X-Ray Photoelectron Spectroscopic Studies of Catalysts
—Chromia–Alumina Catalysts—

Yasuaki Okamoto, Masaki Fujii, Toshinobu Imanaka, and Shiichiro Teranishi
Department of Chemical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received June 30, 1975)

The XPS studies of chromia–alumina catalysts were carried out to elucidate the surface of these catalysts. Photoreduction was found to occur during the XPS measurements. Therefore, all spectra were measured rapidly to prevent any photoreduction. It was found that the information about the spin-orbit splitting of the Cr2P level is very useful for determining the valence state of chromium. The surface state of chromium in chromia–alumina catalysts calcined at 500 °C for 5 h is predominantly Cr^{6+} at low chromia concentration catalysts. However, the Cr^{3+} phase appears in catalysts of higher chromium content, and the surface concentration of Cr^{3+} increases with increasing content of supported chromia. The XPS spectra due to Cr^{5+} were observed after mild reduction of the catalysts. Moreover, it was found that almost all surface chromium is present as Cr^{5+} at low chromia content catalysts after mild reductions. Qualitatively, the results obtained by the XPS technique, which gives information about the surface of catalysts, agree well with the results obtained by ESR and other techniques, which gives information about the bulk of catalysts, especially low chromium concentration catalysts. These findings indicate a high dispersion of chromium on γ-Al_2O_3 for low chromium content catalysts.

Since the X-ray photoelectron spectroscopy (XPS or ESCA) measurements reveal both the chemical composition and state of the surface atoms of solids, they provide a new probe for studying the properties of catalysts.[1] From XPS measurements of catalysts, we can obtain three important pieces of information—that is, information about the binding energy, the satellite structure, and the relative intensities of some levels. The information about the binding energy and the satellite structure reveals the chemical and magnetic state of the atom concerned. Recently, the information about the spin-orbit splitting of the 2p level for some transition metals was emphasized to be useful in determining the magnetic state or valence state of the transition metal ions.[2–4] By comparing the XPS peak intensities of different levels, we can obtain knowledge about the surface composition of a catalyst or the surface coverage of supported catalysts on a carrier.

Chromia-alumina catalysts have been studied by many workers[5] using ESR and other techniques, since chromia–alumina catalysts are active in a great variety of reactions such as dehydrocyclization, dehydrogenation, and the polymerization of olefins. On the basis of the results obtained by means of ESR, magnetic susceptibility measurements, titration method, NMR, X-ray diffraction, and optical reflectance spectroscopy, it is revealed that various valence states of chromium are present on chromia–alumina catalysts.[5] However, from these techniques we can only obtain information about the bulk catalysts or thick surface layer of the catalysts.

The advantages of XPS over these techniques are that, in principle, it is capable both of determining the valencies of metal ions on the thin surface layer (~10 Å) of supported oxide and simultaneously of detecting the interaction between catalyst and support.

In this paper, on the basis of the information obtained by XPS measurements for chromia–alumina catalysts, the surface properties of the catalysts will be discussed and compared with the results obtained by other techniques. XPS spectra of some chromium compounds were measured and the spin-orbit splitting of the Cr2p level was emphasized as being very useful for discriminating the valence states of chromium. The first XPS spectra of Cr^{5+} were, to our knowledge, observed in this study. Moreover, it was pointed out that photoreduction phenomena during XPS measurements must be considered in the case of chromia–alumina catalysts.

Experimental

Materials. Chromia–alumina catalysts supported on γ-Al_2O_3 with different compositions were prepared by a conventional impregnation technique using chromium nitrate or chromic oxide. After drying at 120 °C, catalysts were calcined at 500 °C for 5 h in air. In the case of 2 wt% catalysts, the catalysts calcined at 900 °C for 3 h were also investigated. The surface area of γ-Al_2O_3 used in our experiments was 235 m^2/g.

Procedure. Photoelectron spectra were measured on a Hitachi 507 photoelectron spectrometer using Al*Kα* radiation. The power of X-ray radiation was 500 W (10 kV, 50 mA) in all measurements. The spectrometer was linked to a multichannel analyser in the multiscaler mode, which was useful for the study of time dependent spectra. Powdered samples were mounted on a sample holder made of stainless steel mounted with mesh. The spectrometer operating pressure was *ca.* 1×10^{-6} Torr. After the samples were pretreated in a pretreatment chamber (*ca.* 5×10^{-5} Torr), they were introduced into the analyser.

