Effect of ZnO Addition on Cobalt-Alumina Interaction Species

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The effect of ZnO addition on cobalt-alumina interaction modes was studied using TPR and XPS. It was found that the addition of 2 wt% ZnO markedly affects the distribution of the cobalt species in CoO/Al_2O_3 (5 wt% CoO): cobalt-alumina surface interaction species are removed and migration of cobalt into an alumina subsurface phase is promoted by ZnO. A formation of Co-Zn-O mixed oxide is proposed for $ZnO-CoO/Al_2O_3$ at high ZnO content. The dispersion and distribution of ZnO on Al_2O_3 are also strongly modified by the presence of cobalt.

In connection with $CoO-MoO_3/Al_2O_3$ hydrodesulfurization (HDS) catalyst systems, CoO/Al_2O_3 catalysts have been extensively studied using various physicochemical techniques.[1-12] It has been shown that several $CoO-Al_2O_3$ interaction species are formed on CoO/Al_2O_3 catalysts and that the interaction mode depends on the CoO content and calcination temperature. At usual calcination temperatures (670—870 K), (sub)surface cobalt species in tetrahedral configurations (aluminate like species) are selectively formed at an initial dose of cobalt.[2,4,6-9] Formation of surface cobalt species in octahedral symmetries are also proposed on the basis of XPS and ISS studies coupled with H_2-reduction.[8] A crystalline Co_3O_4 phase appears above about 2 wt% CoO and increases precipitously in the amount with a further increase of cobalt content.[2,6,8,10] With CoO/Al_2O_3 systems calcined at various temperatures, a detailed characterization of cobalt species was conducted by Arnoldy and Moulijn[11,12] using temperature-programmed reduction (TPR) techniques. The formations of surface Co^{3+} and Co^{2+} species, Co^{3+}-Al^{3+} mixed oxide, and subsurface Co^{2+} are proposed in addition to Co_3O_4 and aluminate-like species.

The cobalt-alumina interaction modes are expected to be strongly modified by adding metal oxide which interacts with Al_2O_3, such as ZnO. The additive effects on the cobalt-alumina interactions are, accordingly, considered to provide more detailed information of the interaction species. Furthermore, doping of a small amount of a second promoter, such as ZnO, NiO, or MgO, is often claimed to improve the HDS activity and stability of $CoO-MoO_3/Al_2O_3$ catalysts.[13] However, only a few fundamental investigations have been made to reveal the additive effect on cobalt-alumina interaction modes and the beneficial effects of the second promoter.[14-20]

It has been demonstrated in our previous study[21] using XPS that molybdenum oxide-alumina interaction modes are not appreciably affected on the addition of ZnO. This may suggest that ZnO alters the cobalt oxide-alumina or cobalt oxide-molybdenum oxide interaction modes. With $ZnO-CoO/Al_2O_3$ at varying CoO contents and 1 wt% Zn, Chin and Hercules[15] have actually shown by XPS and ISS that the presence of ZnO enhances the formation of cobalt "surface spinel" at $\leqslant$8 wt% Co, while at higher Co loadings the addition of 1% Zn drastically increases the dispersion of cobalt oxide. No further detailed information on $ZnO-CoO/Al_2O_3$ systems has been reported. A more detailed study on $ZnO-CoO/Al_2O_3$ might provide information about the role of the second promoter in $CoO-MoO_3/Al_2O_3$ catalysts as well as cobalt-alumina interaction modes.

In the present study, the effect of ZnO addition was investigated on the cobalt-alumina interaction modes in CoO/Al_2O_3 using TPR and XPS. It was found that the addition of a small amount of ZnO remarkably altered the distribution of cobalt-alumina interaction species.

Experimental

Supported cobalt catalysts were prepared by impregnating γ-Al_2O_3 with an aqueous solution of cobalt salt. γ-Al_2O_3 (pore volume: 0.66 $cm^3\ g^{-1}$, 163 $m^2\ g^{-1}$) was supplied by the Catalysis Society of Japan as a reference catalyst (JRC-ALO-4).[22] The amount of the aqueous solution of cobalt nitrate was adjusted to be 1.3 cm^3 per g-Al_2O_3 to prepare CoO/Al_2O_3 containing 5 wt% CoO. The supported amount of CoO is represented with respect to the support. After the catalyst precursor was dried at 383 K for 16 h, it was calcined at 673, 823, or 1073 K for 5 h in air by using an electric furnace. $ZnO-CoO/Al_2O_3$ samples containing 5 wt% CoO and varying amounts of ZnO were prepared by simultaneous impregnation of appropriate amounts of cobalt and zinc nitrates.

