Adsorption, Catalysis

THERMOANALYTICAL CHARACTERIZATION OF MOLYBDENUM-BASED CATALYTIC MATERIALS

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Abstract

Thermoanalytical techniques, especially temperature-programmed reduction (TPR), were employed for the characterization of oxidic precursors of molybdenum-based catalysts, sulfides derived from them, and three thiomolybdate compounds, employed as models or precursors of hydrodesulfurization atalysts. Correlations were found between TPR data and the presence of single and mixed oxides of Mo and Ni, Co or Fe, as demonstrated by XRD. The same phases and the thiomolybdates were shown to be present in supported catalytic precursors. Differences between the reducibilities of the mixed oxides of Ni–Mo, Co–Mo and Fe–Mo are easily appreciated from TPR, including those of the α- and β- polymorphic modifications of $NiMoO_4$.

Keywords: Co–Mo, Fe–Mo, Mo-based catalysts, Ni–Mo, thiomolybdates; TPR-XRD

Introduction

Catalyst characterization is an important aspect of research in catalysis that allows to rationalize catalytic behavior in terms of the physicochemical peculiarities of the catalysts. In this context thermal analysis techniques play a central role, as both the activation of catalysts and the catalytic reactions themselves are, in general, strongly dependent on temperature. The thermal techniques most commonly employed in catalysis involve linear temperature programmed (TP) regimes – i.e., constant heating rates – while simultaneously physical or chemical events related to transformations of the catalyst are monitored. Examples include the classical TG/DTG (weight changes); DTA/DSC (heat evolution); the more specialized TPD (desorption of adsorbates); TPR, TPO, TPS (reduction, oxidation, sulfiding of catalysts); TPSR (surface reactions), etc [1].

The objective of the present work is to illustrate the usefulness of thermal analysis tecnhiques, particularly TPR, in the study of several materials based on molybdenum, of interest as models or precursors of hydrodesulfurization catalysts.

Experimental

Materials

Unsupported mixed oxides were prepared by coprecipitation from solutions of ammonium heptamolybdate (AHM) and nitrates of nickel (NN) or cobalt (CN) or ferrous ammonium sulfate. The preparation method of the NiMo series was devised by Pratt *et al.* [2], while the synthesis of the stoichiometric α- and β-NiMoO₄, was reported elsewhere [3]. Supported oxidic catalysts were prepared by impregnation of commercial silica gel (Merck) or alumina (Filtrol) with solutions of AHM and NN or CN, followed by drying and calcination [4, 5]. Sulfiding was accomplished by heating the samples to 400°C under inert atmosphere before flowing pure H_2S for 1 h. The thiomolybdate complexes were synthesized by established methods [6] and employed either pure or impregnated from N,N-dimethyl formamide solutions onto alumina or activated carbon (Merck).

Instrumentation

X-ray powder diffraction (XRD) was measured with a Philips PW 1730 instrument, employing Ni filtered CuK_α radiation. Temperature-programmed reduction (TPR) experiments were performed either with a home made apparatus [7] or with a Micromeritics TPD/TPR 2900 unit. Experimental conditions were as described earlier [3–7].

Results and discussion

It has been shown earlier [7] that the presence and size of TPR peaks in a series of NiMo oxides can be correlated with structural XRD data. When the atomic ratio $r=Ni/(Ni+Mo)$ increased from 0 (MoO_3) to 0.5 ($NiMoO_4$) both the XRD (Fig. 1A) and TPR (Fig. 1B) signals due to the former compound decreased while those due to α-NiMoO₄, increased. From $r>0.55$ to $r=1$ only NiO could be detected by XRD (Fig. 1A), Mo being homogeneously distributed in the NiO phase, as shown by analytical electron microscopy [2]. In agreement with this, a main TPR peak is observed for all compositions in this range, at nearly the same temperature as pure NiO (Fig. 1B and C); only a very small additional signal is evident at the higher Mo contents [7].

