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X-Ray Photoelectron Spectroscopic Studies of Catalysts
— Supported Cobalt Catalysts —

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XPS techniques were used to clarify the state of supported cobalt catalysts. In order to characterize Co^{2+} and Co^{3+}, the spin-orbit splitting of the 2p level, which is considered to be affected by the exchange interaction between the unpaired 3d electrons and 2p electrons, was found to be very useful. The interaction between catalyst and support was investigated. The state of supported cobalt was determined: Co_2O_3 on SiO_2, Co_2O_3+ $CoAl_2O_4$ on γ-Al_2O_3, and $LaCoO_3$ on La_2O_3. The order of the strength of the chemical interaction between cobalt and support is as follows:

$$La_2O_3 > \gamma\text{-}Al_2O_3 > SiO_2.$$

This fact was also confirmed by reduction experiments.

Recently, X-ray photoelectron spectroscopy (XPS or ESCA) techniques have been used in the studies of catalysts by many workers.[1–8] The advantage of XPS over the other techniques is that, in principle, it is capable of determining different valencies of supported metal on the surface layer simultaneously and of detecting the presence of any interaction between catalyst and support.

From XPS measurements for catalysts, we can obtain three important pieces of information–that is, information about the binding energy, the satellite, and the relative intensity of each level. On the basis of the binding energy of some inner level of an atom concerned (chemical shift), we can obtain information about the charge density of the atom and, therefore, the valence state of the atom. However, atoms with the same formal charge have different binding energies according to different circumstances, and, in some cases (for example, Ni compounds[9]), we cannot determine the valence states of the atom by the chemical shift alone.

The origins of satellite peaks have been investigated from the physical point of view by many workers.[10,11] According to their results, the paramagnetic species of some first transition-metal compounds show satellites on some levels; the satellites on the 2p-level are conidered to originate from shake-up processes (3d→4s transition), while the 3s-satellites are concluded to result from multiplet splittings by means of exchange interaction with 3d-unpaired electrons. However, the diamagnetic compounds show no such satellites. On the basis of these results, we can determine the magnetic properties of metal complexes or supported metal catalysts. The information about satellites is very useful in order to elucidate the valence state of the metal ion, especially in cases where it is difficult to determine its state by means of the binding energy alone.

From the relative intensities of the peaks for different level, we can obtain information about the surface composition of a catalyst or the surface coverage of the catalyst.[8]

According to the ESR spectra of supported cobalt catalysts,[12] it seems to be difficult to study the valence state of the supported cobalt because of the large spin-orbital interactions. Only very broad and ambiguous signals are obtained by ESR measurements for supported cobalt catalysts, and the cobaltic species are ESR-inactive. Moreover, only the bulk state of a catalyst is given by ESR and other techniques. Therefore, it seems that it would be interesting to investigate these catalysts by means of the XPS technique in order to characterize the surface state of the supported cobalt catalysts.

In this paper, on the basis of the results obtained by XPS measurements, the surface properties of the cobalt catalysts will be discussed. Moreover, we found that the energy differences between the $2p_{1/2}$ and $2p_{3/2}$ subshells of some first-transition metals are sensitive to the magnetic properties of the metal ion, and also that, in some cases, such information is more useful in the study of elucidating the valence state (magnetic properties) of the metal ion than the satellite is. We also studied the interaction between cobalt and support in order to ascertain the role of the support.

Experimental

Materials. The cobalt catalysts were prepared by a conventional impregnation technique using cobaltous nitrate. After drying at 100 °C, the catalysts were calcined at various temperatures for 5 hr in air. The supports examined were γ-Al_2O_3, SiO_2, and La_2O_3; and their surface areas were 235, 390, and 2 m^2/g respectively. The compounds used in this study were all supplied by Nakarai Chemical, Ltd., and Wako Pure Chemical, Ltd., except for the cobaltic compounds and $Co(CN)_2$, which were prepared and characterized according to published methods.[13] The CoO was obtained by the reduction of Co_2O_3 with H_2 or CO *in situ.*

Procedure. The photoelectron spectra were measured on a Hitachi 507 photoelectron spectrometer using AlKα or MgKα radiation. Powdered samples were held on a sample holder made of copper metal. The binding energies were corrected by using the value of 285.0 eV for the Cls level resulting from the contaminated carbon. The reproducibilities of the values thus obtained were within ±0.2 eV; the energy differences were determined with an accuracy of ±0.1 eV.

