STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLIII, 1-2, 1998

PHYSICOCHEMICAL CHARACTERIZATION OF ALUMINA-SUPPORTED COBALT AND MOLYBDENUM MIXED OXIDES
I. TEMPERATURE-PROGRAMMED REDUCTION (TPR) AND OXIDATION (TPO) STUDIES

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ABSTRACT. Two series of Co-Mo-O/γ-Al_2O_3 catalysts having various metal loading and different Co:Mo atomic ratios were prepared by incipient wetness impregnation. The reducibility and reoxidability of reduced samples were investigated by means of TPR/TPO techniques. Three cobalt species were found: Co_3O_4, isolated Co^{3+} or Co^{2+} cations on the surface of alumina and $CoAl_2O_4$, while molybdenum forms a single species whose redox properties are influenced by the support at lower loading. The presence of molybdenum stabilises the isolated Co^{2+} and Co^{3+} species towards reduction.

INTRODUCTION

Alumina-supported cobalt and molybdenum oxides are widely used as catalysts in the hydrodesulphurisation (HDS) of crude oil [1-3], coal liquefaction [4], wastes incineration [5] or in various partial oxidation reactions of hydrocarbons [6]. In spite of their quite a long time application in industrial processes [7, 8] the nature of active sites in the Co-Mo-O/Al_2O_3 catalysts is still controversial. The literature offers very close performance data (activity, selectivity, and life length) for catalysts of very different compositions. The industrial catalysts contain generally about 5-15 % (mass) Mo and 1-5 % (mass) Co, the atomic ratio Co:Mo ranging between 0.2 and 1.0. Nahid et al. [7] found an optimum Co:Mo atomic ratio of 1.0 for their hydrotreating catalysts, while Engel et al. [8], Porter [9] and Sulimov et al. [10] found for the same test-reaction an optimum Co:Mo = 0.2. By studying the promoting effect of cobalt on the alumina-supported molybdenum oxide, Beuther et. al. [11] established an optimum ratio Co:Mo = 0.35.

In the working conditions of hydrodesulphurisation process, the Co-Mo-O/Al_2O_3 catalysts contain among other species, Al_2O_3, $CoAl_2O_4$, CoO, $CoMoO_4$ which are catalytically inactive [12]. The *in-situ* formed Co_9S_8 and MoS_2 have a weak to moderate activity. The highest activity seems to belong to MoO_3 promoted with an irreducible cobalt oxide species [12, 13]. The real nature of the active compound is yet unknown. Richardson [12] tried to elucidate it by measuring the alteration of the magnetic susceptibility before and after catalytic desulphurisation for a series of 10 % MoO_3/Al_2O_3 samples promoted with cobalt (Co:Mo were between 0.1 and 1.0). Other authors tried to correlate the catalytic properties of cobalt promoted molybdenum oxides with spectral features using FTIR [14], UV-VIS [15], Raman [13] or ESCA [16].

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Poncelet et al. [6] present the sinergetic influence of Co and other metals on the catalytic activity of molybdates in the propene partial oxidation.

Dynamic techniques as temperature-programmed desorption (TPD), reduction (TPR) and oxidation (TPO) are widely used in the investigation of oxidic species in bulk and supported catalysts. Grimblot et al. [17] studied the oxidation behaviour of prereduced Co-Mo-O/γ-Al_2O_3-catalysts by means of gravimetric methods. Arnoldy et al. [18, 19] investigated the influence of calcination parameters on the reduction behaviour of Co-Mo-O/Al_2O_3 catalysts.

The redox properties of the oxidic species are of great importance with respect to their catalytic properties in oxido-reduction reactions. The mutual influence of different metal cations yielding sensible modifications of catalytic behaviour can be also highlighted by means of TPR/TPO-features.

The present paper describes preliminary results from a study of Co-Mo-O/γ-Al_2O_3 catalysts, which was undertaken in order to ascertain the oxidic species at the surface of alumina and their redox behaviour. The influence of the total (Co+Mo)-loading and of the Co:Mo atomic ratio, on the formation of and surface distribution of reducible species is studied.