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 catalysts was carried out in the pretreatment chamber using hydrogen with a pressure of about 10 Torr. The severe reductions were accomplished with a conventional flow system using atmospheric hydrogen.

Results and Discussion

1) XPS Spectra of Chromium Compounds. There have been several reports of X-ray photoelectron spectroscopic measurements of chromium compounds.[6–11] The binding energies of the Cr2p level for the chromium compounds examined in this study are listed in Table 1. It is clear from Table 1 that Cr^{6+}, Cr^{3+}, and Cr metal can be distinguished by the binding energy alone. However, recently the XPS spectra of Cr^{4+} compounds have been reported by Ikemoto *et at.*[12] According to their results, the binding energies of CrO_2 and CrOOH are 576.3 and 577.0 eV respectively. They also reported the $Cr2p_{3/2}$ binding energies for Cr_2O_3 and $K_2Cr_2O_7$; their values agree very well with our data in Table 1. These values for Cr^{4+} compounds are located around Cr_2O_3. In the case of CrO_2, its binding energy is even lower than that of Cr_2O_3. These facts will be explained in terms of the solid effects which cancel chemical shifts, as has been discussed by Kim and Winograd.[13] The chemical shift data, therefore, are not considered to be useful for determining the valence state of chromium, as in the case of Co,[2] Ni,[14] Pb,[15] and Cu.[16] As for Cr^{5+}, there have been no reports about XPS spectra in spite of its importance in catalysis.

The XPS spectra of the Cr2p level for Cr^{3+} compounds have weak satellites and their satellite splittings ($\Delta\varepsilon$) of the $Cr2p_{1/2}$ level were shown in Table 1, but the Cr^{6+} compounds give no such satellite peak. The $\Delta\varepsilon$ values and satellite intensities agree well with those reported by many workers.[17,18]

Helmer[9] reported that the spin-orbit intensity of the Cr2p doublet of Cr^{6+} is 0.33, instead of the theoretical value of 0.50. Also in our measurements it was found that the intensity ratios (I) ($Cr2p_{1/2}/2p_{3/2}$) for Cr^{6+} compounds are about 0.40, which are samller than 0.50: these are shown in Table 1. The discrepancy between the theoretical value and the observed values may be due to solid effects. In the case of Cr^{3+} compounds, I values are larger than those of Cr^{6+} compounds. This fact can be well understood by recognizing that the satellite peak of $Cr2p_{3/2}$ overlaps with the main peak of $Cr2p_{1/2}$.

The spin-orbit splittings of Cr^{3+} compounds are larger than those of Cr^{6+} compounds, as has been reported.[2,9] The difference of the spin-orbit splitting between Cr^{3+} and Cr^{6+} compounds can be explained in terms of the exchange interaction between 2p electrons and unpaired 3d electrons.[2-4] Such an interaction makes the 2p level spectra broad, as is shown in the last column of Table 1. Similar but larger effects of unpaired 3d electrons on the XPS spectra of 2p levels have been found for cobalt compounds.[2-4]

From these facts, Cr^{3+} and Cr^{6+} compounds and Cr-metal can be distinguished in terms of the binding energy, the satellite structure, the spin-orbit intensity ratio, and the spin-orbit splitting. However, in the studies of supported catalysts, the spectra obtained are usually weak, especially when the concentration of the catalytic component is low. The information about the satellite is sometimes ambiguous for supported transition metals, especially for supported chromium catalysts, since the satellite intensities are rather weak for chromium compounds. Moreover, the measurements of spin-orbit intensity ratios are considered to be difficult because of the uncertainties in the estimation of the base line. Therefore, we use the information about the binding energy and the spin-orbit splitting in order to distinguish the valence states of chromium supported on the carrier. In the case of the XPS studies of the supported cobalt catalysts,[2] such information has been found to be very useful to discriminate Co^{2+} and Co^{3+} species.

