Bull. Chem. Soc. Jpn., *71*, 2331—2337 (1998)

Studies on Active Species for Selective Catalytic Reduction of NO on Alumina-Supported Cobalt Oxide Catalysts

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(Received May 1, 1998)

Alumina-supported cobalt oxide catalysts were prepared by three different methods: The impregnation and sol/gel methods using either an acid or a base as a precipitant. The catalysts prepared by sol/gel methods, followed by calcination at 773 K, exhibited a significant activity for the selective catalytic reduction (SCR) of NO with propene as a reductant. The catalyst prepared by impregnation showed poor activity when it was calcined at 773 K, but exhibited enhanced activity when calcined at 1073 K. This is attributed to tiny $CoAl_2O_4$ crystallites formed during calcination of the catalyst at 1073 K. However, in sol/gel catalysts, finely-divided $CoAl_2O_4$ crystallites were formed during calcination, even at 773 K, because of the high dispersion of Co ions in the alumina support. Thus, the active species of alumina-supported cobalt oxide catalysts for SCR of NO with propene were concluded to be tiny $CoAl_2O_4$ crystallites dispersed on alumina.

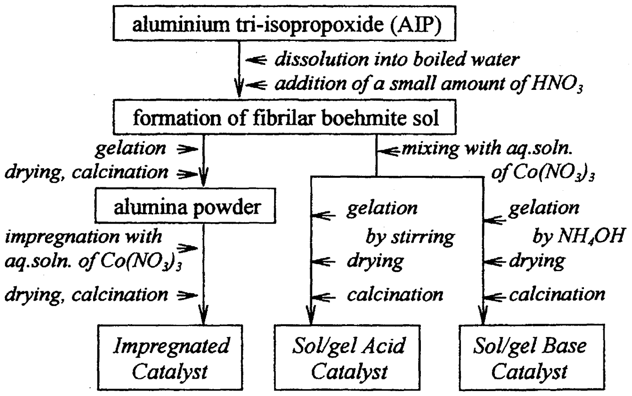
SCR of NO using hydrocarbons as a reductant has been of current interest, since it was reported that alumina as well as zeolite-based catalysts were effective even in an excess amount of oxygen.[1—3] Among zeolite-based catalysts, Cu-ZSM5 exhibited high activity over a wide range of temperatures, but was less durable in the presence of water vapor and/or SO_2 in exhaust gases,[4,5] although Fe-ZSM5 was recently reported to have a high resistance against both water vapor and SO_2.[6,7] Though alumina was more durable in exhausts containing 10% water vapor, it showed poor activity for SCR of NO at low temperatures.[8] Various metal oxides were dispersed on alumina to improve the activity at low temperatures, and were classified into three groups: Cu, Co, Fe, and Cr; they significantly enhanced the activity of alumina, though Ni, Mn, Zn, and V had no effect upon the activity, but Ag, Ca, Pd, and K depressed the activity of alumina at low temperatures.[9] One of the present authors has also studied the effects of metal oxides dispersed on alumina upon the activity for SCR of NO at low temperature, and has reported improved activities of alumina-supported cobalt and iron oxide catalysts.[10]

Alumina-supported cobalt oxides have been extensively studied, partially because of the fundamental interest to study active species for SCR of NO,[11,12] and partially because of applications for practical use. SCR of NO has generally been accepted to initiate the oxidation of NO to NO_2,[13—15] though the direct decomposition of NO to initiate SCR of NO has not been completely denied.[16,17] Since the first step of NO oxidation is the absorption of NO, studies on NO adsorption sites on alumina-supported cobalt oxide catalysts have been extensively pursued. In an early paper, it was reported that NO adsorbed on Co_3O_4, but not on $CoAl_2O_4$, because of the absence of Co ions from the surface of $CoAl_2O_4$, evidenced by means of ion scattering spectroscopy.[18] On the basis of this result and of the fact that SCR of NO did not take place on bulk-like $CoAl_2O_4$ crystallites, active species on alumina-supported cobalt oxides were proposed to be highly dispersed Co_3O_4 crystallites.[19] However, no Co_3O_4 crystallites were detected in the active catalysts prepared in the present work. Accordingly, the purpose of this work is to specify the active species on alumina-supported cobalt oxides for SCR of NO.