EXPERIMENTAL

Catalysts preparation

A series of Co-Mo-O/γ-Al_2O_3 catalysts with various metal loading and Co:Mo atomic ratios were prepared by coimpregnation using aqueous solutions containing the appropriate quantities of $Co(NO_3)_3.6H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ and γ-Al_2O_3 (Condea Hamburg, S_{BET} = 107 m^2/g) as powder having particle size under 200 μm. The solution was brought over the support and water was evaporated in a rotavapor at 40 Torr and room temperature. The samples were then dried at 120 °C and heated for 8 hours at 450 °C in air. The prepared catalysts together with their specific features (surface areas were measured using the BET-method by means of a Fisons-Instrument device type Sorptomatic 1900) are listed in the Table 1.

Table 1.

Characteristics of the Co-Mo-O/γ-Al_2O_3-catalysts

Catalyst	$CoO+MoO_3$ % (mass)	Co:Mo (atomic ratio)	S_{BET} (± 2 %) m^2/g	*)n_{th} considering the oxides as	
				$(CoO+MoO_3)$	or $Co_3O_4+MoO_3)$
a.	5.0	0:100	105	0.20	0.20
b.	5.0	1:100	107	0.21	0.21
c.	5.0	10:100	106	0.22	0.22
d.	5.0	100:100	107	0.19	0.17
e.	5.0	100:10	104	0.22	0.14
f.	5.0	100:1	98	0.22	0.13
g.	5.0	100:0	96	0.22	0.12
h.	1.0	10:100	104	0.04	0.04
i.	3.0	10:100	105	0.13	0.13
j.	10.0	10:100	102	0.44	0.43

*)n_{th} theoretical coverage grade of the support

Temperature-programmed reduction/oxidation

TPR/TPO experiments were made in a conventional device having a quartz U-tube reactor, a cold trap to remove the water generated in the reaction and a thermal conductivity detector (TCD) to measure the hydrogen or oxygen consumption. The temperature was measured using a NiCr-Ni thermoelement situated directly in the catalyst bed. For the TPR experiment a reducing gas containing 10 % (vol.) H_2 in N_2 at a flow rate of 30 ml/min (STP) was passed through the catalyst sample and the temperature was raised with a constant rate of 10 grd/min from 20 °C to 950 °C and then kept constant for 20 min. The reduced sample was cooled and then reoxidated with 40 ml/min (STP) oxidant gas containing 12.5 % (vol.) O_2 in He by heating with a rate of 10 grd/min from 20 °C to 600 °C then keeping it constant for 20 min. The signals of the TCD were calibrated by injecting known volumes of hydrogen or oxygen using a Valco sampling valve, while the reactor contained 100 mg inert quartz powder to avoid hydrodynamic effects.

RESULTS AND DISCUSSION

In order to understand the nature of the active component - support interaction and its role in determining the redox features of the former, low loaded (n_{th} = 4-44 %) metal oxide/alumina catalysts have been prepared. The theoretical coverage grade n_{th} was calculated by considering cobalt and molybdenum oxides as being dispersed in a monolayer on the surface of alumina with the atoms arranged in the <100> plane [20].

The mutual influence of the two metal oxides on the redox properties of the catalyst at Co:Mo ratios varying between 100:0 and 0:100 and constant (Co+Mo) loading are presented in Fig. 1 (A, B).

