ELSEVIER

Thermochimica Acta 379 (2001) 1–5

thermochimica
acta

www.elsevier.com/locate/tca

Characterisation of thermal properties of oxide, reduced and sulphided forms of alumina supported Co(Ni)–Mo(W) catalysts prepared by co-precipitation

Zenon Sarbak

Wydzia Chemii, Uniwersytet im. Adama Mickiewicza, ul. Grunwaldzka 6, 60-780 Poznañ, Poland

Abstract

This study deals with alumina supported Co(Ni)–Mo(W) catalysts prepared in one step by the co-precipitation method. Results of temperature-programmed reduction (TPR) of oxide forms of the catalysts, and differential thermal analysis (DTA) and thermal gravimetry (TG) of the oxide, reduced and simultaneously reduced and sulphided forms of the catalysts are presented. Reduction of the catalysts has been found to begin already at about 150°C. It has been established that at 400°C the CoMo catalyst practically does not reveal any mass loss after 30 min reduction with hydrogen, while the NiMo catalyst shows a large mass loss after 60 min reduction, continuing with time. The catalyst NiW also shows a significant mass loss already after 10 min reduction with hydrogen, and this mass loss continues to occur as the time of reduction increases. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrotreating catalysts; Thermal properties

1. Introduction

Catalytic hydrotreating is one of the main process in the petrochemical industry, playing an important role in refining products used as raw materials in other processes, e.g. hydrocracking, cracking or reforming. Hydrotreating aims at removing, sulphur, nitrogen, oxygen and metal atoms. The catalysts most often used in removal of the above elements are CoMo, NiMo and NiW catalysts supported on alumina. The technological significance of these catalysts has stimulated much research into their structure and the nature of active sites [1–4].

The catalysts studied in this work have been obtained by a procedure different from that currently applied for preparation of catalysts for hydrotreating. The procedure applied in this study is based on co-precipitation, which means that the solutions containing the catalysts components are simultaneously introduced onto the support. The application of this one-step procedure simplifies the method of obtaining the catalysts and can lead to the appearance of surface groups other than those forming on the catalysts obtained in a standard two-step procedure based on incipient wetness method. The methods used in this study for identification of surface species forming in the catalysts studied are differential thermal analysis (DTA), thermal gravimetry, temperature-programmed reduction (TPR).

2. Experimental

2.1. Catalysts preparation

The oxide form of the catalysts denoted as O-Co(Ni)Mo(W)/Al_2O_3 was prepared by one-step co-precipitation of γ-Al_2O_3 (190 m^2/g, 200 mesh).

E-mail address: depchem@amu.edu.pl (Z. Sarbak).

0040-6031/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(01)00567-6

Aqueous solutions of ammonium heptamolybdate or metatungstate and cobalt or nickel nitrate were prepared at a concentration desired and maintained at 70°C and only then were simultaneously added dropwise to a flask containing the support, under stirring. The impregnation was performed at pH 4.0. A slight excess of the solution was used to provide a uniform coating of the alumina surface The mass obtained was dried at 120°C for 16 h, and then, to remove the rest of ammonium nitrate, the temperature was raised to 280°C. Then the sample was moved to a tubular furnace and treated with oxygen passed over the surface of the sample at a flow rate of 30 cm^3/min. Calculation of the catalyst was carried out at 500°C for 6 h.

The oxide samples were activated with hydrogen according to the following procedure. The sample was placed in a glass tube of 2.5 cm diameter, then it was heated to 400°C in the nitrogen atmosphere for 1 h after the temperature stabilised. The process of reduction was initiated by passing hydrogen at a flow rate of 100 cm^3/min through the catalyst bed for 2 h. The reduced form of catalysts were labelled as H-Co(Ni)-Mo(W)/Al_2O_3.

A simultaneous reduction and sulphidation was carried out likewise, with the only difference that, instead of hydrogen, a mixture of gases containing 10 vol.% of H_2S in H_2 was used. The latter samples were labelled as S-Co(Ni)Mo(W)/Al_2O_3.

2.2. *Determination of textural parameters*

Low temperature (−196°C) nitrogen adsorption measurements were carried out with Sartorius microbalance. Prior to the measurement the samples were outguessed at 250°C in vacuum of 10^{-6} Torr. Pore radius and volume were calculated by the method of Cranston–Inkley [5] and the surface area by the BET method.

2.3. *Differential thermal analysis (DTA) and Thermal gravimetry (TG)*

Thermal studies were performed on an OD-102 apparatus (Hungary). The samples were transferred to a ceramic crucible under nitrogen flow and then heated to 1000°C at a rate of 10°C/min in the nitrogen atmosphere.