Experimental

1. Catalyst Preparation. Three kinds of alumina-supported cobalt oxide catalyst were prepared using fibrillar boehmite sols, which were obtained by the hydrolysis of aluminium triisopropoxide (AIP) in the same way as described in a previous paper.[20] The preparation procedures are given in Table 1; in short, one is a conventional impregnation technique using alumina powder prepared from boehmite sols; the other is a sol–gel method using, or not using, aqueous ammonium for gelation. These are designated as "sol/gel base" and "sol/gel acid", respectively. All of the catalysts were dried and calcined at 773 or 1073 K for 3 h before submitting to SCR of NO or other measurements for characterization. Amount of cobalt oxides dispersed was generally settled to be 2 wt% of the

Table 1. Preparation Procedures of Three Kinds of CoO/Al_2O_3 Catalysts



catalysts employed, although the amount was varied to 5, 7 and 10 wt%, if necessary.

2. Characterization of Catalysts. The surface areas and pore structures were analyzed by nitrogen adsorption/desorption measurements at 77 K. Depth profiles of Co ions in the alumina support were monitored by Auger electron spectroscopy using Ar^+ ion sputtering. The electronic states of Co ions were observed by X-ray photoelectron spectroscopy (XPS) in order to distinguish Co_3O_4 from $CoAl_2O_4$ formed during catalyst pretreatments; 7 wt% samples were employed for XPS measurements, where the peak calibration was made using C1s at 284.3 eV. An extended X-ray absorption fine structure (EXAFS) analysis was applied to confirm the local structures around Co ions in the same manner as given elsewhere.[21] A rotating Mo target was operated at 20 kV and 180 mA for X-ray generation, and a Ge(220) single crystallite was used as an X-ray monochromater.

3. Activity Measurements. Activity measurements were carried out using a conventional flow reactor directly connected to a gas chromatograph in order to evaluate NO and hydrocarbon conversions into N_2 and $CO+CO_2$, respectively. Gases consisting of NO (1000 ppm), C_3H_6 (330 ppm), O_2 (10%) and He, as a balance gas, were introduced onto 0.2 g of catalysts at a flow rate of 62 $cm^3 min^{-1}$, corresponding to W/F being 0.19 $g s cm^{-3}$. The reaction temperature was varied from 473 to 873 K. In order to estimate the fraction of exposed Co ions in the catalysts, NO pulse injection was carried out at room temperature to measure the amount of NO chemisorbed in the same way as described in a previous paper.[11]

Results

Table 2 gives the BET surface areas and some parameters concerning pore structure of the prepared catalysts; the pore-size distributions are shown in Fig. 1. AES signals assigned to Co and Al ions were observed at 650—800 and around 1400 eV, respectively. The peak intensity ratio of Co/Al was calculated at several positions of the catalyst surface after every sputtering; the depth profiles of Co ions, normalized by the Al ion concentrations in catalysts calcined at 773 K are depicted in Fig. 2.

Fourier transforms of the EXAFS spectra, phase shifts uncorrected, of the catalysts calcined at 773 and 1073 K are shown in Fig. 3, together with those of the standard Co_3O_4 and $CoAl_2O_4$ crystallites for comparisons. The XPS spectra of Co ions in impregnated catalysts calcined at 773 and 1073 K for 3 h are shown in Fig. 4, where the peak positions were corrected by contaminated carbon (C1s). For a comparison, the XPS spectra of the standard Co_3O_4 and $CoAl_2O_4$ crystallites are also given in Fig. 4. The electronic states of Co ions in the catalysts were investigated using the binding energy of $Co2p_{3/2}$.