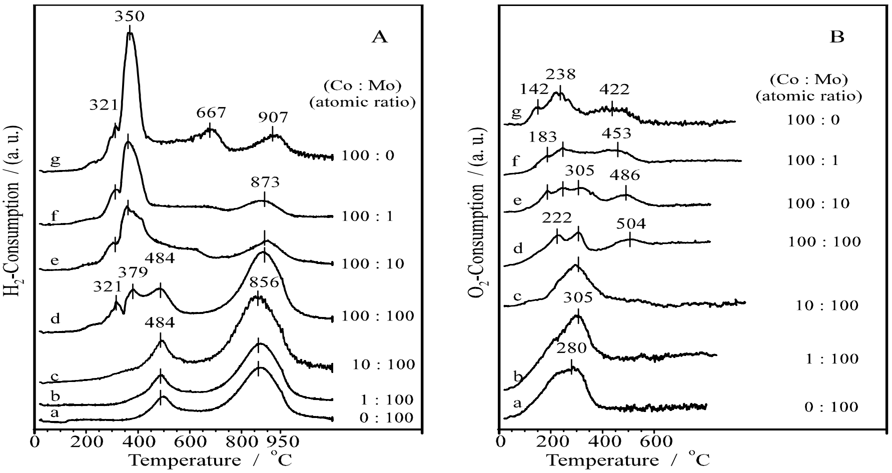

Fig. 1. The TPR (A) and TPO (B) profiles for the catalyst series containing 5 % cobalt and molybdenum oxides, with different Co:Mo atomic ratios

The reduction of alumina-supported molybdenum oxide (profile *a*, Fig. 1 A) takes place in two stages with peaks at 484 °C and 856 °C. The relative H_2 consumption of these peaks is about 1:2 which makes reasonable to assign them to a two-stage reduction of Mo^{6+} cations, first to Mo^{4+} then to Mo^0 in accordance with the reactions [18, 19]:

$$MoO_3 + H_2 \longrightarrow MoO_2 + H_2O \tag{1}$$

$$MoO_2 + 2\,H_2 \longrightarrow Mo + 2\,H_2O \qquad (2)$$

The position and relative intensity of the reduction peaks of molybdenum are not affected by addition of cobalt (Fig 1 A, curves *b* and *c*).

The reduction of alumina supported cobalt oxide (profile *g* in Fig. 1 A) shows four maximums at 290, 350, 667 and 907 °C. On the basis of previous literature data [18] these can be assigned as follows:

- to the reduction of Co_3O_4 spinel at ca. 290 °C;
- to the reduction of Co^{3+} associated with aluminium in compounds of type Co/AlO_6 or isolated Co^{3+} cations on the surface of alumina, at ca. 350 °C;
- to the reduction of surface Co^{2+} cations at ca. 667 °C;
- to the reduction of Co^{2+} incorporated as $CoAl_2O_4$ spinel, at ca. 907 °C.

The different preparation and TPR-experiments conditions [21] could explain the slight differences between the reduction profiles in this paper and those of Arnoldy et al. [18]. The lower calcination temperature employed in the preparation of present catalysts in comparison to those cited restricted the formation of Co_3O_4 and $CoAl_2O_4$ spinels.

The addition of small quantities of molybdenum did not influence the reduction of spinelic cobalt cations and isolated Co^{3+}, but it suppressed the further reduction of the later (isolated Co^{2+} cations), as shown by the disappearance of the reduction peak at 667 °C even at a very high Co:Mo ratio of 100:1 (curve *f* in Fig. 1 A). At higher molybdenum contents (curves *d*, *e* in Fig. 1 A) the first stage of reduction of isolated cobalt ions (Co^{3+} to Co^{2+}, peak at 350 °C) is also hindered.

The TPR/TPO profiles of the catalysts containing 1.0, 3.0, 5.0 and 10.0 % active component considered as $CoO+MoO_3$ (atomic ratio Co:Mo = 10:100) are presented in Fig. 2 A, B.