2.4. *Temperature-programmed reduction (TPR)*

Measurements were performed by the weight method, using an instrument made by Sartorius (Grawimat type 4303). Dried and purified helium was passed through a sample of about 60 mg at the flow rate of 50 cm^3/min at 20°C, until stable weight was obtained. Then the sample was reduced in the atmosphere of the 10% mixture of H_2 in helium passed at the rate of 50 ml/min, for 1 h, then the temperature was increased to 400°C and maintained for 3 h.

3. Results and discussion

Table 1 presents the composition of the oxide forms of the catalysts studied and gives a characteristics of the texture of the oxide forms, hydrogen-reduced forms and the forms simultaneously reduced and sulphided. The surface area of the oxide form of

Table 1
The composition of catalysts and textural properties

Catalyst	Catalyst components (wt.%)				Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore radius (nm)
	CoO	NiO	MoO_3	WO_3			
O-CoMo/Al_2O_3	2.7	–	12.2	–	183	0.33	48.0
H-CoMo/Al_2O_3					161	0.29	43.0
S-CoMo/Al_2O_3					160	0.28	42.1
O-NiMo/Al_2O_3	–	3.5	18.0	–	159	0.25	41.6
H-NiMo/Al_2O_3					147	0.25	42.2
S-NiMo/Al_2O_3					133	0.24	34.2
O-NiW/Al_2O_3	–	5.1	–	22.0	238	0.37	38.8
H-NiW/Al_2O_3					205	0.48	34.2
S-NiW/Al_2O_3					210	0.34	35.3

$CoMo/Al_2O_3$ is somewhat lower than that of the support. For the oxide form of $NiMo/Al_2O_3$, this surface area decrease reaches 16%, while for the oxide form of NiW/Al_2O_3 sample it gets as high as 25%. As follows from the data, the surface area of the samples is slightly decreased as a result of the reduction and the simultaneous reduction and sulphidation. Also no significant changes in the pore volume are observed. Estimation of the mean pore radius and surface area indicates that the samples contain meso- and macropores. On the reduction as well as on the simultaneous reduction and sulphidation the mean pore radius is slightly decreased in the samples $CoMo/Al_2O_3$ and NiW/Al_2O_3, whereas in the sample $NiMo/Al_2O_3$ on the simultaneous reduction and sulphidation (H_2S in H_2) the mean pore radius is decreased by about 18%. This decrease in the mean pore radius is accompanied by a quantitatively similar reduction of the surface area.

Processes of the reduction and the simultaneous reduction and sulphidation of the oxide forms of the catalysts studied have a notable influence on their thermal properties. All forms of the catalysts in the low temperature range (up to 200°C) show endothermic effects (Fig. 1) related to dehydration, followed by exothermic effects. A change from the endo-to exothermic effect is rapid and no transition range can be distinguished. The exothermic effects show a maximum in the range 400–470°C and these effects observed for the oxide forms are related to small mass loss (Fig. 2b). The other thermal effects taking place in the oxide forms in range 750–800°C are accompanied by relatively large mass loss, which is significantly reflected in the DTG and TG curves (Fig. 2a and b).

Similar thermal effects have been observed in the reduced forms $Co(Ni)$-$Mo(W)/Al_2O_3$ catalysts. However, both the endothermic effects related to dehydration and the exothermic effects with maxima in the range 400–450°C are smaller than those for the oxide forms of the catalysts (Fig. 1). In temperatures above 800°C comparatively larger mass loss is observed mainly for CoMo and NiW catalysts (Fig. 2b).

For the samples subjected to the simultaneous reduction and sulphidation, the endothermic effect related to dehydration is small, and its minimum occurs at 100°C for $CoMo/Al_2O_3$ and NiW/Al_2O_3, while for $NiMo/Al_2O_3$ at 170°C (Fig. 1). As seen from the course of the DTG curves (Fig. 2a), the observed effects are two: one taking place in the range 120–150°C, while the other at 325°C for the sample $NiMo/Al_2O_3$ (Fig. 2a) and at about 400°C for the two other samples (Fig. 2a and c). As seen from the above data, sulphidation leads to formation of new groups on the catalysts surface, which then undergo decomposition in temperatures higher than that of dehydration. This second effect can be related to the process of exchange of the oxide ions from the molybdate and tungstate

