CHEMISTRY LETTERS, pp. 241-244, 1974. Published by the Chemical Society of Japan

X-RAY PHOTOELECTRON SPECTROSCOPY STUDIES OF La_2O_3-Cr_2O_3 CATALYSTS

Yasuaki OKAMOTO, Kiyoshi ADACHI,
Toshinobu IMANAKA, and Shiichiro
TERANISHI

Department of Chemistry, Faculty
of Engineering Science, Osaka
University, Toyonaka, Osaka 560

X-ray photoelectron spectra of La_2O_3-Cr_2O_3 catalysts with different compositions were measured. On the basis of the binding energies of $Cr2P_{3/2}$ subshell, it is concluded that there exist the hexa- and tri-valent chromiums in these catalysts, and that when the content of chromia becomes larger, the content of the trivalent chromium becomes predominant.

X-ray photoelectron spectroscopy is a useful tool for the researches of solid surface, and therefore, for the studies of catalysis. Delgass and his co-workers[1) have reviewed the usefulness of the tool for catalytic research. Recently, several reports have been published for the researches of catalysts with this technique, that is, supported Mo-catalysts,[2,3) Rh on charcoal,[4) and tungsten oxide on supports.[5)

We investigated lanthanum oxide-chromia catalysts (La_2O_3-Cr_2O_3) with different compositions using X-ray photoelectron spectroscopy, and compared the results with those obtained by other techniques, i.e., IR, ESR, and X-ray diffraction analysis.

Lanthanum oxide-chromia catalysts with different compositions were prepared by the solid phase reaction of lanthanum oxide and chromia at 750°C for 3 hr in air. Both of lanthanum oxide and chromia were supplied by Nakarai Chemical Ltd. The ketonization of acetic acid on these catalysts were carried out with a conventional pulse reactor at 350°C (carrier gas: He).

Photoelectron spectra were measured on a Hitachi 507 photoelectron spectrometer using MgKα radiation. Powdered samples were mounted on a sample holder made of copper. Binding energies were corrected by using the value of 285.0 eV for C1S level resulting from the contaminated carbon. The reproducibility of the value was within ±0.2 eV.

Figure 1 shows the results obtained by X-ray diffraction analysis of La_2O_3-Cr_2O_3 catalysts with different compositions. The compounds with 2θ of 15.8° and 33.5° correspond to La_2O_3 and Cr_2O_3, respectively. From Figure 1 it is revealed that La_2O_3-Cr_2O_3 catalysts contain two new compounds, A with 2θ of 28.6° and B with 2θ of 32.6°, produced by the reactions of lanthanum oxide and chromia. The amounts of compound A and B have their maximum at 25-30 % and at 50 % chromia content, respectively. From the IR studies, it is shown that A-compound has three absorption bands at 950, 900, and 850 cm^{-1}, which are assigned to CrO_4^{--} ion, and B, a broad band at about 600 cm^{-1}, which is attributed to lattice vibration, in the low frequency region of IR spectra, and also, from the ESR investigations that the intensities of β-phase,$^{6)}$ which indicates the amount of trivalent chromium, corresponds to the amount of B-compound and A-compound is ESR inactive. Therefore, on the basis of these results, A and B compounds seem to be lanthanum chromate($La_2(CrO_4)_3$) and $LaCrO_3$, respectively.