2) XPS Spectra of Chromia-Alumina Catalysts. 2—1 Photoreduction of Chromium on Chromia-Alumina Catalysts: The XPS spectra of chromium on the chromia-alumina catalysts were found to be time-dependent. The Cr2p spectra for a 2 wt% chromia-alumina catalyst, which was prepared by impregnation with chromium nitrate and calcined at 500 °C for 5 h, are shown at various irradiation times in Fig. 1. No change in the spectrum was observed within the irradiation time of 12.5 min. But, after 37.5 min-irradiation, an additional peak appeared at the lower binding energy of *ca.* 578 eV. After 80 min-exposure to X-ray flux, the additional and original peaks became comparable. An additional predominant peak appeared after 300 min irradiation, while a peak at 577.8 eV appeared by further irradiation. The peak obtained by the photoreduction has the spin-orbit splitting (ΔE) of 9.0 eV. Therefore, this chromium compound cannot be attributed to a Cr^{3+} compound, which has larger spin-orbit splitting values, as is shown in Table 1. The valence state this chromium compound will be discussed later. In the case of other chromia-alumina catalysts, similar phenomena were observed; the chromium states obtained were: B. E., 577.7 eV and ΔE, 9.5 eV for 5 wt%; B. E., 577.8 eV and ΔE, 9.7 eV for 10 wt%; and B. E., 577.2 eV and ΔE, 9.9 eV for 20 wt% after several hours irradiation. In the 20 wt% catalyst, the final state of chromium can be attributed to Cr^{3+} compound, because it has a energy of 577.2 eV and the ΔE value of 9.9 eV.

Such a pronounced surface reduction of some 3d transition metal compounds has been observed during XPS measurements. Particularly strong effects were found in copper(II) fluoride and potassium hexa-

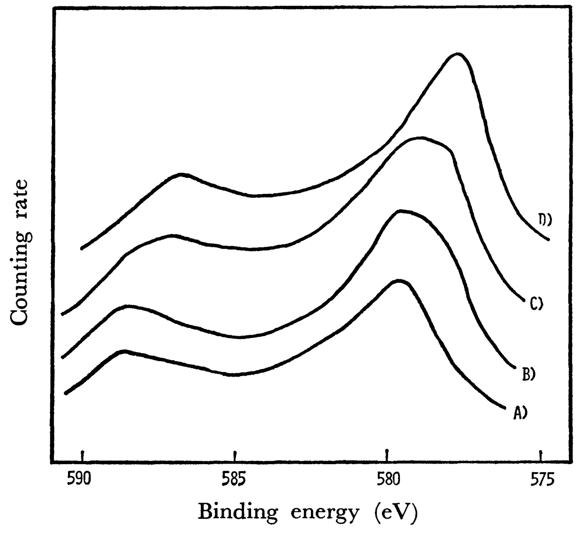

Fig. 1. Time-dependence of Cr2P XPS spectra for a 2 wt% chromia-alumina catalyst.
A) 12.5 min, B) 37.5 min, C) 80 min, D) 300 min-irradiation.

Table 1. Binding energy of $Cr2p_{1/2}$ and $2p_{3/2}$, satellite splitting, spin-orbit splitting of Cr2p level, intensity ratio of $Cr2p_{1/2}$ and $2p_{3/2}$, and full width at half maximum of $Cr2p_{3/2}$

	Compound	Binding energy[a)]		ΔE[b)]	I[c)]	$\Delta\varepsilon$[d)]	FWHM[e)]
		$Cr2p_{1/2}$	$Cr2p_{3/2}$				
1	CrO_3	589.4	580.3	9.1	0.43	—	2.8
2	K_2CrO_4	589.3	580.2	9.1	0.40	—	2.1
3	$K_2Cr_2O_7$	589.1	579.9	9.2	0.40	—	1.9
4	CrF_3	589.1	579.2	9.9	0.67	11.4	3.6
5	$Cr(NO_3)_3$	588.2	578.4	9.8	0.64	9.4	3.2
6	$CrPO_4$	587.9	578.3	9.6	0.56	11.5	4.1
7	$CrCl_3$	587.8	577.8	9.6	0.54	9.5	3.4
8	Cr_2O_3	586.4	576.6	9.8	0.63	10.9	3.6
9	Cr-metal[f)]	583.6	574.5	9.1	nd[g)]	—	nd[g)]

a) eV. b) Spin-orbit splitting (eV). c) Intensity ratio: $Cr2p_{1/2}/Cr2p_{3/2}$. d) Satellite splitting of $Cr2p_{1/2}$ (eV). e) Full width at half maximum (eV). f) Not reduced. g) Not determined.

cyanoferrate (III).[19)] No photoreduction phenomena, however, were observed in the chromium compounds examined in our study. These facts indicate that the chromium on the chromia–alumina catalysts can be easily reduced.