In TPR studies, the cobalt catalyst (0.2 g) was reduced in a 5% H_2/Ar stream (72 cm^3 STP min^{-1}), which was purified by passing through a deoxygenation catalyst layer, followed by a zeolite trap cooled at a methanol-Dry Ice temperature. After evacuation at 623 K for 1 h, the reduction temperature was raised from 300 to ca. 920 K at an uniform heating rate (β) of 2.5 K min^{-1}. The H_2 concentration in the effluent gas was analyzed by a TCD cell at 303 K after removing water vapor by a cold trap at a methanol-Dry Ice temperature.

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The XPS measurements were made on a Hitachi 507 photoelectron spectrometer using Al $K\alpha_{1,2}$ radiation (1486.6 eV). The anode was operated at 9 kV and 50 mA. Assuming linear backgrounds, XPS intensity ratios were obtained by using the planimetered peak areas of the Co 2p, Al 2p, Zn 2p, and Zn($L_3M_{4,5}M_{4,5}$) levels. Binding energies were referenced to the Al 2p level (74.3 eV) of the support, which had been separately determined by using the C 1s band at 285.0 eV due to adventitious carbon.

Results

The TPR profiles for ZnO-CoO/Al$_2$O$_3$ are shown in Fig. 1 as a function of ZnO content and calcination temperature (673 and 823 K). The profiles for CoO/Al$_2$O$_3$ consisted of several distinctly different reduction peaks as reported by Arnoldy and Moulijn.[11] The cobalt species are characterized by the reduction temperatures of 503—553 K (Co-I), 633—643 K (Co-IIA), 693 K (Co-IIB), 753—773 K (Co-III), and 853—873 K (Co-IV) in the present study. The reduction temperatures depended on the calcination temperature and loading level of CoO. Since the rate of temperature increase, flow rate of H$_2$/Ar, and H$_2$-concentration are different, the reduction temperatures in Fig. 1 cannot be directly compared with the values reported by Arnoldy and Moulijn.[11] The present