In Figure 2, the photoelectron spectra of $Cr2P_{3/2}$ level were represented for each catalyst. It is clear from Figure 2 that two valence states of chromium are found in each catalyst, and that when the content of chromia becomes larger, the content of the lower valent chromium becomes predominant. As regard with (3:1) catalyst, the binding energy of higher valence chromium is 579.4 eV, and that of lower one is about 577.0 eV. To compare these values with other known valence state of chromium, we measured the binding energies of $Cr2P_{3/2}$ level for K_2CrO_4, $K_2Cr_2O_7$, CrO_3, Cr_2O_3, and Cr-metal, and obtained the values of 579.5, 579.3, 579.5, 576.7, and 574.1 eV, respectively. Therefore, it is concluded that the chromium with the larger binding energy is hexavalent and that with smaller one is trivalent. In the case of (1:1) catalyst, there also exists hexavalent chromium. The chromium with the $2P_{3/2}$ binding energy of 576.0 eV appears significantly in this catalyst, whose binding energy is 0.7 eV lower than that in Cr_2O_3. Taking into account the behavior of the compound B in Figure 1 and the results obtained by IR and ESR measurements, it is revealed that the lower valence chromium in (1:1) catalyst is trivalent and due to $LaCrO_3$. The trivalent chromium in (3:1) or (2:1) catalyst is, however, attributed to residual Cr_2O_3, whose existence cannot be detected by other techniques. On the basis of the binding energies of $Cr2P_{3/2}$ level for Cr_2O_3 and $LaCrO_3$, the chromium in Cr_2O_3 is more ionic than that in $LaCrO_3$. As regard with the hexavalent chromium, comparing the results obtained by other techniques with that by X-ray photoelectron spectroscopy, it can be attributed to compound A. Therefore, compound A is defined to be lanthanum chromate. The higher valent chromium in (2:1) catalyst, whose binding energy is 0.7 eV higher than that for lanthanum chromate, may be due to lanthanum chromate in different circumstances.

The changes of the O1S level in La_2O_3-Cr_2O_3 catalysts with compositions are shown in Figure 3. On the basis of the similar discussions about the valence state of chromium, the oxygens with the O1S binding energy of 528.1, 529.1, 530.4, 530.6, and 531.0 eV can be assigned to those in La_2O_3, $LaCrO_3$, Cr_2O_3, $La_2(CrO_4)_3$, and $La(OH)_3$, respectively. From the O1S spectra of La_2O_3, it is clear that the surface of La_2O_3 is considerably hydrated. In the case of (3:1) catalyst, the O1S spectra from lanthanum chromate can be expected from Figure 2. But, since the catalyst contains excess La_2O_3 and the chemical shift between the O1S binding energies of lanthanum chromate and $La(OH)_3$ is very small (0.4 eV), the O1S spectrum of lanthanum chromate is considered to be obscured by that of $La(OH)_3$. As regard with (2:1) and (1:1) catalyst, it is considered that the O1S spectrum of $La(OH)_3$ is obscured by that of lanthanum chromate in contrast with (3:1) catalyst. The ionic character of the

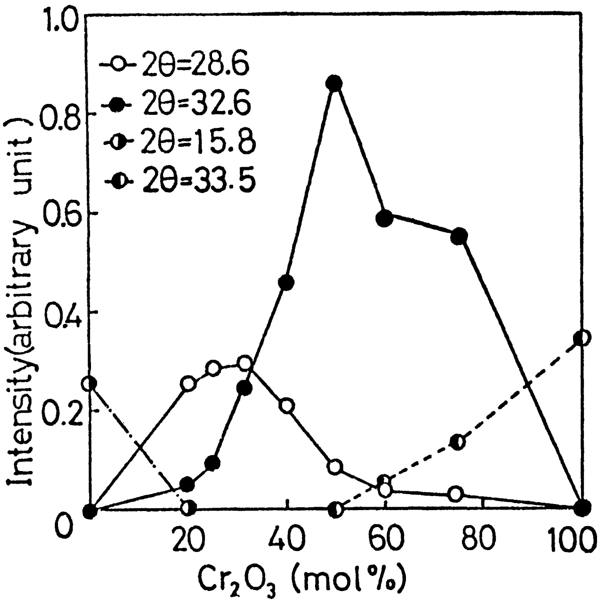

Fig. 1

Dependencies of the X-ray diffraction intensities for La_2O_3-Cr_2O_3 catalysts on the contents of chromia