2—2 Surface State of Chromium on Chromia–Alumina Catalysts: As has been discussed above, the surface reduction of the catalyst during XPS measurements was found to be negligible within 12.5 min irradiation. Therefore, all spectra were measured within 4—12.5 min exposure to X-ray flux. In Fig. 2, the XPS spectra of the Cr2p level for 1, 2, 5, 10, and 20 wt% chromia–alumina catalysts (impregnated with chromium nitrate and calcined) are shown. The binding energies of the $Cr2p_{3/2}$ level and the spin-orbit splitting (ΔE) for the Cr2p level for these catalysts are listed in Table 2. In the case of 1 and 2 wt% catalyst, the valence state of surface chromium is considered to be almost entirely Cr^{6+} (B. E, 579.7 eV and ΔE, 9.0 eV), whereas the spectrum for a 5 wt% catalyst has a weak shoulder at the lower binding energy side. The shoulder intensity increases with increasing the supported amount of chromia. According to Table 2, the valence state of chromium with lower binding energy can be assigned to Cr^{3+} (B. E., 577.7 eV and ΔE, 9.8 eV). Then, the amount of the Cr^{3+} on the catalyst surface increases with increasing the chromia concentration. This tendency was also ascertained in the bulk analysis of the catalysts examined in our studies† by means of ESR (Cr^{3+}) and chemical analysis (Cr^{6+}; Bunsen-Rupp method). It has been reported by Matsunaga[20)] that essentially all of the chromium ions were oxidized at 450 °C to the Cr^{6+} state for low chromia concentration catalysts, which were prepared by impregnation with chromic oxide and reduced in a stream of hydrogen for 5 h at 360 °C after calcination at 350 °C. Poole and MacIver[21)] suggested, based on their optical measurements, that the Cr^{6+} detected is probably present on the catalyst surface and not in the catalyst bulk. The surface compositions obtained by XPS techniques support their results for low concentration catalysts. At higher chromium content catalysts, the Cr^{6+} content on the catalyst surface seems to be a little larger than that in a bulk catalyst. For example, in the case of a 20 wt% catalyst about half of chromium was found to be present as Cr^{6+}, according to chemical analysis by Bunsen-Rupp method, whereas the Cr^{3+} peak, as is shown in Fig. 2, is observed only as a shoulder of the Cr^{6+} one.

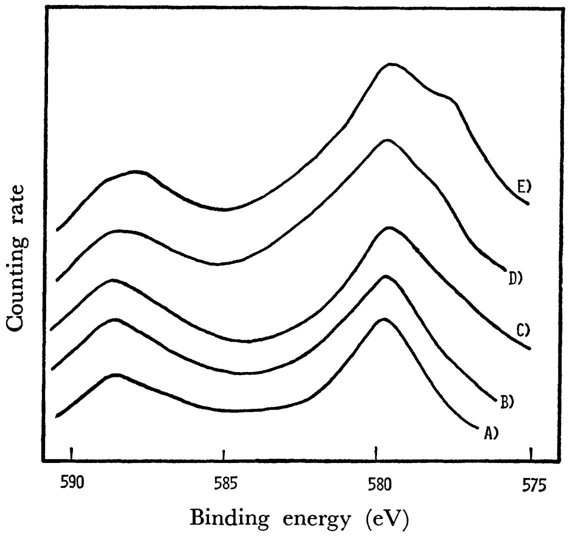

Fig. 2. XPS spectra of Cr2p level for impregnated chromia–alumina catalysts with chromium nitrate, which are calcined at 500 °C for 5 h.
A) 1 wt%, B) 2 wt%, C) 5 wt%, D) 10 wt%, E) 20 wt% catalyst.