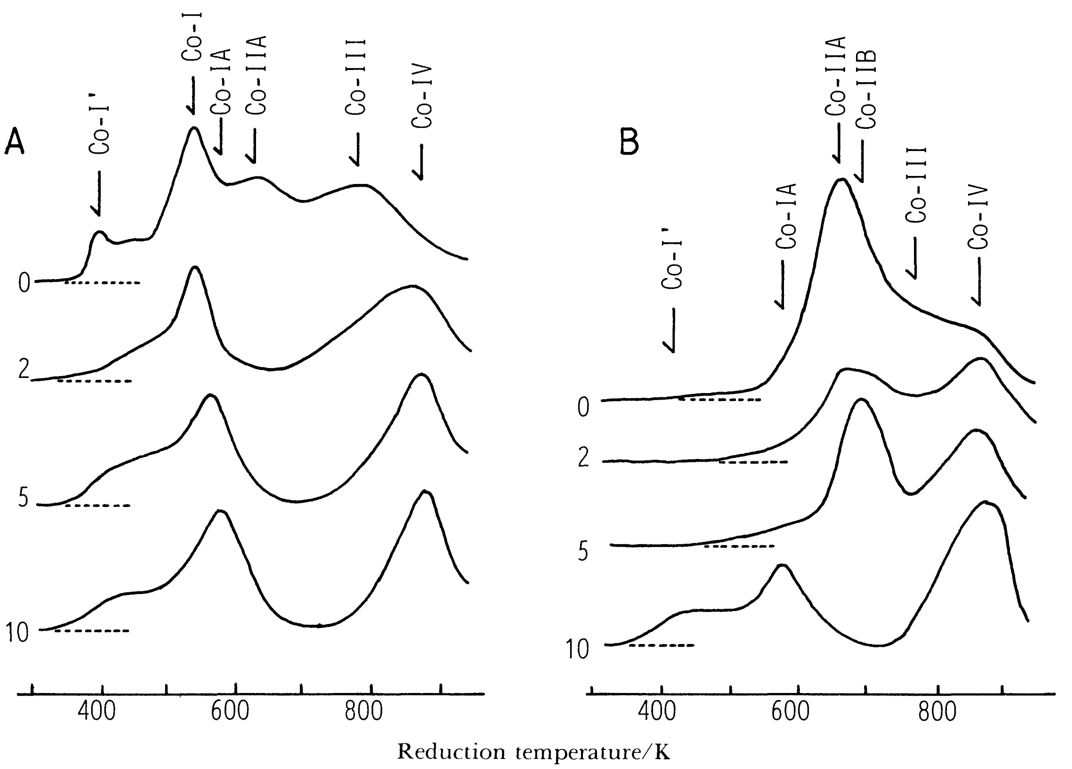

Fig. 1. TPR profiles of ZnO-CoO/Al$_2$O$_3$ (CoO; 5 wt%) as a function of ZnO content and calcination temperature. (A): calcined at 673 K and (B): 823 K. Numbers in the figure denote ZnO content (wt%). Dotted lines show backgrounds after vertical replacements. β=2.5 K min^{-1}.

Table 1. TPR Results on CoO/Al$_2$O$_3$

Cobalt species	Reduction temperature/K		Assignments[a]
	Moulijn et al.[a]	This work[b]	
Co-I'	—	400—450	Amorphous Co-oxide[c]
Co-I	600	503—553	Crystalline Co$_3$O$_4$
Co-IA	—	580	Co-Zn-O[b]
Co-IIA	750	633—643	Surface Co^{3+}
Co-IIB	750	693	Co^{3+}-Al^{3+}-oxide
Co-III	900	753—773	Surface Co^{2+}
Co-IV	1130—1240	853—873	(Sub)surface Co^{2+}
Co-V[d]	1150—1230	>920	Co$_x$Al$_{(8/3-2x/3)}$O$_4$ CoAl$_2$O$_4$

a) Refs. 11 and 12, β=10 K min^{-1}. b) β=2.5 K min^{-1}, this work. c) Ref. 26. d) Co-IVC and IVD in Refs. 11 and 12.

reduction temperatures of cobalt species are compared in Table 1 with those in Ref. 11. A good parallel correlation in Table 1 indicates that the cobalt species detected here correspond well to those observed by Arnoldy and Moulijn.[11] The reduction peaks are denoted as in Table 1 according to Arnoldy et at.[11,12] in the order of the reduction temperature. Co-IVC and Co-IVD observed at 1150—1230 K by Arnoldy and Moulijn[11] are supposed to be detected at >920 K in the present study. Hydrogen consumptions at >920 K in the TPR profiles in Fig. 1 indicate the presence of these reduction peaks (denoted Co-V here). In addition to Co-I—V peaks, Co-I′ appeared at 400—450 K in the present study.

The TPR profile of Co_3O_4 consisted of a slightly asymmetric single peak. The reduction temperature depended on the particle size of Co_3O_4 and the samples with the particle diameter of 50 and 1200 nm (SEM observations) showed the TPR peaks at 570 and 590 K, respectively.

The addition of ZnO into CoO/Al_2O_3 was found to strongly affect the TPR profiles. As shown in Fig. 1, the addition of 2 wt% ZnO into 5 wt% CoO/Al_2O_3 catalyst (673 K) removed almost completely Co-IIA and most of Co-III. Further additions of ZnO completely eliminated Co-III. Although the TPR intensity of Co-I was not signicantly altered by the addition of 5 and 10 wt% ZnO, the reduction temperature of Co-I (538 K) increased by 20 K at 5 wt% ZnO and additionally augmented by 20 K, reaching 580 K at 10 wt% ZnO. Co-I species could not be found at such a high temperature of 580 K for supported CoO systems, for instance, CoO/Al_2O_3 and CoO/SiO_2 containing up to 20 wt% CoO. No appreciable change in the crystallite size of Co_3O_4 was observed by means of XRD on the addition of ZnO. Accordingly, the reduction peak at 580 K is concluded to be ascribed to a new cobalt phase and denoted Co-IA here.

With $ZnO-CoO/Al_2O_3$ calcined at 823 K, the intensities of Co-IIA and III were significantly decreased by the addition of 2 wt% ZnO as observed with the sample calcined at 673 K. The presence of Co-IIB became clearly observable by the elimination of Co-IIA. Co-IIB remaind intact on the addition of 5 wt% ZnO. On the other hand, the addition of 10 wt% ZnO removed Co-IIB and brought about the formations of Co-IA and I′. The intensity of Co-IV increased at 2 wt% ZnO but was not strongly affected by a further addition of ZnO, irrespective of the calcination temperature. As for ZnO/Al_2O_3 systems (below 10 wt% ZnO), no reduction peaks were observed below 900 K under the present TPR conditions.