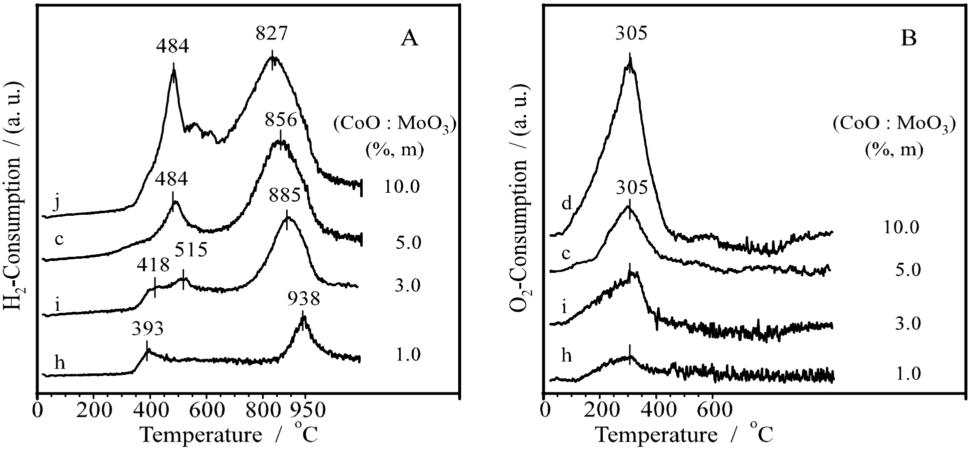

Fig. 2. The TPR (A) and TPO (B) profiles for the Co-Mo-O/γ-Al_2O_3 catalysts having different loading, at a constant Co:Mo atomic ratio of 10:100.

As the active components loading increased from 1 to 3 and 5 %, the first molybdenum reduction peak at 393 °C shifted to higher temperatures (418 and 484°C, respectively) while another increase to 10 % active component brought no other change of this peak. The second reduction maximum of molybdenum shifted towards lower temperatures (from 938 to 827 °C) as the loading increased. The first effect can be assigned to a higher reactivity of oxygen anions bounded to isolated Mo^{6+} cations at lower loading [19] and the second, to the change of coordination number of Mo^{4+} cations from 4 to 8 which hinders their reduction [14]. The higher coordination number is promoted by the presence of OH groups of alumina support around the Mo^{4+} cation therefore it occurs most probably at lower loading where molybdenum is highly dispersed. At higher loading the influence of the support diminishes and the second reduction stage takes place at lower temperatures. The reduction of spinelic cobalt ions can be seen as a shoulder on the left side of the first molybdenum reduction peak (Co_3O_4 species) and another one on the right side of the second peak ($CoAl_2O_4$ species). The reduction of isolated cobalt ions does not appear, being hindered by the presence of molybdenum as shown before. An interesting reduction feature appears at the 10 % catalyst (considered as $CoO+MoO_3$) on the temperature range of about 550-650 °C. As it didn't show at any other catalysts with lower loading, or in the TPR-profiles of single cobalt or molybdenum oxides, we assign it to a binary Co-Mo-O oxide of type cobalt molybdate which can form only at sufficiently high cobalt and molybdenum loading. Such oxides are common active catalysts in the partial oxidation of alchenes [6, 22] and are supposed to be the active phases for the HDS activity [23].

The reoxidation profiles of samples containing mainly molybdenum is shown in Fig. 1 B (curves *a*, *b*, *c*) and consist of a single broad peak at 280 °C which shifts weakly towards higher temperature (305 °C) in the presence of cobalt. The reduced alumina-supported cobalt sample (profile *g* in Fig. 1 B) shows on the contrary several oxidation maxima at 142, 238 and 422 °C, most likely due to the presence of different cobalt species on the surface. The addition of even small quantities of molybdenum suppresses the first oxidation peak at 142 °C, which makes possible to assign it to the isolated cobalt ions, which were not reduced in the presence of molybdenum.

CONCLUSIONS

The investigation of reduction-oxidation features of the $Co-Mo-O/\gamma-Al_2O_3$ catalysts by means of the TPR/TPO technique leads to the following conclusions:

(1) Molybdenum oxide shows a very good dispersion on the surface of alumina. The interaction support-active component is strong at low loading and diminishes at higher molybdenum contents. The oxygen atoms bound on Mo^{6+} isolated cations are more active, yet these cations are more stable towards total reduction due to the influence of the support.

(2) The presence of cobalt does not influence the redox properties of molybdenum.

(3) Cobalt oxide deposited on the surface of alumina forms several species: Co_3O_4, dispersed Co^{3+} or Co^{2+} cations and $CoAl_2O_4$. Oxygen atoms bound on Co^{3+} in Co_3O_4 or isolated Co^{3+} are more reactive as those bound on Mo^{6+}.