The reduction of the cobalt catalysts was carried out *in situ* using hydrogen with a pressure of 10 mmHg.

Results and Discussion

Spin-orbit Splitting of the 2p Level. There have been only a few reports of X-ray photoelectron spec-

TABLE 1. BINDING ENERGY, SATELLITE SPLITTING OF 2p LEVEL, SATELLITE TYPE, AND ΔE FOR COBALT COMPOUNDS

	Compound	Satellite type[a)]	$Co2p_{1/2}$		$Co2p_{3/2}$		ΔE[d)]
			B. E.[b)]	S. S.[c)]	B. E.[b)]	S. S.[c)]	
1	CoF_2	B	798.1	6.0	782.1	4.6	16.0
2	$Co(NO_3)_2$	B	797.6	5.5	781.8	4.8	15.8
3	$CoSO_4$	A	797.5	5.0	781.4	3.7	16.1
4	$Co(CH_3COO)_2$	B	797.0	5.2	781.1	4.8	16.1
5	$Co_3(PO_4)_2$	A	797.0	5.2	781.0	4.8	16.0
6	$CoCrO_4$	B	796.8	6.5	780.9	5.6	15.9
7	$Co(CN)_2$	D	796.0	—	780.9	—	15.1
8	$CoCl_2$	A	796.6	6.2	780.7	5.6	15.9
9	$2CoCO_3\cdot 3Co(OH)_2$	B	796.7	5.7	780.7	4.5	16.0
10	$CoBr_2$	A	796.3	6.7	780.3	5.2	16.0
11	CoO	B	796.0	6.1	780.3	5.5	15.7
12	Co_3O_4	C	794.6	9.2	779.6	9.5	15.0
13	Co_2O_3	C	794.5	9.3	779.4	8.9	15.1
14	$K_3Co(CN)_6$	D	796.7	—	781.7	—	15.0
15	$[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_4$	C	796.3	6.9	781.2	9.5	15.1
16	$[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_5$	C	796.5	9.3	781.5	9.4	15.0
17	$[Co(NH_3)_6]Cl_3$	C	796.7	8.4	781.7	9.6	15.0
18	$[Co(NH_3)_6]Br_3$	C	796.3	9.0	781.3	10.3	15.0
19	$[Co(NH_3)_5Br]Br_2$	C	796.1	8.0	781.0	8.9	15.1
20	$[Co(NH_3)_6](NO_3)_3$	C	796.4	8.7	781.5	9.4	14.9
21	$[Co(en)_3]Cl_3$	C	794.9	8.9	780.2	9.3	14.7
22	$[Co(en)_2Cl_2]Cl$	C	794.9	8.7	780.0	8.2	14.9
23	Co-metal	D	792.9	—	777.8	—	15.1

a) see Fig. 1. b) binding energy (eV). c) satellite splitting (eV). d) spin-orbit splitting of 2p level (eV).

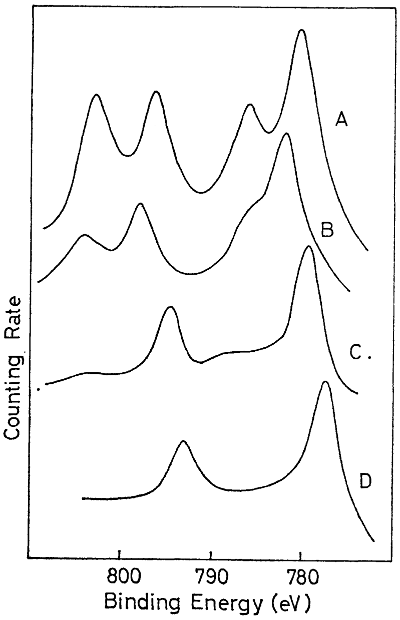

Fig. 1. XPS spectra of Co2p level for cobalt compounds, A∼D indicate satellite type, A: $CoCl_2$, B: CoF_2, C: Co_2O_3, D: Co-metal.