The intensity of TPR profile was found to depend on the ZnO content. The total TPR areas between room temperature and 920 K are shown in Fig. 2 as a function of ZnO content. It was found that the addition of ZnO also strongly affected the TPR intensity of CoO/Al_2O_3 (5 wt% CoO). The TPR areas decreased by 40% at 2 wt% ZnO and were almost invariant on a further addition of ZnO at the calcination temperatures of 673 and 823 K. On the basis of the XPS study of CoO/Al_2O_3 (8 wt% Co) calcined at 673 K, Chin and Hercules[15] have reported that the fraction of cobalt which is H_2-reducible at 623 K decreases from 20 to 15% (by 25% decrease) on the addition of 1% Zn. The TPR results in Fig. 2 are in line with their XPS observations.

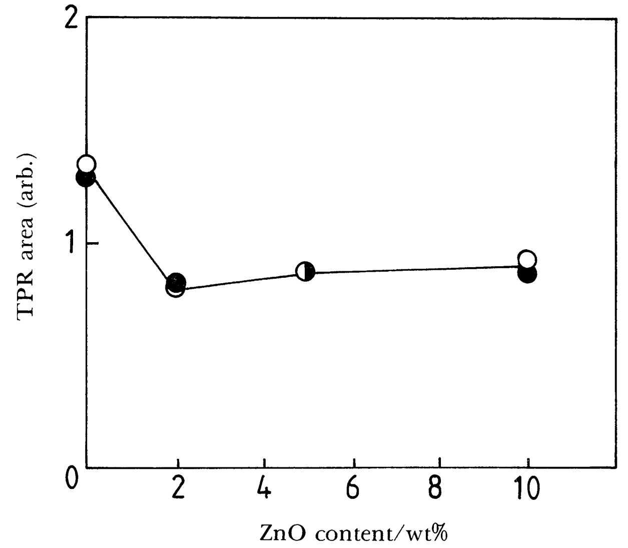

Fig. 2. Variations of the TPR area intensity with ZnO content (wt%) for $ZnO-CoO/Al_2O_3$ catalysts (5 wt% CoO) calcined at 673 K (○) and at 823 K (●).

XPS characterization of the $ZnO-CoO/Al_2O_3$ systems was carried out as a function of ZnO loading. The BE values of Co $2p_{3/2}$ band for 5 wt% CoO/Al_2O_3 calcined at 673 and 823 K were 780.3 and 781.2 eV, respectively. They are in between those for $CoAl_2O_4$ (781.3—782.2 eV)[4,6-8] and Co_3O_4 (779.6—779.8 eV).[6,7] When CoO/Al_2O_3 was calcined at 1073 K, the BE of Co $2p_{3/2}$ band (781.5 eV) was very close to that of $CoAl_2O_4$. The Co $2p_{3/2}$ BE was not influenced by the addition of ZnO within experimental accuracy (±0.2 eV). The BE of Zn 2p level and the kinetic energy (KE) of $Zn(L_3M_{4,5}M_{4,5})$ Auger band were independent of ZnO and CoO contents and calcination temperature and were 1021.8 and 987.5 eV, respectively. These BE and KE values for Zn indicate that Zn^{2+} cations are in an aluminate-like phase.[21,23]

The Co 2p/Al 2p or Zn 2p/Al 2p XPS intensity ratio depends on both dispersion and surface concentration of Co or Zn. A higher XPS intensity ratio is expected for higher dispersion and/or higher surface concentration of Co or Zn.[24] The effect of ZnO addition on the Co 2p/Al 2p ratio for CoO/Al_2O_3 is shown in Fig. 3 as a function of ZnO content. When $ZnO-CoO/Al_2O_3$ was calcined at 673 or 823 K, no appreciable change in the Co 2p/Al 2p ratio was detected, except for the 2 wt% ZnO sample calcined at 673 K, while the ratio for $ZnO-CoO/Al_2O_3$ calcined at 1073 K decreased gradually with increasing ZnO content. A small decrease in the Co 2p/Al 2p ratio for 2 wt% CoO/Al_2O_3 calcined at 673 K is consistent with the observations by Chin and Hercules.15)