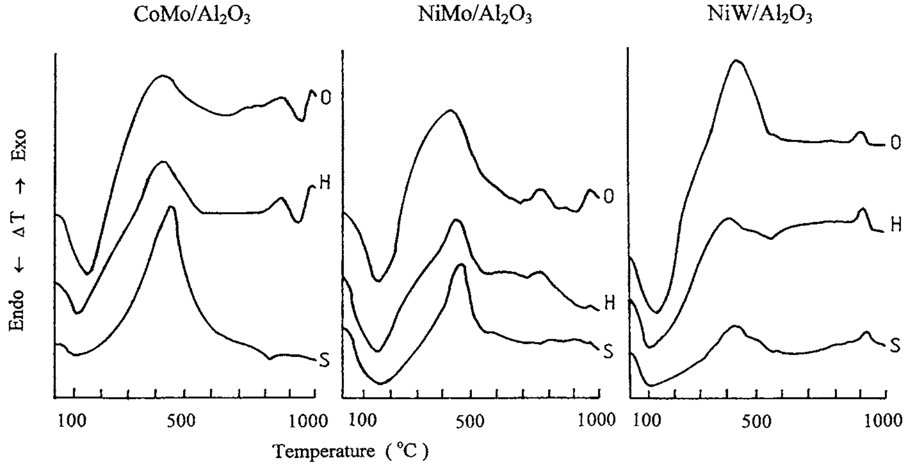


Fig. 1. DTA of oxide (O), reduced (H) and simultaneously reduced and sulphided (S) forms of $Co(Ni)$–$Mo(W)/Al_2O_3$ catalysts.

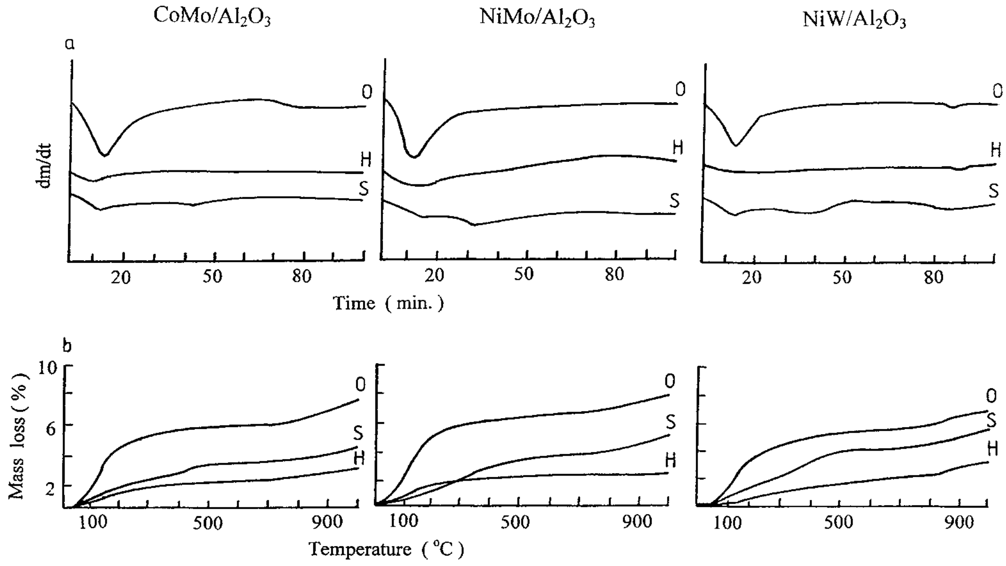
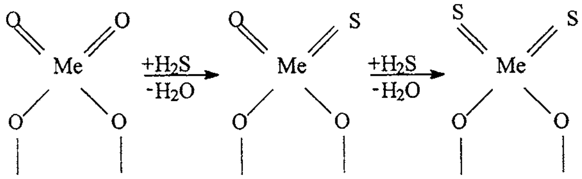


Fig. 2. Mass loss of oxide (O), reduced (H) and simultaneously reduced and sulphided (S) forms of Co(Ni)Mo(W)/Al_2O_3 catalysts.

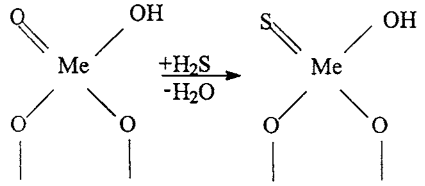
surface species into the sulphide ions, and to desorption of the water molecules formed in the processes, according to the Schemes 1 and 2 in which Me stands for Mo or W.

These processes are followed by dehydroxylation of the product of sulphidation formed according to Scheme 3.

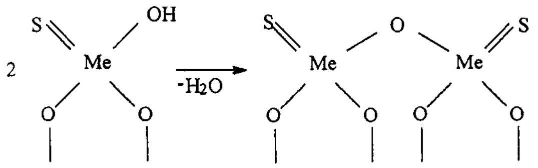
Fig. 2b present the mass loss versus temperature. The course of the curves indicates that the greatest mass loss upon heating occurs for the oxide forms, while the smallest for the reduced forms. For the samples, simultaneously subjected to reduction and sulphiding the mass loss takes an intermediate value. This fact means that the reduction of the oxide forms may involve dehydroxylation besides metal reduction and dimeric species can be obtained according to Scheme 4.