The amount of NO adsorbed on the catalysts, measured by NO pulse injection, are summarized in Table 3. The cat-

Table 2. Surface Area and Pore Volume of 2 wt% CoO/Al_2O_3 Catalysts

Prepn. method	CoO loading	Caln. temp	Surf. area	Pore volume
	%	K	$m^2 g^{-1}$	$cm^3 g^{-1}$
Impregnation	2	773	190	0.21
Sol–gel (acid)	2	773	180	0.21
Sol–gel (base)	2	773	200	0.42

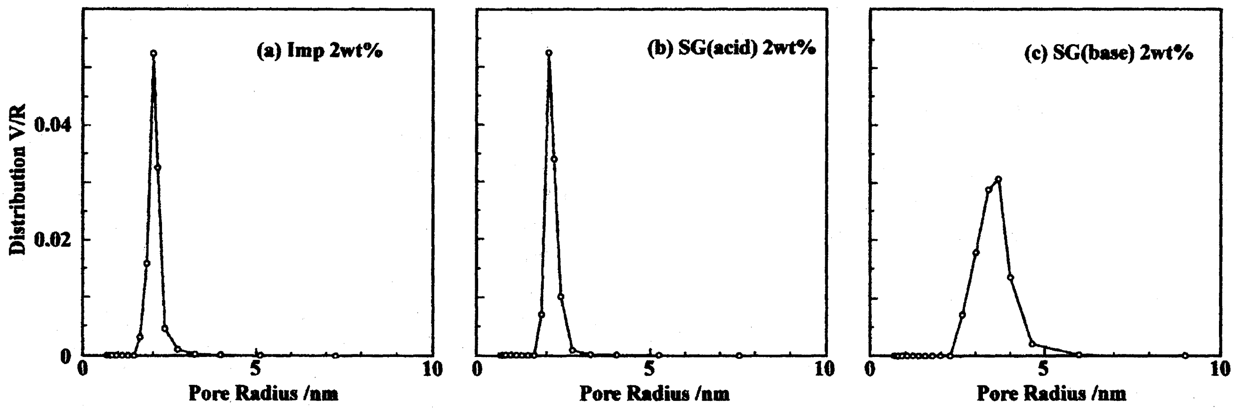


Fig. 1. Pore size distribution of the catalysts calcined at 773 K. (a) impregnated catalyst, (b) sol/gel acid catalyst, (c) sol/gel base catalyst.