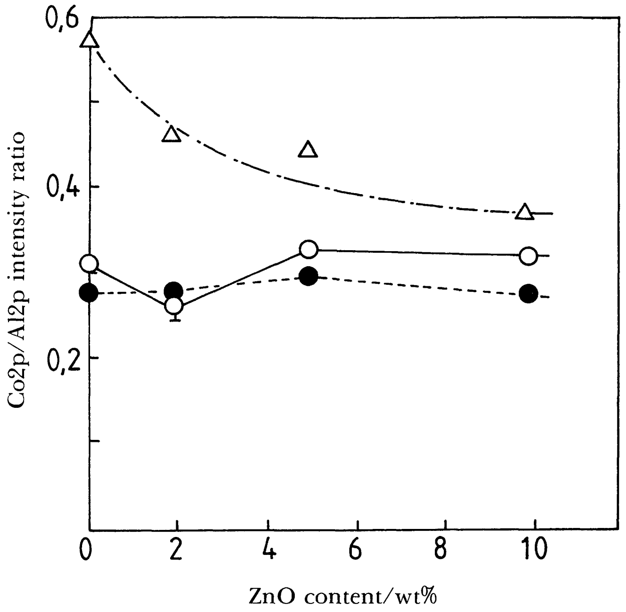

Fig. 3. Dependencies of the Co 2p/Al 2p XPS intensity ratio on ZnO content (wt%) for $ZnO-CoO/Al_2O_3$ (CoO; 5 wt%) calcined at 673 K (○), 823 K (●), and 1073 K (△).

Figure 4 depicts the Zn 2p/Al 2p (A) and Zn(LMM)/Zn 2p (B) intensity ratios to estimate the dispersion and depth profile of Zn^{2+} cations in $ZnO-CoO/Al_2O_3$ samples containing 5 wt% CoO. According to Penn,25) the escape depths of the photo- and Auger-electrons are estimated to be 0.8 and 1.5 nm, respectively. The Zn-Auger/Zn 2p ratio for pure ZnO was 1.2 for the present spectrometer.21)

The Zn 2p/Al 2p ratio for $ZnO-CoO/Al_2O_3$ decreased with increasing calcination temperature, whereas the Zn Auger/Zn 2p ratio increased. These behaviors are analogous to those for ZnO/Al_2O_3 samples21) as presented in Fig. 4. However, it was found that when $ZnO-CoO/Al_2O_3$ is calcined at 673 or 823 K the coimpregnation of CoO significantly decreases the Zn 2p/Al 2p intensity ratios compared to those for ZnO/Al_2O_3, whereas the presence of CoO increases the Zn(LMM)/Zn 2p ratio. Both ratios for the samples calcined at 1073 K were not affected by the presence of CoO (5 wt%).

Discussion

The TPR and XPS studies of $ZnO-CoO/Al_2O_3$ catalysts with varying ZnO contents were carried out to reveal the effect of ZnO addition on the cobalt-alumina interaction species. In the present study, it has been definitely demonstrated for the first time that the addition of a small amount of ZnO greatly affects the cobalt-alumina interaction modes and the distribution of cobalt species.

In the TPR experiments, it is assumed that the respective reduction peaks correspond to distinct