◑; La_2O_3, ◐; Cr_2O_3, ○; A-compound, and ●; B-compound

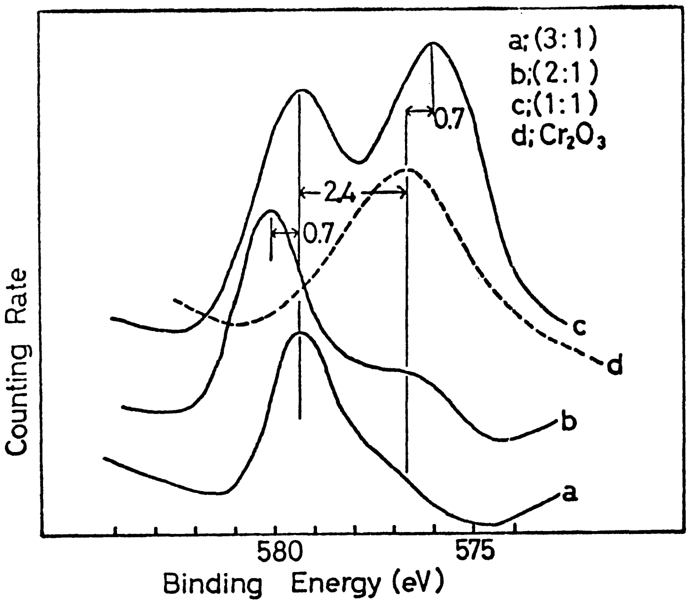

Fig. 2

Photoelectron spectra of Cr2$p_{3/2}$ subshell for La_2O_3-Cr_2O_3 catalysts
The number in parentheses; (the mole of La_2O_3: the mole of Cr_2O_3)

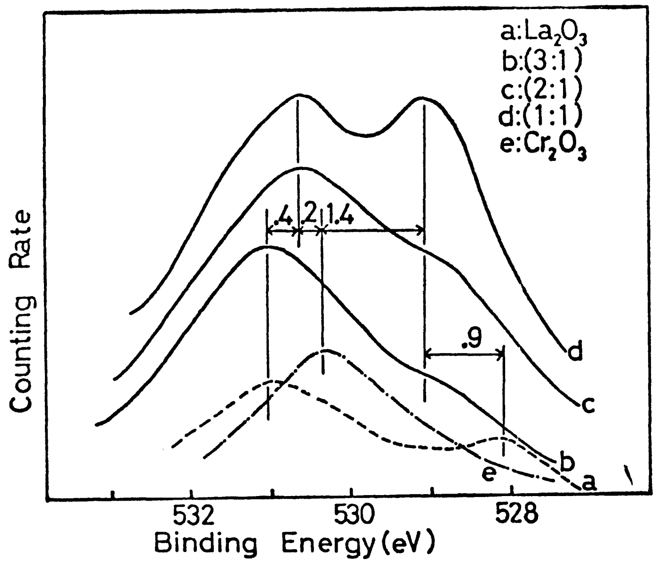

Fig. 3

Photoelectron spectra of O1S shell for La_2O_3-Cr_2O_3 catalysts
The number in parentheses; (the mole of La_2O_3: the mole of Cr_2O_3)

oxygen in these compounds decreases in the following order; La_2O_3>$LaCrO_3$>Cr_2O_3 >$La_2(CrO_4)_3$>$La(OH)_3$. On the other hand, no change was observed for these compounds according to the photoelectron spectra of $La3d_{5/2}$, La4p, and La4d shells and their respective satelites.

To compare the surface state of the catalysts obtained by X-ray photoelectron spectroscopy with the catalytic reaction, the ketonization of acetic acid on these catalysts were carried out. According to our results,7) the reaction intermediates may involve both acetic anion and acyl cation. Consequently, the bifunctional catalysts, which have both acidic and basic sites, seem to be favorable for this reaction. As La_2O_3-Cr_2O_3 catalysts contain lanthanum oxide and the compound with the hexavalent chromium, it is considered that these catalysts are bifunctional, and therefore, that they have higher activities for this reaction than the catalysts before calcination which have no significant acidic character. Actually, it is confirmed that higher activities were obtained for La_2O_3-Cr_2O_3 catalysts than those predicted for the catalysts before calcination.

Reference

1) W.N.Delgass, T.R.Hughes, and C.S.Fadley, Cat. Rev., 4, 179 (1970).
2) A.W.Miller, W.Atkinson, M.Barber, and P.Swift, J. Cat., 22, 140 (1971).
3) D.A.Whan, M.Barber, and P.Swift, Chem. Comm., 1972, 198.
4) J.S.Brinen and A.Melera, J. Phys. Chem., 76, 2525 (1972).
5) P.Biloen and T.Pott, J. Cat., 30, 169 (1973).
6) C.P.Poole and D.S.MacIver, Adv. Catalysis, 17, 224 (1967).
7) T.Imanaka, T.Tanemoto, and S.Teranishi, Proc. Intern. Congr. Catalysis, 5th, Florida 1972, No.4.

(Received November 27, 1973)