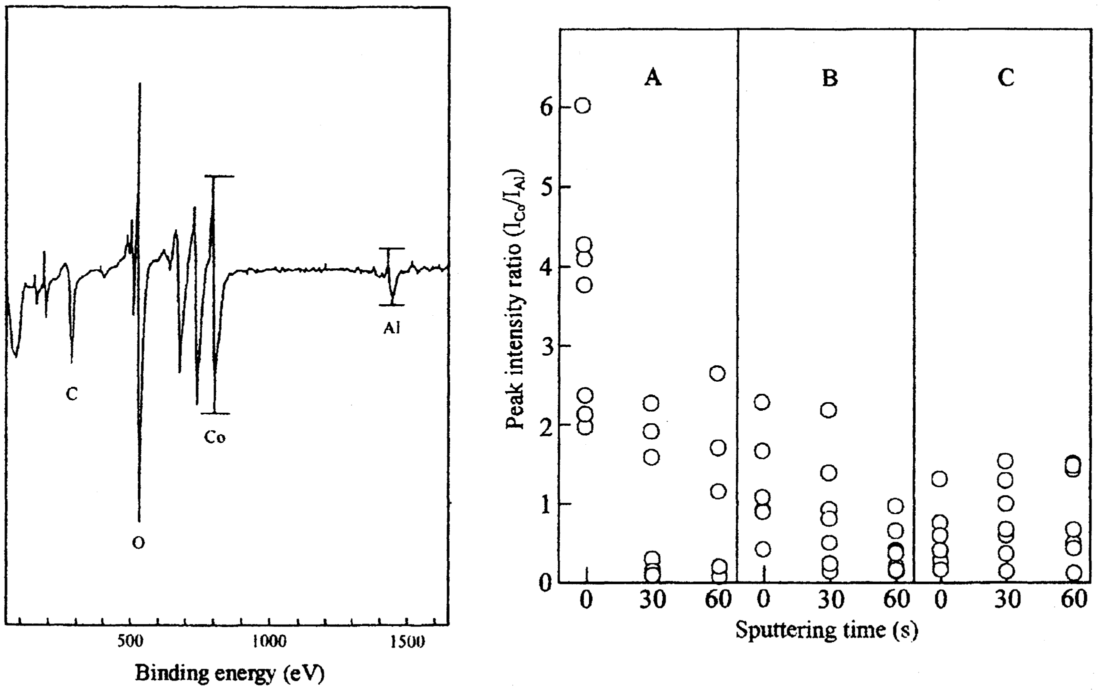


Fig. 2. Auger spectrum of CoO/Al_2O_3 catalyst calcined at 773 K (left), and distribution state of Co ions in the catalysts measured by sputtering Auger spectroscopy. A: impregnated catalyst, B: sol/gel acid catalyst, C: sol/gel base catalyst.

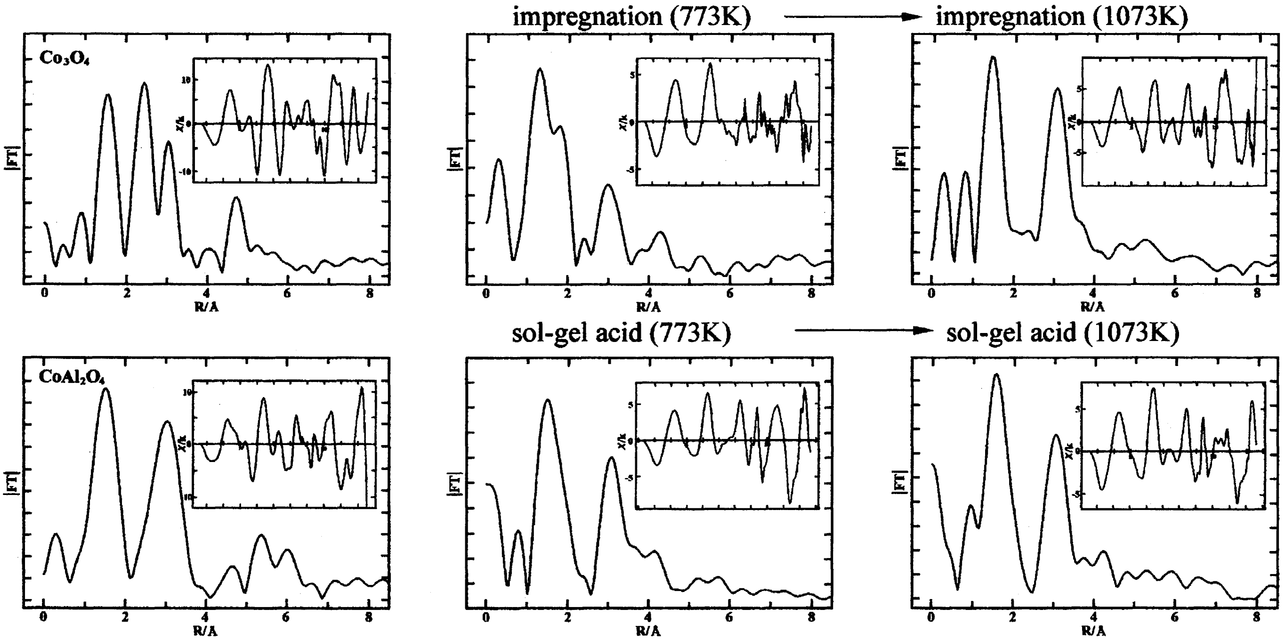


Fig. 3. Fourier transforms of EXAFS oscillations of the standard Co_3O_4 and $CoAl_2O_4$ crystallites (left), and those of impregnated and sol/gel acid catalysts calcined at 773 and 1073 K, respectively (right).

alytic activities were evaluated by NO and C_3H_6 conversions into N_2 and $CO+CO_2$, respectively; the results obtained for catalysts calcined at 773 K are given in Fig. 5 and those for catalysts calcined at 1073 K are in Fig. 6. These results show that the activity for SCR-NO is inversely related to that for propene combustion.

Discussion

Discussions are made in the following sections: One concerns the effects of the physical properties such as the pore structures and dispersion states of metal ions, upon the catalytic activity for SCR of NO. The effects of the crystallographic structure of cobalt oxides upon the activity will be discussed based on the EXAFS results. The characterization of Co ions in the active species formed on alumina-supported cobalt oxides will also be discussed.