Regarding the chromia–alumina catalysts prepared by impregnation with chromic oxide, the spectra were the same as those in Fig. 2 at low concentration of chromia, that is, almost all of the chromium are Cr^{6+}, while in the case of a 20 wt% catalyst the amount of Cr^{6+} is a little larger than that on the 20 wt% catalyst impregnated with chromium nitrate.

The Cr^{6+} binding energies are essentially the same among the calcined catalysts impregnated with different

---

† The ESR signal intensity of Cr^{5+} decreases with increasing the amount of supported chromium, indicating the maximum at 1 wt% catalyst. This fact suggests that the main valence state of chromium in the bulk is Cr^{5+}, but that the surface of the catalyst calcined in air is covered with Cr^{6+}.

starting compounds and uncalcined catalysts impregnated with chromium(III) oxide. They are slightly lower compared with that of CrO_3. The small changes in the binding energy may be attributed to charging effects, differences in crystal structure, or interactions between chromium and γ-Al_2O_3. Therefore, we cannot determine precisely the chemical state of the Cr^{6+} compound on γ-Al_2O_3 after calcination. However, the binding energies of Cr^{3+} on the surface of chromia–alumina catalysts are considerably increased (1.0—1.4 eV), comparing with that for Cr_2O_3. This fact is considered to indicate the presence of the interaction between small crystallines of Cr_2O_3[5] and γ-Al_2O_3, that is, the electron flow from Cr_2O_3 to γ-Al_2O_3 and be expected.

Before calcination, the valence states of chromium were Cr^{3+} (B. E., 578.0 eV and ΔE, 9.8 eV) for the catalysts prepared from chromium nitrate. This result coincides with that obtained by Poole *et al.*[22] using reflectance spectroscopy. In the case of the catalysts prepared from chromium(III) oxide, the chromium is Cr^{6+} (B. E., 579.8 eV and ΔE, 9.0 eV) before calcination.

The changes in the Cr2p spectra for chromia–alumina catalysts were observed by evacuation at elevated temperature or by reduction with hydrogen. These results are summarized in Table 2. In the case of a 2 wt% catalyst, the binding energy of $Cr2p_{3/2}$ become lower (1.9 eV), while the spin-orbit splitting was invariant (9.0 eV) even after evacuation at 230 °C for 20 min or at 350 °C for 1 h. The binding energy of 577.8 eV is close to that of Cr^{3+} compound, but the ΔE value of 9.0 eV is much smaller than that of Cr^{3+} compound. The XPS spectrum of this chromium was the same as that in Fig. 1 (D), which was observed by photoreduction. We cannot attribute this chromium to Cr^{3+} or Cr^{6+}.

The catalysts are considerably reduced by heating them in a pretreatment vacuum chamber. For example, the pronounced reduction of molybdena–alumina catalysts (Mo^{6+}—Mo^{5+}, Mo^{4+}) were observed by evacuation at 300—400 °C in our sample pretreatment chamber, which is evacuated with a cryogenic pump.[23] Therefore, the sexivalent chromium in the original catalyst is considered to be reduced to the chromium with the binding energy of 577.8 eV and the ΔE of 9.0 eV. In fact, the treatment of the catalyst with hydrogen at the pressure of 7.8 Torr gave the same valence state of chromium produced by the treatment of the evacuation or the photoreduction, as is shown in Table 2.

To determine the state of chromium observed after the evacuation at high temperature or the mild reduction with hydrogen, we consider the correlation between spin-orbit splitting (ΔE) and the number of the 3d unpaired electrons. In Table 3, these correlations are listed. When the number of unpaired 3d electron is one, no or only a small change in ΔE was observed, as for the cases of V, Co, and Cu. But when the unpaired 3d electron number is larger than two, a considerable change in ΔE was observed. The fact that ΔE values increase with increasing the number of 3d unpaired electrons can be explained qualitatively in terms of the exchange interaction between 2p electrons and 3d unpaired electrons.[2] From these facts, we can conclude that the number of 3d unpaired electrons in chromium obtained by the reduction is one or zero. The initial state of chromium is Cr^{6+}, as has been discussed. Therefore, the valence state of chromium is considered to be Cr^{5+}, which has one 3d unpaired electron. As discussed above, the chemical shifts data are not useful for determining the valence