More recently it has been found that the two normal pressure polymorphic modifications of NiMoO₄, namely α- and β-phases, are easily differentiated by TPR [3]: The low temperature α-phase (Mo in octahedral environment) is easier to reduce than (β-NiMoO₄ (Mo in tetrahedral symmetry) (Fig. 2A, B). However, in the case of the two similar polymorphs of both CoMoO₄ and FeMoO₄ (Fig. 2C, D, and E, F, respectively) the patterns are essentially the same except for minor differences in the shapes of some peaks, notably the lower temperature one in CoMoO₄. The explanation of these results is that the α to β transition in both these compounds occurs at lower temperatures than the onset of the reduction [8]. However, it is evident that the three divalent molybdates can be easily differentiated by TPR
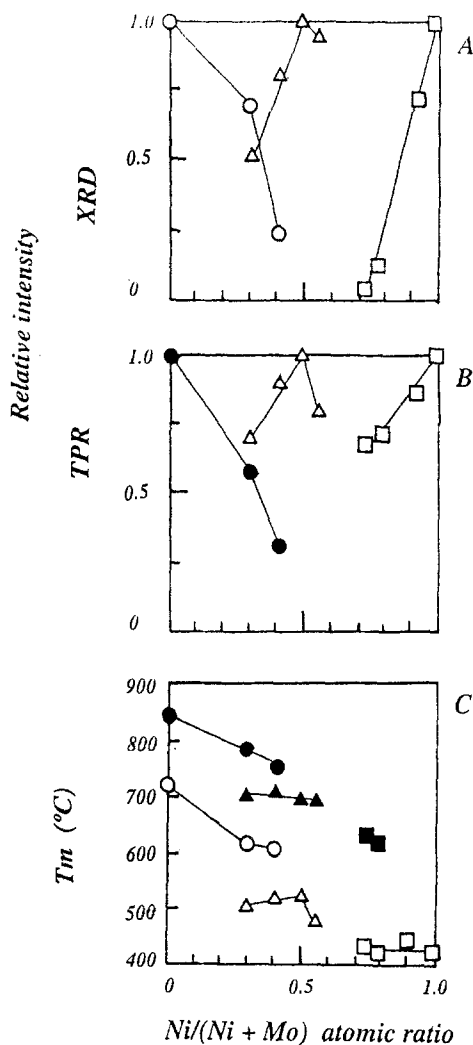
Fig. 1 Variation -in function of the atomic ratio r =Ni/(Ni+Mo) of: A) relative intensity of the main XRD peak; B) relative intensity of TPR signal; C) T_m (temperature at the maxima) of TPR signal of compounds detected in the NiMo mixed oxide series. Circles, MoO_3; triangles, α-$NiMoO_4$; squares, NiO; in B and C, open symbols refer to low T_m peaks and filled symbols to high T_m signals

by both the distinct shapes of the patterns and temperatures of the TPR signals. The Fe(III) molybdate compound also exhibits a distinct TPR pattern from $FeMoO_4$, showing a low temperature (~650°C) complex signal due to the reduction of $Fe_2(MoO_4)_3$ to β-$FeMoO_4$ [9].

TPR also shows differences between the two polymorphs α- and β-$NiMoO_4$ after sulfiding. These differences are qualitatively similar to those observed for the
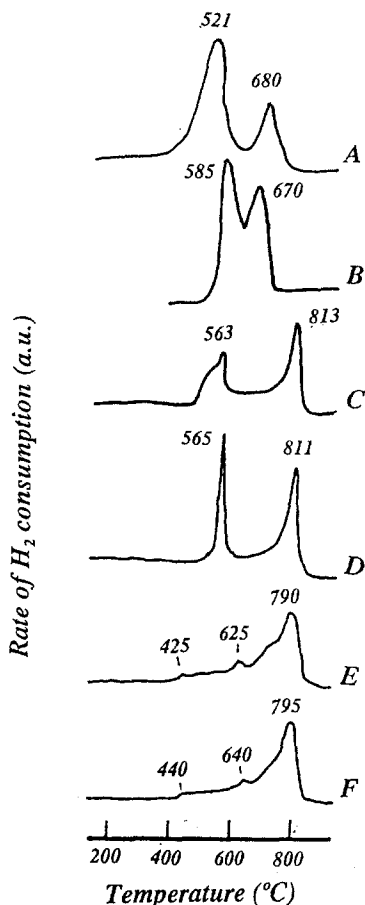
Fig. 2 PR profiles of: A) α-NiMoO$_4$; B) β-NiMoO$_4$; C) α-CoMoO$_4$; D) β-CoMoO$_4$;
E) α-FeMoO$_4$; F) β-FeMoO$_4$

oxides, i.e., the β- phase is more difficult to reduce than the sulfided α- polymorph (350 *vs.* 333°C, respecitively [3]). The reason for this is not clear as, being the sulfides completely amorphous and intensely dark colored or black solids, there are not many techniques which could be employed to gather structural information. Currently, we are starting an EXAFS study with the sulfided polymorphs of the NiMoO$_4$ compound, aiming at explaining both the differences in reducibility and the higher HDS catalytic activity of the β-NiMoO$_4$ phase. In the future, it will also be attempted to detect its presence in industrial-type supported catalysts.

