_4$-Al_2O_3 catalysts for $NO+C_2H_4+O_2$ as a function of reaction temperature. RM showed higher activity than Al_2O_3(800) below *ca.* 500 °C, although the activity of $CoAl_2O_4$ alone (0.06 g, weight of Co in RM) was quite small (max conv. = 2%). These results indicate that $CoAl_2O_4$ in RM promoted the reaction in cooperation with Al_2O_3. WMC-500 showed higher activity than RM, implying the degree of contact between $CoAl_2O_4$ and Al_2O_3 particles is correlated to the activity. Interestingly, when WMC-500 which was once used in $NO+C_2H_4+O_2$ at 200-800 °C was used again without further calcination, the activity was higher than that of fresh WMC-500. This could be ascribed to the fact that fresh WMC-500 was heated at high temperatures around 800 °C during the reaction. In order to prove this hypothesis, WMC-800 was also examined. As expected, WMC-800 showed higher activity than the spent WMC-500. It is also noted that the active temperature region of WMC-800 includes that of Co(5)/Al_2O_3(800, MD). The activities of the three types of $CoAl_2O_4$-Al_2O_3 catalysts for the oxidation of ethene in $NO+C_2H_4+O_2$ decreased in the order, WMC-800 > spent WMC-500 > WMC-500 > RM. This order was quite similar to that for the reduction of NO to N_2 in $NO+C_2H_4+O_2$.

As can be seen in Figure 2, the binding energy (BE) of WMC-800 was higher than that of WMC-500. Since BE shift to the higher energy side is generally ascribed to more positively-charged metal species, the Co species of WMC-800 is considered to be positively charged too. This would be due to the strong interaction between the Co species of $CoAl_2O_4$ and Al_2O_3. In this sense, it is interesting that the BE of WMC-800 was higher than that of Co(5)/Al_2O_3(800, MD). In addition, it is noted that the BE of WMC-500 was higher than those of RM and $CoAl_2O_4$(1000). This suggests that the interaction between the Co species of $CoAl_2O_4$ and Al_2O_3 appeared in WMC-500 too.

Figure 3 shows the pore size distribution of WMC-500 and WMC-800. The pore volume of WMC-800 at the pore radius of *ca.* 0.8 nm and ca. 2 nm was smaller than that of WMC-500 and instead in case of WMC-800 macropores appeared. The BET surface area (162 $m^2 \cdot g^{-1}$) of WMC-800 was slightly lower than that (169 $m^2 \cdot g^{-1}$) of WMC-500. The XRD patterns of WMC-500 and WMC-800 were similar except their diffraction intensities (not shown). The intensities of the strongest diffraction line due to $CoAl_2O_4$ were 1074 cps and 882 cps for WMC-500 and WMC-800, respectively. The fact that the intensity for WMC-800 was slightly lower than that for WMC-500 indicates that the amount of $CoAl_2O_4$ in WMC-800 decreased; $CoAl_2O_4$ would react with Al_2O_3 in part.

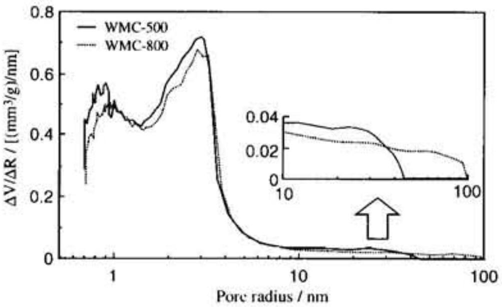

Figure 3. Pore size distribution of WMC-500 and WMC-800.

In view of the results of the above characterization, $CoAl_2O_4$ particles are considered to contact closely with Al_2O_3 particles to form well-grown interfaces. In contrast, in the case of WMC-500, necking between $CoAl_2O_4$ particles and Al_2O_3 particles would hardly be developed because of the low calcination temperature.

Over Co/Al_2O_3, $NO+C_2H_4+O_2$ proceeds via the following reaction pathway: $NO + O_2 \rightarrow NO_2$, $NO_2 + C_2H_4 \rightarrow N_2$.[3,4] The Co species and Al_2O_3 of Co/Al_2O_3 catalysts are believed to catalyze the first step and the second step, respectively.[5] In the catalysts used in the present experiments, the Co species exist as only $CoAl_2O_4$. $CoAl_2O_4$ can catalyze the first step.[7] According to the definition of catalyst, $CoAl_2O_4$ can catalyze the reverse reaction of the first step, $NO_2 \rightarrow NO + O_2$ too. Therefore, if NO_2 produced on $CoAl_2O_4$, does not move immediately to the surface of Al_2O_3 but stays or adsorbs on $CoAl_2O_4$ a moment, NO_2 will convert to NO. This situation means that the second step is hindered. In contrast, if NO_2 moves promptly from $CoAl_2O_4$ to the surface of Al_2O_3, NO_2 will react with C_2H_4 to form N_2. In WMC-800, the well-grown interfaces may assist this prompt transfer or may newly-generated active sites on the interfaces may catalyze $NO_2+C_2H_4$ to form N_2. Anyhow, the degree of sintering between $CoAl_2O_4$ particles and Al_2O_3 particles is considered to be a critical factor for generating a maximal activity of $CoAl_2O_4$-Al_2O_3 catalyst. The fact that the active temperature region of Co(5)/Al_2O_3(800, MD) was included in that of WMC-800 suggests that in the former catalyst also, $CoAl_2O_4$ particles and Al_2O_3 particles are subjected to sintering slightly to generate its high activity.

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