Changes in Surface Composition of a Cobalt–Molybdenum Binary Oxide Catalyst during Various Treatments Studied by *X*-Ray Photoelectron Spectroscopy

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Summary The surface composition of a Co–Mo binary oxide catalyst changes drastically during contacts with reactive gases; surface Mo enrichments were accomplished by reactions with H_2 and thiophen–H_2, while Co enrichment was attained by using H_2S–H_2.

It is well known that enrichment of one component of a binary alloy occurs when the alloy is exposed to reactive gases.[1] We have used *X*-ray photoelectron spectroscopy (XPS) to show that considerable changes occur in the surface composition of binary oxide catalyst systems when they are in contact with reactive gases.

The Co–Mo binary oxide catalyst [Co : (Co+Mo) = 0·3 : 1] was prepared by the wet mixing method using ammonium paramolybdate and cobalt(II) nitrate, followed by calcination in air at 550 °C for 5 h. XPS spectra were measured on a Hitachi 507 photoelectron spectrometer using Al-$K_{\alpha 1,2}$ radiation. All binding energies were referenced to the contaminant carbon [C(1*s*) = 285·0 eV]. The peak area intensities of Mo (3*d*), Co ($2p_{3/2}$), and S (2*p*) levels were used to obtain the Co : Mo and S : Mo intensity ratios. Catalyst treatments were carried out at 400 °C with 10 Torr of reaction gases (thiophen–H_2, H_2S–H_2, H_2, and O_2) in a pretreatment chamber. Thiophen : H_2 and H_2S : H_2 ratios were 1 : 15.

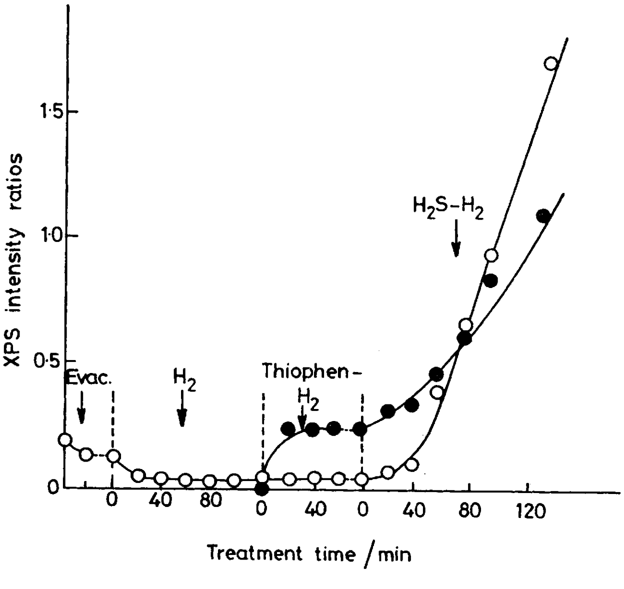

Figure. Surface composition and sulphur content of the catalyst during consecutive treatments: evacuation, H_2, thiophen–H_2, and H_2S–H_2. ○, Co : Mo; ●, S : Mo.

The Figure shows a typical run. After evacuation at 400 °C for 1 h, some Mo^{6+} [Mo ($3d_{5/2}$) = 233·2 eV] was reduced to Mo^{4+} [Mo($3d_{5/2}$) = 228·8 eV] with decreased Co:Mo intensity ratio. Further reduction of the catalyst with H_2 resulted in the formation of MoO_2 [Mo ($3d_{5/2}$) = 228·8 eV] and Co metal [Co($2p_{3/2}$) = 778·7 eV], accompanied by a further decrease in the Co:Mo intensity ratio to one-fifth of that for the calcined catalyst. When the catalyst was exposed to thiophen–H_2, there was not such a large change in the Co:Mo intensity ratio, but the sulphur content of the catalyst reached a constant value after 20 min with a chemical shift of 0·7 eV in the Mo ($3d_{5/2}$) level. The Mo ($3d_{5/2}$) binding energy (229·5 eV) and S:Mo intensity ratio agreed well with those of MoS_2, assuming that the sulphur was bonded to Mo. This was confirmed in separate experiments which showed that Co metal did not form a sulphide when treated with thiophen–H_2 under similar conditions. Following exposure to thiophen–H_2, the catalyst was brought in contact with H_2S–H_2. As shown in the Figure, the Co:Mo intensity ratio increased considerably with the increase in the sulphur content (*i.e.*, the S:Mo ratio). This indicates that surface enrichment occurs, together with the formation of sulphide species of cobalt. The Co ($2p_{3/2}$) binding energy did not change during the formation of the sulphide species, as has been reported.[2] Admission of thiophen–H_2 after evacuation at 400 °C for 1 h caused a gradual decrease in the Co:Mo intensity ratio which reached the same value after 60 min as shown in the Figure. Introduction of H_2 to a catalyst which had formed sulphide species by treatment with H_2S–H_2 resulted in a slight decrease in the Co:Mo and S:Mo intensity ratios. However, when O_2 was used, the Co:Mo and S:Mo intensity ratios decreased markedly and some Co and Mo were oxidized to form CoO [Co ($2p_{3/2}$) = 782·0 eV] and MoO_3 [Mo ($3d_{5/2}$) = 233·2 eV], respectively; an oxidized sulphur species [*S* ($2p$) = 169·5 eV] was also detected. In the case of thiophen vapour, the rate of formation of sulphide species was very slow with a gradual decrease in the Co:Mo intensity ratio.

Thus, surface Mo enrichment was accomplished by thiophen–H_2 and H_2, while surface Co enrichment was attained by H_2S–H_2. These findings are believed to be related to the fact that Mo activates hydrodesulphurization (HDS) reactions of thiophen but Co does not. Drastic changes in surface composition can also be expected in the cases of supported Co–Mo (Co–Mo–Al_2O_3) catalysts with various pretreatments; different activities for HDS reactions will therefore be expected for different pretreatments and reaction conditions, since it has been assumed that for a Co–Mo–Al_2O_3 catalyst some Mo and Co species migrate and segregate easily on to the outer surface of the catalyst to form Co–Mo binary oxides and/or sulphides during the usual HDS reaction conditions.[3]

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[1] See, for example, V. Ponec, *Catalysis Rev.*, 1975, **11**, 1.

[2] J. P. Bonnelle, J. Grimglot, and A. D'Huysser, *J. Electronic Spectroscopy Relat. Phenom.*, 1975, **7**, 151.

[3] Y. Okamoto, H. Nakano, T. Shimokawa, T. Imanaka, and S. Teranishi, *J. Catalysis*, in the press.