1. Effects of the Physical Properties upon the Activity for SCR of NO. Although the catalyst compositions are

Table 3. Amounts of NO Adsorbed on the Catalysts Calcined at 773 and 1073 K

Prepn. method	CoO loading	Caln. temp	Amount of chem. NO	Fraction of exposed Co
	%	K	$cm^3\ g^{-1}$	%
Impregnation	2	773	0.146	5.1
Sol/gel acid	2	773	0.049	1.6
Sol/gel base	2	773	0.047	1.6
Impregnation	2	1073	0.067	2.2
Sol/gel acid	2	1073	0.054	1.8
Sol/gel base	2	1073	0.075	2.6

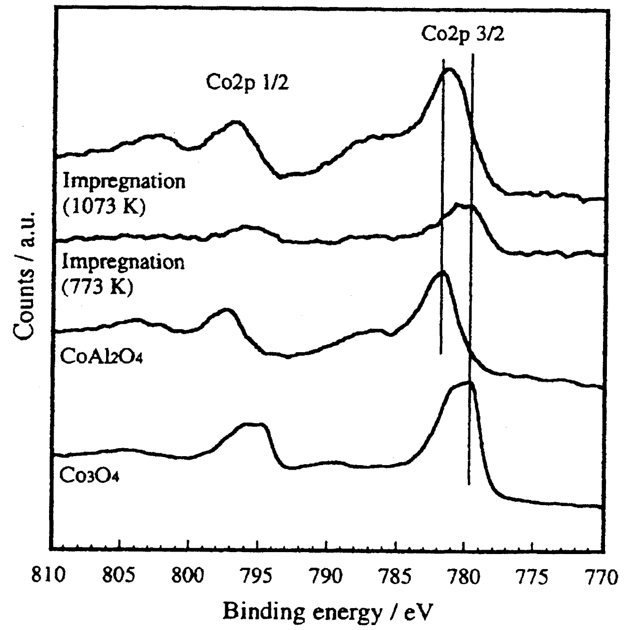


Fig. 4. XPS spectra of the standard Co_3O_4 and $CoAl_2O_4$ crystallites and of impregnated catalysts calcined at 773 and 1073 K, respectively.

the same, the catalytic activity and selectivity happen to depend upon the catalyst preparation routes.[22] This is generally ascribed to either impurities contaminated in the catalysts or differences in the dispersion states of the active species and in the physical properties of the supports employed. It has been well-known that the SCR of NO on alumina-supported cobalt oxides depends upon the impurities of Na and S ions,[12] and upon the counter anions in catalyst precursors.[11] In order to avoid any troublesome problems caused by impurities, we employed alumina from AIP and guaranteed-grade $Co(NO_3)_2 \cdot 6H_2O$ as starting materials for the preparation, since alumina from AIP has been considered to be free from impurities and NO_3 ions from $Co(NO_3)_2 \cdot 6H_2O$ were removed by heating them at temperatures higher than 573 K.[23] Accordingly, we consider the effects of the physical properties of these catalysts upon the activity for SCR of NO below.

As can be seen in Table 2, the BET surface areas of all catalysts calcined at 773 K were almost the same, but the pore structure of the sol/gel base catalyst was different from those of the impregnation and sol/gel acid catalysts. The difference in the pore structure is obviously depicted in Fig. 1, where a broad distribution curve centered around 4.0 nm is shown for a sol/gel base catalyst, and a sharp one centered around 2.0 nm is shown for the impregnation and sol/gel acid catalysts,