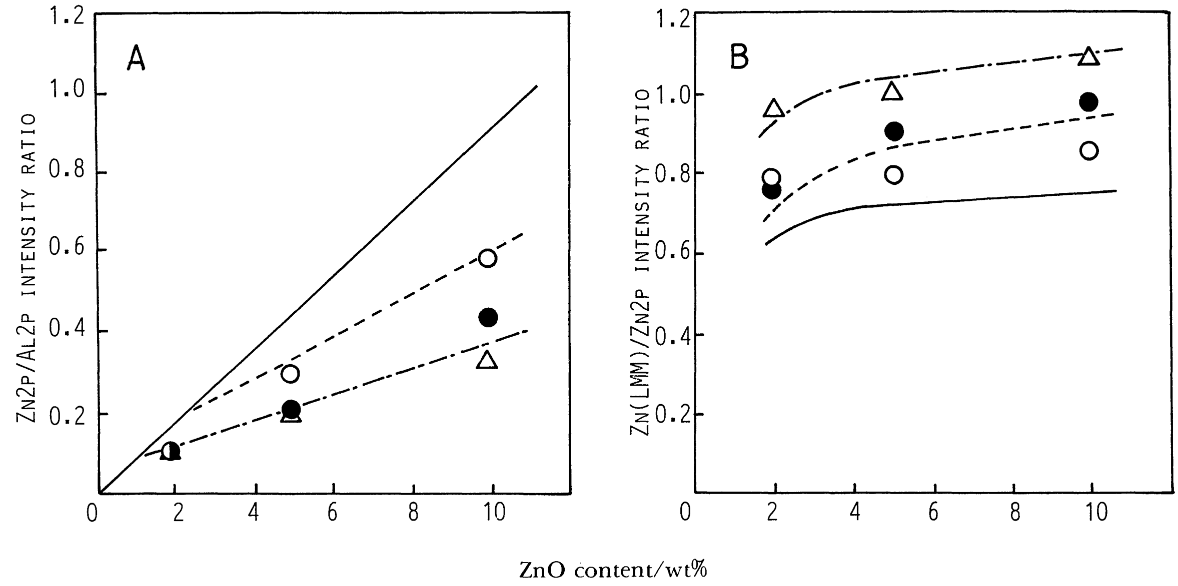

Fig. 4. Zn 2p/Al 2p XPS intensity ratio (A) and Zn(LMM)/Al 2p intensity ratio (B) vs. ZnO content (wt%) for $ZnO-CoO/Al_2O_3$ (CoO; 5 wt%). ○: calcined at 673 K, ●: 823 K, and △: 1073 K. Solid line: ZnO/Al_2O_3 calcined at 673 K, dotted line: 823 K, and dashed line: 1073 K.21)

cobalt species in different oxidation states and/or different chemical environments, since the reduction of Co_3O_4 showed only a relatively narrow peak with slight shoulder and since the peak separations among Co-I—IV seem to be too large to assign them to successive reduction processes of cobalt, e.g. Co^{3+} to Co^{2+} and Co^{2+} to Co metal. The TPR peaks for CoO/Al_2O_3 have been assigned by Moulijn et al.[11,12] as summarized in Table 1 on the basis of XRD and the amount of H_2-consumption. A combined TPR and XPS study[26] on CoO/Al_2O_3 with varying CoO loadings essentially support their assignments in Table 1.

It is demonstrated from the TPR spectra in Fig. 1 that dramatic alterations in cobalt–alumina interaction modes in CoO/Al_2O_3 are brought about by the addition of ZnO. The addition of 2 wt% ZnO effectively eliminates surface cobalt–alumina interaction species (Co-IIA and III) and enhances a formation of (sub)surface spinel species, while the amount of bulk Co_3O_4 phase is not affected in the presence of ZnO. On the base of XPS and ISS studies on ZnO–CoO/Al_2O_3, Chin and Hercules[15] suggested that the formation of cobalt "surface spinel" is enhanced by the addition of 1 or 2% Zn at $\leqslant$8 wt% Co. The TPR results in Figs. 1 and 2 definitely support their conclusions and provide more convincing and detailed information on the effect of ZnO on CoO–Al_2O_3 interaction modes.

The changes in cobalt species on the addition of ZnO are considered to result from competitive occupations of limited numbers of surface and bulk sites of Al_2O_3 by Co^{2+}, Co^{3+}, Al^{3+}, and Zn^{2+} cations. The structure of γ-Al_2O_3 is described as a defect spinel[27] and these cations occupy octahedral and/or tetrahedral sites of Al_2O_3 on solid state reactions during calcination.[1,2,28—30] Before discussing the cobalt species in ZnO–CoO/Al_2O_3, it is considered first how the distribution and dispersion of Zn^{2+} cations in ZnO/Al_2O_3 are affected by the cobalt addition.

The escape depth of the Zn(LMM) Auger band is higher than that of the Zn 2p band. Since the Zn(LMM)/Zn 2p ratios for ZnO/Al_2O_3 (673 K) are significantly lower than that of pure ZnO, in which zinc is expected to be homogeneously distributed in depth, it is concluded that Zn^{2+} cations are segregated in the surface layer of ZnO/Al_2O_3 at 673 K.[21] The intensity ratio of Zn(LMM)/Zn 2p can be expressed as follows for Al_2O_3 with a zinc–aluminate surface layer of thickness, d.