(4) The presence of molybdenum stabilises isolated Co^{2+} ions and, in higher quantities, even isolated Co^{3+}, towards reduction.

ACKNOWLEDGEMENTS. The authors express their gratitude to Mr. Prof. D. Hönicke (Technische Universität Chemnitz) for supporting this research and Mr. Dipl. Chem. H. Eisenhuth for experimental contributions.

REFERENCES

1. R. Iwamoto, K. Inamura, T. Nozaki, A. Lino, *Appl. Catal. A-Gen.,* ***163(1-2)*** (1997) 217.
2. K. Hiroshima, T. Mochizuki, T. Honma, T. Shimizu, M. Yamada, *Appl. Surf. Sci.,* ***121*** (1997) 433.
3. P. Grange, X. Vanhaeren, *Catal. Today,* ***36(4)*** (1997) 375.
4. J. A. Legarreta, B. M. Caballero, I. Demarco, M. J. Chomon, P. M. Uria, *Fuel,* ***76(13)*** (1997) 1309.
5. M. J. Gordon, S. Gaur, S. Kelkar, R. M. Baldwin, *Catal. Today,* ***28(4)*** (1996), 305.
6. H. Poncelet, J.M.M. Millet, G. Coudurier and J.C. Védrine in: *ACS Symp. Ser*., vol. 523, New York 1993, p. 262.
7. P.G. Nahin and H.C. Huffman, US Patent 2,510,189 (June 06,1950).
8. W. F. Engel and H. Hoog, US Patent 2,697,683 (December 21, 1954).
9. F.W.B. Porter, *J. Inst. Petrol.*, ***41***, (1954) 18.
10. A.D. Sulimov, M.V. Lobeev, I.N. Kozhina, A.E. Al'tshnler, A.B. Gutman and V.M. Satyogov, *Khim. Sera-Org. Soedinenii Soderzhasheh. v. Naft. i Nefteprodukt., Akad. Nauk SSSR Bashkir. Filial., Materialy Vtoroi Sessii,* 1956, 135; CA ***53***, 1958, 10720a.
11. H. Beuther, R.A. Flinn and J.B. McKinley, *Ind. Eng. Chem.,* ***51***, (1959) 1349.
12. J.T. Richardson, *Ind. Eng. Chem. -Fundamentals,* ***3(2)***, (1964) 154.
13. P.L. Villa, F. Trifiró and I. Pasquon, *React. Kin. Catal. Lett.,* ***1(3)***, (1974) 341.
14. T. Fransen, O van der Meer and P. Mars, *J. Catal.,* ***42***, (1976) 79.
15. N.P. Martinez, P.C.H. Mitchell and P. Chiplunker, in *"Proc. of the Climax 2nd Int. Conf.on the Chemistry and Use of Molybdenum",* Climax Molybdenum Ltd., London 1977, p. 164.
16. T.A. Patterson, J.C. Carver, D.E. Leyden and D.M. Hercules, *Spectr. Lett.,* ***9(1)***, (1976) 65.
17. J. Grimblot, A. D'Huysser, J.P. Bonnelle and J.-P. Beaufils, *J. Electron Spectrosc. Relat. Phenom.,* ***6(1)***, (1975) 71.
18. P. Arnoldy, M.C. Franken, B. Scheffer and J.A. Moulijn, *J. Catal.,* ***96***, (1985) 381.
19. P. Arnoldy and J.A. Moulijn, *J. Catal.,* ***93***, (1985) 38.
20. H. Eisenhuth, *Seminararbeit*, Technische Universität Chemnitz, 1995.
21. D.E.M. Monti and A. Baiker, *J. Catal.*, ***83***, (1983) 323.
22. O. Lezla, E. Bordes, P. Courtine, G. Hecquet, *J. Catal.,* ***170(2)*** (1997) 346.
23. R. G. Leliveld, A. J. Vandillen, J. W. Geus, D. C. Koningsberger, *J. Catal.,* ***171(1)*** (1997) 115.