TABLE 2. BINDING ENERGY OF $Cr2p_{3/2}$ AND SPIN-ORBIT SPLITTING OF Cr2p LEVEL FOR VARIOUS CHROMIA-ALUMINA CATALYSTS[a] PREPARED BY IMPREGNATION WITH CHROMIUM NITRATE

Catalyst (wt%)	Treatment	Binding energy of $Cr2p_{3/2}$ (eV)	ΔE (eV)	Assignment[c]
1	no treatment	579.7	9.0	6+
2	no treatment	579.7	8.9	6+
	evac. at 320 °C for 20 min	577.8	9.0	5+
	evac. at 350 °C for 1 h.	577.8	9.0	5+
	reduced with H_2 (7.8 Torr) at 300 °C for 5 min	577.8	9.1	5+
	reduced with atmospheric H_2 at 440 °C for 2 h	577.8	9.4	5+, (3+)
	reduced with atmospheric H_2 at 440 °C for 10 h	557.8	9.6	3+, (5+)
2[b]	no treatment	579.5	8.5	6+, (3+)
	evac. at 300 °C for 15 min	578.0	9.9	3+
5	no treatment	579.8[d]	9.0	6+, (3+)
	evac. at 340 °C for 15 min	577.5	9.4	5+, (3+)
10	no treatment	579.8	9.0	6+
		ca. 578.0	nd[e]	3+
	evac. at 330 °C for 50 min	577.5	9.6	3+, (5+)
20	no treatment	579.0	9.0	6+
		577.7	9.8	3+
	evac. at 340 °C for 30 min	577.5	9.6	3+, (5+)
	reduced with H_2 (10 Torr) at 200 °C for 10 min	577.6	9.8	3+

a) Calcined at 500 °C for 5 h in air. b) Calcined at 900 °C for 3 h. c) Valence state in parentheses indicates minor one. d) This peak has a weak shoulder at lower binding energy side. e) Not determined.

Table 3. Dependence of ΔE value on the number of unpaired 3d electrons for some transition metals

Metal	Valence state	Number of unpaired 3d electrons	ΔE (eV)	Compound
V	5+	0	7.5	NH_4VO_3
	4+	1	7.6	$VOSO_4$
Cr	6+	0	9.1	Table 1
	4+	2	9.8	CrO_2,[a] CrOOH
	3+	3	9.8	Table 1
	0	—	9.1	Table 1
Ni	2+	2	17.6	NiO, $Ni(HCOO)_2$
	0	—	17.2	Ni-metal
Co[b]	3+	0	15.0	
	2+	3	16.0	
		1	15.0	
	0	—	15.0	
Cu	2+	1	20.1	CuO
	1+	0	20.0	Cu_2O
	0	—	20.0	Cu-metal

a) Ikemoto *et al.* Ref. 12. b) Okamoto *et al.* Ref. 2.

state of chromium, and ΔE values are considered to be more powerful and reliable in discriminating the valence state of chromium. Therefore, the valence state of chromium obtained by the mild reduction of Cr^{6+} is concluded to be Cr^{5+}, though the binding energy is lower than expected. The low binding energy of Cr^{5+} will be explained in terms of solid effects,[13] as in the case of Cr^{4+}. Moreover, it is considered, based on our assignment, that almost all chromium is present as the Cr^{5+} state after such mild reduction at low chromia concentration catalysts. According to Cossee *et al.*,[24] the mild reductions of chromia–alumina catalysts produce over 95% Cr^{5+} in total chromium in the case of low concentration of chromium. Our XPS results coincide with their ESR results. These facts show that our assignment is reasonable. However, it is not easy to define the chemical state of Cr^{5+} precisely, since there have been no reports, to our knowledge, about the XPS spectrum for Cr^{5+}.