$$[\mathrm{Zn(LMM)/Zn\,2p}] = [\mathrm{Zn(LMM)/Zn\,2p}]_0 \times [1 - \exp(-d/\lambda_{\mathrm{Zn(LMM)}})]/[1 - \exp(-d/\lambda_{\mathrm{Zn\,2p}})] \quad (1)$$

where $[\mathrm{Zn(LMM)/Zn\,2p}]_0$ indicates the intensity ratio for an infinitely thick, homogeneous Zn-layer and is observed to be 1.2 for ZnO.[21] $\lambda_{\mathrm{Zn(LMM)}}$ and $\lambda_{\mathrm{Zn\,2p}}$ denote the escape depths of the Zn(LMM) Auger- and Zn 2p photo-electrons and are 1.5 and 0.8 nm, respectively. The intensity ratios are calculated to be 0.68, 0.82, 0.96, and 1.13 from Eq. 1 for Zn-containing layers of thickness of 0.2 (monolayer), 1, 2, and 4 nm, respectively. A comparison with the results in Fig. 4-B implies that Zn^{2+} cations preferentially occupy surface sites forming a monolayer in ZnO/Al_2O_3 calcinated at 673 K and containing less than about 6 wt% ZnO.

The increase in the Zn(LMM)/Zn 2p ratio with increasing calcination temperature indicates the diffusion of Zn^{2+} cations into the Al_2O_3 bulk (1—2 nm at 823 K and 2—5 nm at 1073 K). The increase in the thickness of Zn layer is obviously observed as ZnO content increases. These findings are a consequence of enhanced diffusivity of Zn^{2+} cations at a higher temperature and limited surface sites for Zn^{2+} cations. These behaviors of Zn^{2+} cations in ZnO/Al_2O_3 were qualitatively confirmed by Ar^+ sputtering techniques.[21]

With the ZnO–CoO/Al_2O_3 systems calcined at 673 and 823 K, the Zn(LMM)/Zn 2p intensity ratios increased on the addition of CoO, indicating that the cobalt addition enhances the diffusion of Zn^{2+} cations into the Al_2O_3 bulk phase. This is also supported by the decrease in the Zn 2p/Al 2p XPS intensity ratios on the addition of CoO. On the other hand, it should be noted that the Zn(LMM)/Zn 2p ratios for ZnO–CoO/Al_2O_3 are still far below the ratio for pure ZnO and, in consequence, that a considerable proportion of Zn^{2+} cations occupies surface sites in ZnO–CoO/Al_2O_3 calcined at 673 or 823 K. A significant depletion of Zn^{2+} at surface would lead to the ratio Zn(LMM)/Zn 2p>1.2, which is contrary to the experimental observations.

The differences in the site preference between Zn^{2+}, Co^{2+}, Co^{3+}, and Al^{3+} cations are considered to determine the site distributions of cations in the ZnO–CoO/Al_2O_3 systems. Surface Zn^{2+} cations are expected to occupy tetrahedral sites of Al_2O_3 because of low stability in octahedral sites (octahedral preference energy: $+7.6\ \mathrm{kcal\,mol^{-1}}$) as compared to Al^{3+} ($-10.6\ \mathrm{kcal\,mol^{-1}}$).[31] This was confirmed by the BE of Zn 2p band and KE of Zn(LMM) level for ZnO/Al_2O_3 and ZnO–CoO/Al_2O_3. Divalent cobalt cations are also anticipated to be present mainly in tetrahedral sites (95% in $CoAl_2O_4$ spinel structure) ($+3\ \mathrm{kcal\,mol^{-1}}$). On the other hand, it is suggested by Arnoldy and Moulijn[11] using a ligand field theory that Co^{3+} shows a tendency to occupy octahedral sites in an Al_2O_3 lattice. The order of tetrahedral site preference in spinel structures is, accordingly, estimated to be $Zn^{2+}>Co^{2+}>Al^{3+}>Co^{3+}$.

As aforementioned, the Zn^{2+} cations in ZnO–CoO/Al_2O_3 occupy preferentially surface tetrahedral sites of Al_2O_3 at a low ZnO content. This eventually results in an occupation of octahedral sites with Al^{3+} cations as in $ZnAl_2O_4$. It is deduced that the preferential incorporation of Zn^{2+} cations in surface tetrahedral sites significantly retards formations of both surface Co^{2+} (Co-IIA) and Co^{3+} (Co-III) species in octahedral and tetrahedral sites, respectively, in conformity with the TPR profiles in Fig. 1. The cobalt cations expelled from the surface sites are expected to be incorporated into tetrahedral sites in an Al_2O_3 lattice as long as these sites are available because of higher thermodynamic stability of cobalt aluminate formation. The enhanced diffusions of Zn^{2+} and Co^{2+} cations into subsurface layer of Al_2O_3 result from competitive occupations of surface and bulk sites.