Scheme 1.

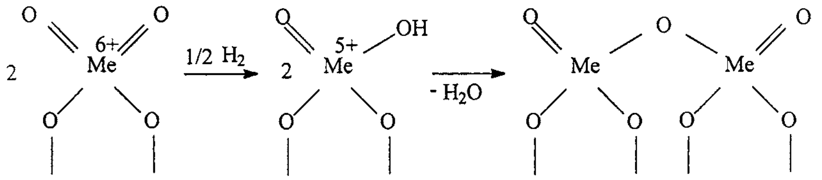


Scheme 2.



Scheme 3.

According to the results of the detailed temperature studies in the programmed reduction of the samples Co(Ni)–Mo(W)/Al_2O_3, with increasing temperature the mass loss increases. The dependence presented in Fig. 3 implies that the reduction of the samples begins at 150°C and at 400°C the process is not completed yet. Analysis of the sample reduced at 400°C (Fig. 4) has shown that already after 10 min the NiW/Al_2O_3 catalyst was almost completely reduced, but a small increase in the mass loss is observed with time of reduction. The complete



Scheme 4.

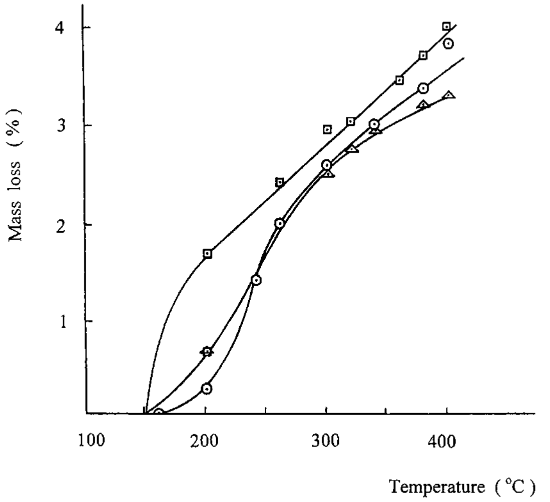


Fig. 3. Relationship between mass loss and reduction temperature of oxide forms of catalysts: (○) CoMo/Al_2O_3; (△) NiMo/Al_2O_3 and (□) NiW/Al_2O_3.

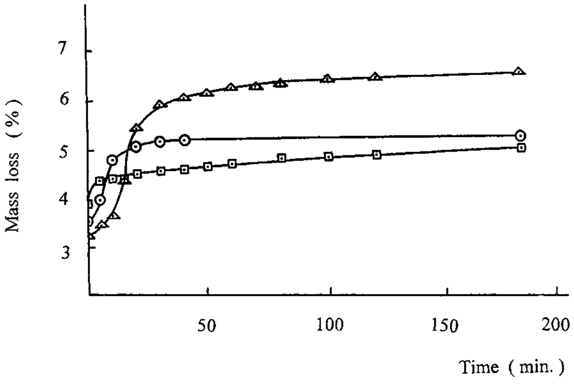


Fig. 4. Mass loss as a function of reduction time of oxide forms of catalysts: (○) CoMo/Al_2O_3; (△) NiMo/Al_2O_3 and (□) NiW/Al_2O_3.

reduction of the catalyst CoMo/Al_2O_3 took place after about 30 min. However, for the catalyst NiMo/Al_2O_3 the time needed for significant reduction is about 1 h and then reduction is continued slowly with time.

4. Conclusions

As seen from the above discussed results, the application of a one-step procedure based on co-precipitation leads to the catalysts containing both meso- and macro-pores. On the surface of such catalysts the appearance of surface groups easily undergoing reduction has been established, since the reduction begins already at a temperature about 150°C. At 400°C, the catalysts NiMo show large mass loss up to 60 min of reduction and then is continued with time, while the catalyst CoMo does not show mass loss after 30 min of reduction. The catalyst NiW shows a large mass loss already after 10 min of reduction, but the reduction does not stop and the mass loss continuously increases with time.

References

[1] B.C. Gates, J.R. Katzer, G.C.A. Schuit, Chemistry of Catalytic Processes, McGraw-Hill, New York, 1979.

[2] T. Weber, R. Prins, R.A.V. Santen (Eds.), Transition Metal Sulphides, Kluwer Academic Publishers, Dordrecht, 1998.

[3] H. Topsøe, B.C. Clausen, F.E. Masoth, Hydrotreating Catalysis, Springer, Berlin, 1996.

[4] T. Kabe, A. Ishihara, W. Qian, Hydrodesulphurisation and Hydrodenitrogenation — Chemistry and Engineering, Kodansha, Tokyo, 1999.

[5] R.W. Cranston, F.A. Inkley, Adv. Catal. 9 (1957) 143.