In the case of the high chromia concentration catalysts, the binding energy and ΔE value of the surface state of chromium were 577.5 eV and 9.4—9.6 eV respectively after evacuation at high temperature. The XPS spectra for these chromiums were similar to that in Fig. 1 (D) except for the ΔE value. The spectra containing both Cr^{3+} and Cr^{5+} are deduced to have ΔE of a intermediate value between 9.0 and 9.9 eV, when the spectra of Cr^{3+} and Cr^{5+}, whose binding energies are almost the same, overlap each other. After the evacuation the ΔE values were 9.4, 9.6, and 9.6 eV for 5, 10, and 20 wt% catalysts, respectively. Therefore, it is concluded that these high chromia content catalysts contain both Cr^{3+} and Cr^{5+} after evacuation and that the higher the chromia content is, the larger is the amount of Cr^{3+} produced.

On the basis of a discussion similar to the above, it is considered that the Cr^{3+} phase can be produced at first by severe reductions at low chromia concentration catalysts, as is shown in Table 2. Accordingly, it is concluded that at lower chromia content catalysts, such as a 2 wt% catalyst, Cr^{5+} phase is rather stable, while at higher chromia content catalysts Cr^{3+} phase can be easily produced.

In the case of a 2 wt% catalyst calcined at 900 °C for 3 h, however, chromium was easily reduced by the mild reduction and gave almost entirely Cr^{3+} state, as is listed in Table 2. These findings seem to correlate with the fact that the catalysts calcined at high temperature give a weaker γ-phase intensity in ESR spectra than the catalysts calcined at 500 °C.[5]

On the basis of these results, the assignments for the valence states of surface chromium before and after the treatments were accomplished and listed in the last column of Table 2. Qualitatively, these surface properties of chromia–alumina catalysts obtained by XPS technique agree very well with the results obtained by ESR or other techniques, especially at low chromium concentration catalysts. These facts indicate the good dispersion of chromium on γ-Al_2O_3 at low chromium content catalysts.

References

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

2) Y. Okamoto, H. Nakano, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, **48**, 1163 (1975).

3) D. C. Frost, C. A. MacDowell, and I. S. Woolsey, *Chem. Phys. Lett.*, **17**, 320 (1972).

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

5) C. P. Pool and D. S. MacIver, *Advan. Catal.*, **17**, 224 (1967).

6) D. N. Hendrickson, J. M. Hollandar, and W. L. Jolly, *Inorg. Chem.*, **9**, 612 (1970).

7) M. V. Zeller and R. G. Hayes, *Chem. Phys. Lett.*, **10**, 610 (1971).

8) J. C. Carver, G. K. Schweitzer, and T. A. Carlson, *J. Chem. Phys.*, **57**, 973 (1972).

9) J. C. Helmer, *J. Electron Spectrosc.*, **1**, 259 (1972/73).

10) G. C. Allen, M. T. Curtis, A. J. Hooper, and P. M. Ticler, *J. Chem. Soc., Dalton*, **1973**, 1675.

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

12) I. Ikemoto, K. Ishii, S. Kinoshita, H. Kuroda, M. A. Franco, and J. M. Thomas, Preprint for the 32nd Annual Meeting of Chemical Society of Japan, Tokyo, April, 1975.

13) K. S. Kim and N. Winograd, *Chem. Phys. Lett.*, **30**, 91 (1975).

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

15) K. S. Kim, T. J. O'Leary, and N. Winograd, *Anal. Chem.*, **45**, 2213 (1973).

16) P. E. Larson, *J. Electron Spectrosc.*, **4**, 213 (1974).

17) T. A. Carlson, J. C. Carver, L. J. Saethre, F. G. Santibanez, and G. A. Vernon, *J. Electron Spectrosc*, **5**, 247 (1974).

18) B. Wallbank, I. G. Main, and C. E. Johnson, *J. Electron Spectrosc.*, **5**, 259 (1974).

19) B. Wallbank, C. E. Johnson, and I. G. Main, *J. Electron Spectrosc.*, **4**, 263 (1974).

20) Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **30**, 868 (1957).

21) C. P. Poole and D. S. MacIver, *J. Chem. Phys.*, **41**, 1500 (1964).

22) C.P. Poole and J.F. Itzel, *J. Chem. Phys.*, **39**, 3445 (1963).

23) Y. Okamoto, H. Nakano, T. Imanaka, and S. Teranishi, unpublished.

24) P. Cossee and L. L. Reigen, Proc. 2nd Int. Congr. Cat., Paris (1960).