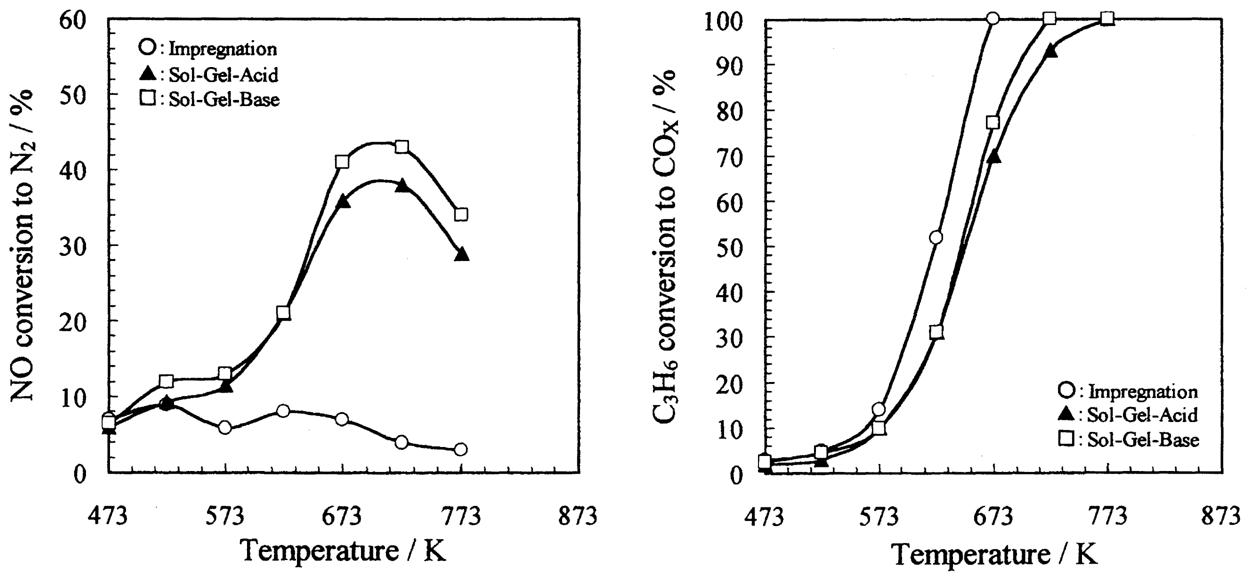


Fig. 5. NO_x and propene conversion on the catalysts calcined at 773 K.

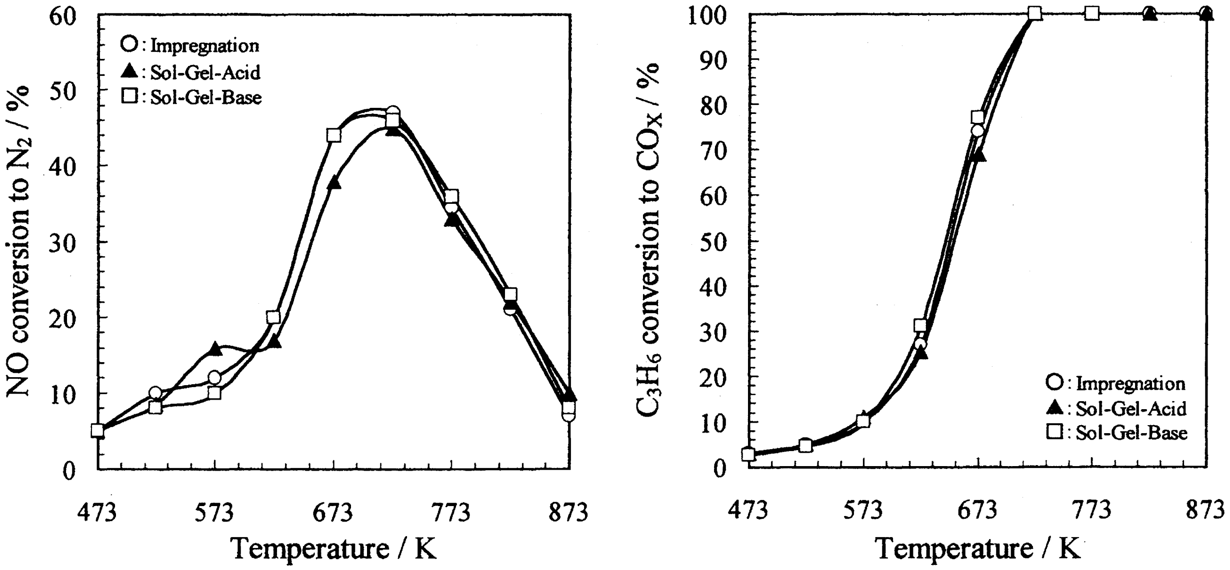


Fig. 6. NO_x and propene conversion on the catalysts calcined at 1073 K.