troscopic measurements of cobalt compounds.[14)] The binding energies of the cobalt compounds examined are listed in Table 1. The chemical shift is generally used to distinguish the oxidation states of the atom. However, as is shown in Table 1, the binding energies of the cobaltous compounds (Co^{2+}) examined are distributed between 782.1 eV for CoF_2 and 780.3 eV for $CoBr_2$, while those of cobaltic compounds (Co^{3+}) are distributed between 781.7 eV for $K_3Co(CN)_6$ and 779.4 eV for Co_2O_3, according to their chemical environments. Therefore, from the binding energy alone, we cannot clarify the oxidation state of these cobalt compounds. In the case of copper compounds, cuprous and cupric compounds can be distinguished by the chemical shift alone, as has been reported by Frost *et al.*,[15)] whereas, in the case of cobalt compounds, as has been reported for nickel compounds,[9)] the chemical shift is not a useful measure for discriminating the valence states.

The photoelectron spectra of the 2p level for some representative cobalt compounds are shown in Fig. 1. In some cases of a first-transition metal, it is well known that paramagnetic compounds show satellite(s) on the 2p level as a result of a shake-up process, while diamagnetic compounds do not. According to our systematic studies of cobalt compounds, all the cobaltous compounds except $Co(CN)_2$ have intense satellites, as is shown in Fig. 1, but none of the cobaltic compounds examined, cobalt metal, or $Co(CN)_2$ showed any such strong satellite. According to the intensity of the satellite, we classified the spectra into 4 types(A–D), as is shown in Fig. 1. The intensity ratio of the satellite and its main peak ($2p_{3/2}$) is >0.8 for Type A, >0.6 for Type B, ~ 0.1 for Type C, and ~ 0 for Type D. In Table 1, the satellite splittings and types are summarized for the cobalt compounds studied. Negative relations were observed between the satellite splittings and the binding energies for both the $2p_{1/2}$ and $2p_{3/2}$ subshells of cobaltous compounds, as has been reported by Frost *et al.*[15] for cupric compounds. That is, when the covalency becomes smaller or the electronegativities of ligands become larger, the satellite splittings become smaller. These facts can be explained in terms of a shake-up process under the influence of the chemical environment, as has been indicated by Frost and his co-workers.[15] Therefore, the information about satellites may be used in conjunction with binding energy to predict the relative degree of covalency between the ligand and the central ion.

In the case of $Co(CN)_2$, the electronic configuration of this compound is a low-spin state; that is, $Co(CN)_2$ has one unpaired electron and the magnetic moment (μ_{eff}) of this compound is 3.11.[16] The other cobaltous compounds examined have high-spin configurations ($\mu_{eff} \fallingdotseq 5.2$). Moreover, the unpaired spin must be distributed over cyano ligands because of their large nephelauxetic effect. Therefore, $Co(CN)_2$ may behave like diamagnetic compounds in the XPS study of 2p satellites, since the spin density of the cobalt ion in $Co(CN)_2$ is low. The cobalt complex $[(NH_3)_5Co(O_2)Co(NH_3)_5]\ Cl_5$ is paramagnetic; it contains Co^{3+} and Co^{4+} and has one unpaired electron.[17] However, this compound also behaves in a diamagnetic manner for the 2p satellite, for the same reason as $Co(CN)_2$. However, an ambiguous weak satellite can be observed on the 3s level for both compounds; this indicates that the compounds are paramagnetic, as estimated from the magnetic properties.[16] It is considered that the different behavior of 2p and 3s satellites is a result of their different interaction strengths with 3d unpaired electrons.

Cobaltous compounds cannot be distinguished from cobaltic compounds by the chemical shift alone, but they can be discriminated by the satellite structure (magnetic properties). Since the chemical shift reflects the over-all electron density, and since the satellite structure shows the electronic configuration of the 3d level, it may be considered that the electron densities of the central metal ions, which are, of course, affected by the electronegativities of the ligands, are similar for cobaltous and cobaltic compounds, but that the electron configurations of the 3d levels for these compounds are influenced only very slightly by the ligands. It is estimated that the electrons of level higher than 3d (4s, 4p electrons) are responsible to a considerable degree for the bonding to the surrounding ligands.