Supported Mo/Al$_2$O$_3$ and Mo/SiO$_2$ catalysts of compositions close to that of the industrial HDS catalysts (~8–10% Mo) present no XRD signals due to MoO$_3$ (except when calcined at high temperatures, see below) [4, 5]. Other characterization techniques, notably the vibrational spectroscopies (IR and Raman), suggest that the surface Mo compounds consist primarily of polymolybdate-like phases (10, 11).
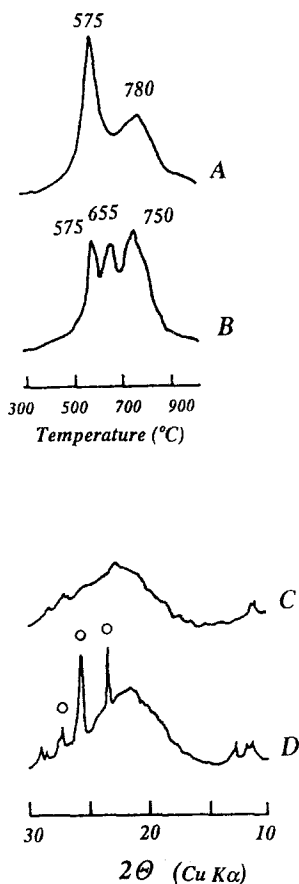
Fig. 3 TPR and XRD profiles of Mo/SiO₂ catalysts. A, B) TPR; C, D) XRD. Catalysts cal-
cined at: A and C 500°C; B and D 600°C

The TPR patterns of either catalyst are very distinctive, and show no resemblance
to that of bulk MoO_3. In particular, although generally there exist two well differ-
entiated peaks, the ratio of the sizes of the low to the high temperature signals is
rather different to the 1:2 value that characterizes the $Mo^{6+} > Mo^{4+} > Mo^0$ process
in crystalline MoO_3 [7].

When the Mo/SiO₂ catalyst is calcined at 500°C or lower temperatures, the typi-
cal two peaks TPR profile is observed (Fig. 3A) which has been reported by several
workers [4 and references therein]. However, after calcination at 600°C, a third ad-
ditional peak appears at an intermediate temperature, while the high temperature
signal increases in size (Fig. 3B). The positions of both these new or modified sig-
nals are close to those of bulk MoO_3 diluted in a matrix of other oxides, as in
Fig. 1C for r ~0.4. In agreement with all of this, the XRD trace clearly shows the
presence of crystalline MoO_3 in the sample calcined at 600°C (compare Fig. 3C

and D). Thus, again the TPR results correlate fairly well with the structural infonnation derived from XRD and other techniques.

The sulfided supported catalysts are rather ill understood. The results of TPR indicate than upon sulfiding supported catalysts, the temperatures of the observed peaks are lower than those of the precursor oxides, in a similar way to what was noted above for the unsupported molybdates. This suggests that the sulfides, in general, are better activating the H_2 molecule than the oxides.

Three thiomolybdate complexes of formulas $(NH_4)_2MoS_4$, $(NH_4)_2Mo_2S_{12}$ and $(NH_4)_2Mo_3S_{13}$ (monomer, dimer and trimer, respectively) were studied by TG/DTG in both inert and H_2 atmospheres and by TPR [12]. The TPR traces were characteristic for each compound and were interpreted, along with the gravimetric data, in terms of the differences in structure between the three crystalline compounds. When supported on Al_2O_3 the general differences in the temperatures of reduction are maintained. However, after supporting onto activated carbon (and particularly in the presence of a promotor such as Ni) the resulting catalysts are nearly indistinguishable. This behavior is interpreted assuming that the complexes retain their structures after breing supported on Al_2O_3 (although they are no longer detectable by XRD suggesting microcrystallinity), but react with the activated carbon surface, producing a similar surface phase independent of the complex employed in the preparation.

In conclusion, the present results show the usefulness of TPR in the identification of crystalline and microcrystalline compounds present in molybdenum-based catalysts, which was especially easy to demonstrate in the case of the oxidic samples. Further work is required to complement the results obtained in the case of the amorphous and the supported sulfided samples.

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References

1 S. Bhatia, J. Beltramini and D. D. Do, Catal. Today, 7 (1990) 309.
2 J. V. Sanders and K. C. Pratt, J. Catal., 67 (1981) 331.
3 J. L. Brito, A. L. Barbosa, A. Albornoz, F. Severino and J. Laine, Catal. Lett., 26 (1994) 329.
4 J. Laine, J. L. Brito and F. Severino, J. Catal. 131 (1991) 385.
5 J. L. Brito and J. Laine, J. Catal., 139 (1993) 540.
6 J. L. Brito, M. Ilija and P. Hernández, Thermochim. Acta, 256 (1995) 325.
7 J. L. Brito, J. Laine and K. C. Pratt, J. Mater. Sci., 24 (1989) 425.
8 J. Haber and J. Janas, in Proc. 25th Int. Meet. Soc. Chim. Phys., Reaction Kinetics in Heterogeneous Chemical Systems (P. Barret, ed.). Elsevier, Amsterdam, 1975. pp. 737–744.
9 H. Zhang, J. Shen and X. Ge, J. Solid State Chem., 117 (1995) 127.
10 S. R. Seyedmonir, S. Abdo and R. F. Howe, J. Phys. Chem., 86 (1982) 1233.
11 H. Jeziorowsky and H. Knözinger, J. Phys. Chem., 83 (1979) 1166.
12 J. L. Brito, M. Ilija and P. Hernández, Thermochim. Acta, 256 (1995) 325.