respectively. It has already been reported that the gelation by basic additives affected on the pore size distribution of the resultant metal oxide powders.[24] As for the dispersion states of Co ions in the catalyst, however, most of the Co ions were concentrated on the surface vicinity of the impregnated catalyst, while they were homogeneously dispersed either on the surfaces or the insides of both the sol/gel acid and base catalysts, as evidenced by the AES depth profiles given in Fig. 2. This suggests that large crystallites of cobalt oxides were formed on the impregnated catalyst, and finely-divided crystallites were homogeneously distributed in both the sol/gel acid and base catalysts. Consequently, it was found that the impregnated and the sol/gel acid catalysts possess a similar pore structure, and that the sol/gel acid and base catalysts have a similar dispersion state of Co ions.

Which contributes more to the present SCR of NO on alumina-supported cobalt oxide catalysts: the pore structure or the dispersion state of Co ions? Figure 5 gives the conversions of NO into N_2 on these catalysts calcined at 773 K, indicating that the sol/gel acid and base catalysts exhibit the same activity, and that the impregnated one shows much less activity than the sol/gel catalysts. Accordingly, a high dispersion of Co ions in the catalysts was concluded to contribute more to SCR of NO. It is also shown in Fig. 5 that the conversion of propene on the impregnated catalysts was, inversely, higher than on the sol/gel catalysts at lower temperatures. An enhanced combustion of propene is due to the large crystallites of cobalt oxides on the impregnated catalyst. Although no X-ray diffraction peaks were detected for the 2 wt% CoO/Al_2O_3 catalysts employed, large crystallites on the impregnated catalyst calcined at 773 K are likely to be Co_3O_4 because of the significant activity for hydrocarbon combustion at lower tem-peratures.[11,12,25]

2. Effects of the Crystallographic Structure of Cobalt Oxides upon the SCR of NO Activity. An extremely improved NO conversion, associated with the depression of propene combustion at lower temperatures, was observed on the impregnated catalyst calcined at 1073 K, as given in Fig. 6. However, for the sol/gel catalysts, slight changes for NO and propene conversions were measured when calcined at 1073 K. The improvement in the NO conversion on the impregnated catalyst calcined at 1073 K can be considered to be due to the generation of active species for SCR of NO. Then, a study about the crystallographic structure of cobalt oxides calcined at 773 and 1073 K becomes important.

EXAFS measurements were carried out to reveal the local structures around Co ions in impregnated catalysts, since no X-ray diffraction peaks were observed for 2 wt% CoO/Al_2O_3 calcined at 773 and 1073 K. Figure 4 gives the Fourier transforms of EXAFS oscillation of both impregnated and sol/gel acid catalysts calcined at 773 and 1073 K. Although the EXAFS results obtained for sol/gel base catalysts are not given here, they are the same as those obtained for sol/gel acid catalysts.

As given in Fig. 3, although two peaks are observed in the EXAFS Fourier transform of the standard $CoAl_2O_4$ in the distance range of 1—4 Å, three distinct peaks are observed for the standard Co_3O_4 in the same range, which is the key to distinguish $CoAl_2O_4$ from Co_3O_4 crystallites. Comparing the Fourier transforms of cobalt oxides in the catalysts calcined at 1073 K with the those of the standard crystallites, the formation of $CoAl_2O_4$ was confirmed for all catalysts calcined at 1073 K for 3 h. This suggests that the active species for SCR of NO with propene are $CoAl_2O_4$ crystallites, since all of the catalysts calcined at 1073 K are very active for SCR of NO, as shown in Fig. 6. More exactly looking at the Fourier transform of the standard $CoAl_2O_4$ crystallites, another peak is observed at around 5.3 Å with a shoulder at 6.0 Å, suggesting a long-range order of the crystallites.[26] In the Fourier transforms of all the catalysts calcined at 1073 K, no peaks were recognized at a distance greater than 4 Å, indicating no long-range order of the present $CoAl_2O_4$ crystallites In other words, tiny $CoAl_2O_4$ crystallites were formed in the catalysts calcined at 1073 K.