From the XPS measurments, Co_2O_3 and Co_3O_4, which contains both Co^{2+} and Co^{3+}, could not be distinguished by chemical shift or satellite. This suggests that the surface layer of Co_3O_4 is similar to that of Co_2O_3.

As has been discussed above, the chemical shift and satellite peaks give information about the oxidation state and the chemical environment of a metal ion or a catalyst surface. However, in the studies of supported catalysts, the spectra obtained are usually weak, especially when the concentration of the catalytic components is low. Therefore, the information about the satellite is sometimes ambiguous, and it becomes difficult to characterize the catalyst.

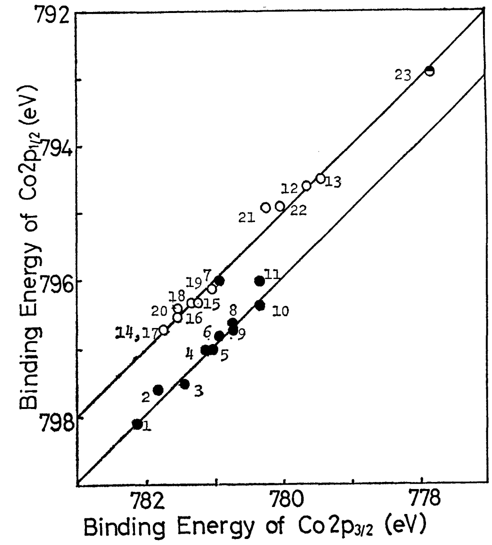

Fig. 2. Correlations of the binding energies of $Co2p_{3/2}$ and those of $Co2p_{1/2}$ for cobalt compounds. See Table 1 for a listing of the compounds

Table 2. ΔE values for Ni, Cr, and Cu compounds observed

Metal	ΔE (eV)	Compounds
Ni	17.6	Ni^{2+} compounds[1]
	17.2	Ni-metal
Cr	9.2	Cr^{6+} compounds
	9.7	Cr^{3+} compounds
	9.1	Cr-metal
Cu	20.1	Cu^{2+} compounds
	20.0	Cu^{+} compounds, Cu-metal

[1] Paramagnetic compounds.

The spin-orbit splittings of the 2p level (ΔE) of the cobalt compounds examined are shown in Table 1. The relation between the binding energies of the $2p_{1/2}$ subshells and those of the $2p_{3/2}$ subshells is shown in Fig. 2. It is interesting that two different linear corelations are obtained for the cobaltous and cobaltic compounds. It is clear from Fig. 2 that, for cobaltous compounds, $\Delta E = 16.0$ eV, while for cobaltic compounds, $Co(CN)_2$, and cobalt metal, $\Delta E = 15.0$ eV. Hence, we can distinguish the oxidation states of the cobalt compounds by means of the value of ΔE. Recently, such correlations between the oxidation state and ΔE have been reported for several cobalt compounds by Frost *et al.*[14] The ΔE values for nickel, chromium, and copper compounds are shown in Table 2.

On the basis of these results, it seems to be established that the ΔE values for paramagnetic compounds are larger than those for diamagnetic compounds or metal, and that the energy difference in ΔE between paramagnetic and diamagnetic (or metal) compounds depends on the number of the unpaired electrons of the paramagnetic compounds. These results suggest that the origin of the change in ΔE is as follows. In the case of a paramagnetic 3d transition metal, the satellite peaks of the 3s level are generally observed and the origin of the satellite is considered to be due to the exchange interaction between the 3s electron and the 3d unpaired electrons.[10] According to Basch,[10] the satellite splitting due to the exchange interaction is given as follows:

$$\Delta\varepsilon_\mu = \sum(N_t^\alpha - N_t^\beta)K_{\mu t} \tag{1}$$

where $\Delta\varepsilon_\mu$ is a satellite splitting of the μ-level, where N_t^α and N_t^β are the numbers of α and β spins respectively in the t-level, and where $K_{\mu t}$ is the exchange integral between t- and μ-levels. Such an effect of unpaired spins in the 3d band has been clearly observed on the 3s and 3p levels,[18] but for the 2p-level no such clear evidence of multiplet splitting has been found because of the smaller value of $K_{2p,3d}$ relative to $K_{3s,3d}$. According to the UHF calculations by Moskowitz *et al.*,[19] which predict a 3s-level splitting of 5.2 eV (compared to the 4.0 eV observed), the exchange splitting of the 2p level of NiF_6^{4-} is calculated to be about 2 eV. Therefore, the expected splitting of less than 2 eV would be difficult to observe with non-monochromatized X-ray sources, which give spectra with band widths at half height, typically about 2.5 eV. Recently, however, Frost *et al.*[15] reported that the widths of the main peaks of the 2p level from the cuprous compounds are narrower than that of cupric. These facts can be considered to be indirect evidence in favor of such splitting.

If we consider the case in which one unpaired electron exists in the 3d level and the orbital angular momentum, l, of the electron is spherically averaged (its state is expressed by $^2S_{1/2}$), for the sake of simplicity, the hole state of $2p_{1/2}$ and $2p_{3/2}$ subshells, after the emission of photoelectrons (whose states are expressed by $^2P_{1/2}$ and $^2P_{3/2}$ respectively), is split by exchange interaction with the 3d unpaired electron into two terms[20]:

$$^2S_{1/2}{}^2P_{1/2} \rightarrow {}^3P_0 \text{ and } {}^3P_1$$

$$^2S_{1/2}{}^2P_{3/2} \rightarrow {}^3P_2 \text{ and } {}^1P_1$$

In Fig. 3, some schematic spectra are shown. From Eq. (1), the energy differences between $^3P_0$ and $^3P_1$, or between $^3P_2$ and $^1P_1$ are given. The energy diagram of the sp configuration in an intermediate coupling[20] must be inverted in our case, since the hole states are involved in the XPS. From Fig. 3, we can expect a larger ΔE value for a paramagnetic compound than for a diamagnetic one. In real systems, the conditions are much more complicated, but the ΔE value for a paramagnetic compound may be expected to be larger than that for a diamagnetic compound. As has been discussed above, the change in ΔE is considered to be due to the multiplet splitting of the 2p level and to be indirect evidence for exchange interaction between the 2p and 3d levels. The dependence of the difference in the ΔE values between paramagnetic and diamagnetic compounds upon the number of unpaired spins can be explained by Eq. (1)

If the spin-orbit splitting of the 2p level is considered to be due to the multiplet splitting by the exchange interaction with 3d unpaired electrons, the widths of the 2p-level spectra for paramagnetic cobaltous compounds must be broader than those for diamagnetic cobaltic compounds. In fact, the full widths at half height are about 3.4 eV and 2.9 eV for cobaltous and cobaltic compounds respectively. These facts support the multiplet splitting mechanism.

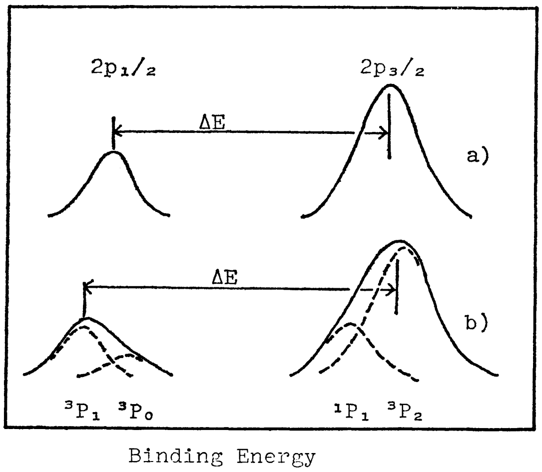

Fig. 3. Schematic spectra with and without exchange interaction between 2p and 3d levels.
a) without interaction b) with interaction.