The ratio of bulk oxide (Co-I and IIB) and (sub)-surface cobalt species may depend on the calcination temperature and ZnO content, but actually it was almost invariant at 673 and 823 K (Fig. 2). The bulk oxide species are conjectured to be produced via oxidation of Co^{2+} to Co^{3+} during calcination.[26] The proportion of Co^{3+} depends strongly on the starting salt but weakly on the calcination temperature ($\leqslant$823 K) and ZnO content. This is because the calcination temperature of 673 or 823 K is too low for the cations to attain equilibrium distributions in an Al_2O_3 lattice (Tammann temperature: ca. 1140 K) as suggested by Burggraf et al.[9] On the contrary, diffusions of Co^{2+} and Zn^{2+} are significantly enhanced at 1073 K because of competitive site occupation and elevated calcination temperature which facilitates bulk diffusion to attain equilibrium distribution.

The formation of Co-IA was observed at high ZnO content. It is proposed that the high reduction temperature of Co-IA as compared to that of Co_3O_4 is attributed to the dissolution of Zn^{2+} into Co_3O_4 phase. The Zn^{2+} cations are expected to occupy tetrahedral sites in Co_3O_4 as in $ZnCo_2O_4$ (normal spinel structure).[30] The amount of Co-IA is very close to Co_3O_4 (Co-I) at 673 K, indicating no formation of Co_3O_4 is promoted by the addition of ZnO at this temperature. On the other hand, when 10 wt% $ZnO-CoO/Al_2O_3$ was calcined at 823 K, Co-IA was produced in spite of the absence of precursor Co_3O_4 (Fig. 1-B). This finding is interpreted in terms of an extensive occupation of tetrahedral sites of an Al_2O_3 lattice with Zn^{2+} cations due to an enhanced diffusivity at 823 K and a large number of Zn^{2+} cations doped.

Mixed oxide formation between dispersed Co_3O_4 particles and the support constituent increases the reduction temperature of cobalt as a consequence of enhanced polarization of Co–O bondings.[11] The incorporation of Al^{3+} into octahedral interstices of Co_3O_4 (Co-IIB) significantly increase the reduction temperature (ca. 150 K) of Co_3O_4. Formation of $Si^{4+}{}_{x/2}Co^{2+}{}_{1-x}Co^{3+}{}_2O_4$ with spinel structure is proposed for CoO/SiO_2 and the reduction temperature increases by 55 K compared with Co_3O_4.[32] The effect of cation incorporation is in the order $Al^{3+} \gg Si^{4+} > Zn^{2+}$ as might be expected, taking into account a cation charge and a low concentration of Si^{4+} in the lattice.

Analogously to the enhanced bulk diffusion of Zn^{2+} in the presence of Co^{2+}, the diffusion of Co^{2+} cations into the bulk phase is promoted by a simultaneous impregnation of ZnO as evidenced by a considerable decrease in the TPR area in Fig. 2. This is partly substantiated by the decrease in the Co 2p/Al 2p XPS intensity ratio at 2 wt% ZnO in Fig. 3 for $ZnO-CoO/Al_2O_3$ (673 K) in line with the observations by Chin and Hercules.[15] With $ZnO-CoO/Al_2O_3$ at high ZnO or calcined at 823 K, however, the Co 2p/Al 2p XPS intensity ratios are not appreciably affected by the addition of ZnO in spite of the bulk diffusion of cobalt species. This may be interpreted in terms of compensating effects on the XPS intensity ratio, that is, diffusion of the surface cobalt species into a bulk phase deeper than the sampling depth of XPS (2—3 nm) and the increase in cobalt dispersion due to the reactions with Al_2O_3 (formations of Co-IV and V at the expense of Co-IIB).

In summary, it was found that the addition of 2 wt% ZnO markedly affected the cobalt–alumina interaction modes. The distribution of the cobalt species in CoO/Al_2O_3 was greatly altered: cobalt–alumina surface interaction species were removed and migration of cobalt into alumina subsurface phase was promoted by ZnO. A formation of Co–Zn–O mixed oxide is proposed for $ZnO-CoO/Al_2O_3$ at high ZnO contents (5—10 wt%).

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