Thw situation is the same in the sol/gel catalysts calcined at 773 K, where tiny $CoAl_2O_4$ crystallites were formed by calcination even at 773 K. This is probably because of the high dispersion of Co ions in the sol/gel catalysts. However, the Fourier transform of the impregnated catalyst calcined at 773 K is rather complicated, and it resembles the transforms of neither Co_3O_4 nor $CoAl_2O_4$ crystallites. One of the possible assignments is as follows: Cobalt oxides in this catalyst consist of both Co_3O_4 and $CoAl_2O_4$ crystallites, because the compensation of each oscillation wave occurs during the Fourier analysis if both crystallites are mixed in a proper proportion. XPS is also an effective tool to distinguish Co_3O_4 from $CoAl_2O_4$ crystallites, since signals due to $Co2p_{3/2}$ and $Co2p_{1/2}$ in the Co_3O_4 crystallites are observed at 780.0 and 795.3 eV, respectively, and those in $CoAl_2O_4$ are at 781.0 and 796.5 eV.[11,12,27] The XPS spectrum of the impregnated catalyst calcined at 773 K is given in Fig. 4, indicating that cobalt oxides in the catalyst mainly consist of Co_3O_4 crystallites, probably mixed with a small amount of $CoAl_2O_4$.

3. Characterization of Co Ions in the Active Species on Alumina-Supported Cobalt Oxides. From the discussion above, the active species for the SCR of NO with propene were concluded to be finely-divided $CoAl_2O_4$ crystallites, formed during calcination of the sol/gel catalyst at 773 K and the impregnated catalyst at 1073 K, respectively. However, it has been reported that NO absorbed on Co ions in Co_3O_4, but not on Co ions in the $CoAl_2O_4$ spinel crystallites because of the absence of Co ions on the surface of spinel crystallites,[18] which caused a problem of how Co ions in spinel crystallites contributed to the SCR of NO through NO adsorption on them. Table 3 gives the amounts of NO absorbed on catalysts calcined at 773 and 1073 K, indicating more NO absorbed on the impregnated catalysts calcined at 773 K. This is ascribed to the Co_3O_4 crystallites, predominating in the impregnated catalysts calcined at 773 K. Table 3 further indicates that NO did adsorb on $CoAl_2O_4$ in the sol/gel and in the impregnated catalysts, although the amounts of NO adsorbed were less than a half of that on Co_3O_4 crystallites in the impregnated catalyst calcined at 773 K. The number of Co ions exposed was estimated based on the assumption that one NO molecule may adsorb on one Co ion in the catalyst. The results are also given in Table 3, showing that only less than 2% of the Co ions in the $CoAl_2O_4$ crystallites are responsible for NO absorption. In the normal spinel structure Co(II) ions are located at tetrahedral sites and Al(III) are at octahedral sites; however in the inverse spinel a part of Co(II) ions substitute with Al(III) to occupy the octahedral sites in the spinel structure. According to papers by Okamoto et al.[28] and by Topsoe et al.,[29] NO does not adsorb on the Co ions at tetrahedral sites, but adsorbs on Co ions at octahedral sites in the inverse spinel crystallites. Hence, it may be speculated that a trace of $CoAl_2O_4$ crystallites formed in the catalysts will be in the inverse spinel structure and Co ions in octahedral coordination will enhance the SCR of NO though NO adsorption, although no evidence has been reported so far. It is hard even by EXAFS measurements to detect the presence of a trace amount of inverse spinel in a normal spinel matrix. EXAFS gives information merely about the normal spinel.

It must be noted that catalysts loading more than 5 wt% CoO showed depressed activities for SCR-NO, even after calcination at 1073 K. This is because of the limitation of Co ions, which could migrate into the alumina lattice to form $CoAl_2O_4$.[30,31] Thus, Co ions remaining on the alumina surfaces are aggregated into large Co_3O_4 crystallites, which enhance the combustion of propene and depress NO conversion.

A part of this work was carried out as a research project of The Japan Petroleum Institute commissioned by the Petroleum Energy Center with the support of the Ministry of International Trade and Industry.

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