TABLE 3. BINDING ENERGY OF $2p_{3/2}$ LEVEL AND ΔE FOR SUPPORTED COBALT CATALYST

Support	wt%	Calcination temperature (°C)	B. E. (eV)	ΔE (eV)
γ-Al_2O_3	5.0	100	780.8	15.8
	5.0	500	780.7	15.6
	5.0	1000	780.4	15.3
	10.0	500	781.0	15.1
La_2O_3	5.0	100	780.5	15.7
	5.0	500	779.7	15.0
	5.0	1000	779.6	15.0
	10.0	500	780.2	15.0
SiO_2	10.0	500	779.1	15.3

Consequently, in the study of catalysts with XPS, we can also use the ΔE value as a useful piece of information for elucidating the oxidation state of a catalyst component as well as the binding energy and the satellite.

Supported Cobalt Catalysts. The cobalt catalysts supported on γ-Al_2O_3, SiO_2, and La_2O_3 were also investigated. The catalysts examined are shown in Table 3; their binding energies of the $2p_{3/2}$ subshell and the ΔE values are also listed. In the case of cabalt catalysts, the ΔE values fall between 15.0 and 16.0 eV. This fact indicates the coexistence of Co^{2+} and Co^{3+} on the surface of cobalt catalysts.

In Fig. 4, the spectra of the 2p level for the supported cobalt (5 wt%) on γ-Al_2O_3 (a) are shown. As with the cobalt-alumina catalysts, after drying at 100°C the oxidation state of a large proportion of the cobalt is considered to be Co^{2+}, as expected, on the basis of the satellite and ΔE value, listed in Table

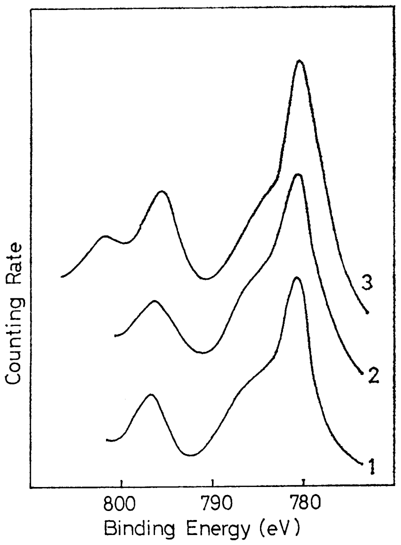

Fig. 4a. XPS spectra of Co2p level for cobalt supported (5 wt%) on γ-Al_2O_3, 1) after drying at 100 °C, 2) after calcination at 500 °C for 5 hr, 3) after calcination at 1000 °C for 5 hr.

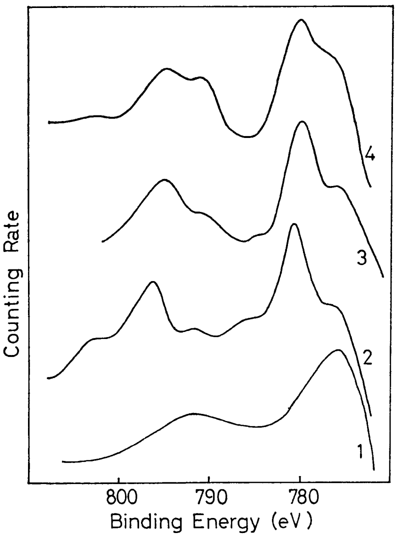

Fig. 4b. XPS spectra of Co2p level for cobalt supported (5 wt%) on La_2O_3, 1) back ground spectrum of La_2O_3, 2) after drying at 100 °C, 3) after calcined at 500 °C for 5 hr, 4) calcined at 1000 °C for 2 hr.

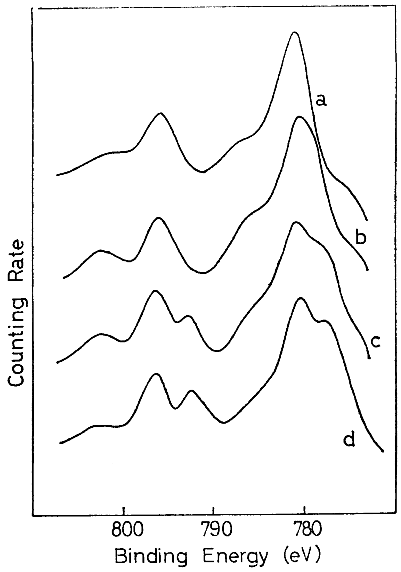

Fig. 5. XPS spectra of Co2p level for cobalt-alumina catalyst (10 wt%) reduced by H_2 (10 mmHg) at 400 °C.

a) after calcination at 500 °C for 5 hr, b) 20 min reduction, c) 80 min reduction, d) 250 min reduction

3. After the catalysts were calcined in air at 500 °C or 1000 °C, only very small chemical shifts for the $2p_{3/2}$ sublevel are observed, but ΔE changes 0.5 eV among these catalysts. In the case of the catalyst calcined at 500 °C, a weak satellite is observed (Fig. 4a) and the spin-orbit splitting is about 15.6 eV. Therefore, both Co^{2+} and Co^{3+} exist in comparable amounts on the 500 °C-calcined catalyst. However, with regard to the cobalt-alumina catalyst calcined at 1000 °C, it is considered that a large proportion of the cobalt is Co^{3+}, while only a small amount of Co^{2+} is present. This is confirmed by the ambiguous satellite peak for this catalyst shown in Fig. 4a. It may be concluded from Table 3 that the Co^{3+} content becomes larger with calcination at higher temperatures and with an increase in the amount of supported cobalt. It may be of interest to mention here that all the Co–Al_2O_3 catalysts calcined above 800 °C were blue in color, revealing the presence of Co^{2+} ions in a tetrahedral surrounding of O^{2-} ions,[21] and that X-ray diffraction analysis of this catalyst suggests the presence of $CoAl_2O_4$. Contrary to these results, a large proportion of the cobalt is Co^{3+}, as is shown by XPS measurements. The discrepancy between these results is considered to be due to different types of information about the catalyst; that is, the information about the surface layer is obtained by XPS (<20Å), about the much thicker layer, by means of the visible spectra ($<1\,\mu$), and about the "bulk" of the catalyst, by X-ray diffraction analysis. Comparing the chemical shift data in Tables 1 and 3, it is considered that the state of cobalt over γ-alumina calcined at 100°C is more covalent than that of cobaltous oxide. Moreover, after calcination at 500 °C or 1000 °C, the binding energies of $Co2p_{3/2}$ for these catalyst do not fall between those for CoO and Co_2O_3. These facts indicate an interaction (chemical or physical) between cobalt and γ-alumina, even after drying at 100 °C.

Such an interaction is supported by such reduction experiments as are shown in Fig. 5. After calcination at 500 °C (a), the cobalt-alumina catalyst (10 wt%) contains mainly Co^{3+}, as is to be expected from its spectrum (weak satellite) and ΔE value (15.1 eV). However, after a 20-min reduction at 400 °C (b), the main peak of the $2p_{3/2}$ subshell becomes broader, the satellite intensity becomes larger relative to the main peak, and the ΔE value increases to 15.5 eV. That is, the appearance of Co^{2+} can be expected. After further reduction (80 min) at 400 °C (c), a metal peak appears as a shoulder at about 778.1 eV. The higher binding energy peak of the $2p_{3/2}$ subshell with an ambiguous satellite is considered to be that of Co^{2+}, probably due to $CoAl_2O_4$, judging from the ΔE value (15.8 eV). No further intense change in the spectrum was observed even after a 250-min reduction at the same temperature (d). However, in the case of unsupported Co_2O_3, a peak due to CoO appeared after a 10-min reduction at 400 °C and a metal peak appeared clearly after a 15-min reduction at the same temperature. The spectrum of a pure metal was obtained after only a 40-min reduction. These facts indicate a strong interaction between cobalt and γ-Al_2O_3.

In the case of silica gel, it is considered that Co_2O_3 is formed on the surface; it is then easily reduced to cobalt metal as Co_2O_3. Therefore, no specific interaction between cobalt and silica gel is found.

As regards the cobalt catalysts supported on La_2O_3, a cobaltic compound can be expected after calcination over 500 °C. Comparing the chemical shifts of cobaltic compounds in Table 1, the chemical environment of cobaltic compounds on La_2O_3 is considered to be similar to that of Co_2O_3. It is clear from Fig. 4b the intensity of the cobalt 2p level, compared to the background peak of La_2O_3, becomes weaker with the calcination temperature; this indicates that the cobalt ion diffuses into La_2O_3 or that new compounds of cobalt and La_2O_3 are formed. In the cases of alumina and silica gel, no such intense change in the intensity of the cobalt peaks was observed upon treatment. On the basis of the X-ray diffraction studies, it is found that $LaCoO_3$ is formed. To confirm this conclusion, reduction experiments were carried out. After a 1-hr reduction, Co^{2+} appeared ($\Delta E = 15.5$ eV); no metal peak was observed clearly until after a 2-hr reduction at 400 °C. Therefore, cobalt on La_2O_3 is the most difficult to reduce among the cobalts on all the supports examined. These facts confirm that the new compound ($LaCoO_3$) is formed on the catalyst surface.

Summarizing these results, it is determined that the states of supported cobalt are; Co_2O_3 on SiO_2, $Co_2O_3 + CoAl_2O_4$ on γ-Al_2O_3, and $LaCoO_3$ on La_2O_3. Consequently, it is concluded that the chemical interaction between support and cobalt catalyst decreases as follows:

$$La_2O_3 > \gamma\text{-}Al_2O_3 > SiO_2$$

References

1) W. N. Delgass, T. R. Hughes, and C. S. Fadley, *Catal. Rev.*, **4**, 179 (1970).

2) A. W. Miller, W. Atkinson, M. Barber, and P. Swift, *J. Catal.*, **22**, 140 (1971).

3) D. A. Whan, M. Barber, and P. Swift, *Chem. Commun.*, **1972**, 198.

4) J. S. Brinen and A. Melera, *J. Phys. Chem.*, **76**, 2525 (1972).

5) P. Biloen and G. T. Pott *J. Catal.*, **30**, 169 (1973).

6) J. Escard, C. Leclere, and J. P. Contour *ibid.*, **29**, 31 (1973).

7) Y. Okamoto, K. Adachi, T. Imanaka, and S. Teranishi, *Chem. Lett.*, **1974**, 241.

8) Y. Okamoto, M. Fujii, T. Imanaka, and S. Teranishi, unpublished.

9) L. J. Matienzo, L. I. Yin, S. O. Grim, and W. E. Swartz, *Inorg. Chem.*, **12**, 2762 (1973).

10) H. Basch, *Chem. Phys. Lett.*, **20**, 233 (1973) and the literature therein.

11) L. Yin, I. Adler, T. Tsang, L. J. Matienzo, and S. O. Grim, *Chem. Phys. Lett.*, **24**, 81 (1974) and the literature therein.

12) H. Ueda, *J. Catal.*, **27**, 281 (1972).

13) "Inorganic Synthesis," Vol 1–12, McGraw-Hill Book Comp. New York and London (1939–1970).

14) D. C. Frost, C. A. McDowell, and I. S. Woolsey *Mol. Phys.* **27**, 1473 (1974).

15) D. C. Frost, A. Ishitani, and C. A. McDowell *ibid.*, **24**, 861 (1972).

16) "American Institute of Physics Handbook," 3rd Ed. McGrow-Hill Book Company, New York (1972).

17) F. A. Cotton and G. Wilkinson "Advanced Inorganic Chemistry," 2nd Ed. Interscience Publishers, New York, London, Sydony, 1966.

18) C. S. Fadley and D. S. Shirley, *Phys. Rev.*, **2A**, 1109 (1970).

19) J. W. Moskowitz, C. Hollister, C. J. Hornback, and H. Basch, *J. Chem Phys.*, **53**, 2570 (1970)

20) E. C. Condon, and G. H. Shortley "The Theory of Atomic Spectra," Cambridge University Press (1970), p. 272.

21) J. H. Ashley and P. C. Mitchell, *J. Chem. Soc. Ser. A*, **1968**, 2821.