

Structural and textural study of Ni and/or Co in a common molybdate lattice as catalysts

H. Boukhrouf, R. Benrabaa and A. Barama

Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, Faculté de Chimie, USTHB, BP. 32, El-Alia, 16111 Bab Ezzouar, Alger, Algérie

Abstract. This work deals with the search for new molybdate catalyst formulations, which are known to be active in light alkane oxidative dehydrogenation, a process which could be replaced in the near future by the common steam cracking and pure dehydrogenation processes currently used for the production of alkenes. Co, Ni and mixed Ni-Co molybdates of various compositions are prepared by a modified coprecipitation procedure from metal nitrates and ammonium heptamolybdate. Their structural and textural properties were studied by XRD, Raman, B.E.T and XPS. Textural and structural properties of the materials are correlated to the composition.

1. INTRODUCTION

Transition metal molybdates are important families of inorganic materials which have been a subject of intensive research due to their many applications such as photoluminescence, magnetic properties, electronic properties [1–6] and catalysts in a large variety of industrial processes that involve the activation or conversion of hydrocarbons [7–11]. For example, cobalt and nickel molybdates are important components of industrial catalysts for the partial oxidation of hydrocarbons and precursors in the synthesis of sulfide, nitride, and carbide materials [12]. The MMoO_4 compounds are ideal for exploring possible correlations among the structural, electronic and chemical properties of mixed-metal oxide catalysts, a subject that is receiving a lot of attention. The interest for these compounds is furthermore enhanced by the perspectives of synthesizing new molybdate MMoO_4 and mixed Ni-Co molybdates with improved catalytic properties. It is initiated that the investigations on a series of binary nickel-cobalt molybdates displaying improved catalytic properties, whose XRD patterns let conclude that the structures of these mixed compounds are solid solutions of NiMoO_4 and CoMoO_4 . In the present work, MMoO_4 ($M = \text{Ni}$ or Co) oxides were synthesized by coprecipitation method and characterized by different techniques. The purpose is to evaluate the effect of Ni or Co on the structural and textural properties of nanomaterials MMoO_4 ($M = \text{Ni}$ or Co) and the mixed oxide Ni-Co-Mo-O.

2. EXPERIMENTAL

2.1. Catalysts preparation

The catalysts ($M\text{-Mo-O}$ with $M = \text{Ni}, \text{Co}$) were prepared by coprecipitation method as described in references [13]. The adequate amounts of $M(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($M = \text{Ni}$ or Co) (Aldrich +99%) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Merck +99%) are dissolved separately in deionized water to

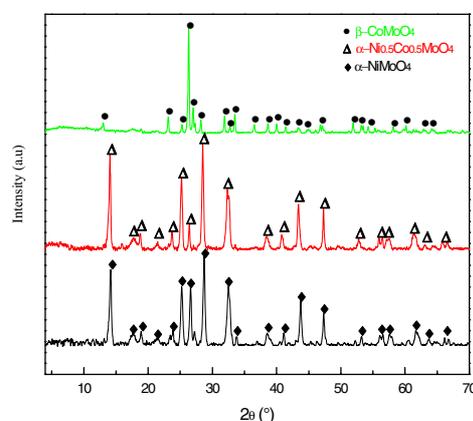


Figure 1. X-ray diffraction patterns of catalysts.

obtain aqueous solutions (0.25M) with the molybdate composition $M/\text{Mo} = 1.0$. The obtained solution was mixed at 85°C ; and introduced drop wise into a vigorously stirred ammonia solution (2M).

2.2. Physicochemical analyses

A number of physicochemical methods were used for characterization of solids before and after calcination, the details of these methods are reported early in [13, 14].

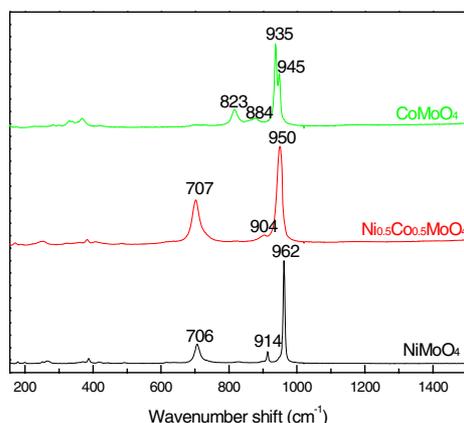
3. RESULTS AND DISCUSSION

Structural properties of catalysts were studied by XRD and Raman techniques at room temperature, the obtained results are shown in Figures 1 and 2. The results of both techniques are in the same direction. The XRD analysis (Figure 1) showed for the Ni-Mo-O system after calcination at 550°C , the presence of $\alpha\text{-NiMoO}_4$ phase (file 33-0948) with octahedral Mo coordination is through its well-defined pattern displaying peaks at d-spacing values of 3.095, 3.513 and 2.746 Å and the

Table 1. XPS results of NiMoO₄ and CoMoO₄.

Catalyst	Mo ^{IV+}				Ni ^{II+}		Co ^{II+}		Ni+Co/Mo
	1Mo3d		5Mo3d		3Ni2p		3Co2p		
	BE	At.%	BE	At.%	BE	At.%	BE	At.%	
NiMoO ₄	232.4	18.41	232.5	18.46	855.8	41.52	-	-	1.12
CoMoO ₄	232.5	22.79	232.7	22.67	-	-	781.2	33.77	0.74

Ni (+II), Co (+II) and Mo (+IV) are detected. Both systems present a different surface composition, NiMoO₄ showed a surface rich on Ni species while CoMoO₄ a surface rich on Mo species.

**Figure 2.** Raman spectra of catalysts.

β -CoMoO₄ (file 21-0868) for Co-Mo-O system, with tetrahedral Mo coordination. For the mixed oxide Ni-Co-Mo-O corresponding to the formulation Ni_{0.5}Co_{0.5}MoO₄ prepared by the same method, the α -phase is always detected for NiMoO₄ and CoMoO₄ in the common molybdenum lattice.

Raman spectra (Figure 2) showed that in all cases, the spectra characteristic of the solid solutions exhibit bands corresponding essentially to the α -phase. According to the literature sampling of α -NiMoO₄ is assumed to result in the formation of the so-called α' -phase, which is a distorted form of α -NiMoO₄, and this has been confirmed in our case. In all the other cases, the presence of the β -phase is inferred from the occurrence of two neighbor bands in the range 935-945 cm⁻¹, resulting in a broad band without clear resolution. The Raman spectra of catalysts whose XRD pattern revealed the presence of both α - and β -phases only displayed the bands corresponding essentially to the β -phase.

Textural characteristics of catalysts were studied by their specific surface area by B.E.T and XPS methods. The specific surface areas (S_{BET}) largely depend on the element M (Ni or Co). S_{BET} is not very high for all solids (<40 m²/g), the best surface is observed for NiMoO₄ (37 m²/g), the system CoMoO₄ and the mixed oxide Ni_{0.5}Co_{0.5}MoO₄ present S_{BET} almost similar (14 m²/g for CoMoO₄ and 17 m²/g for the mixed oxide Ni_{0.5}Co_{0.5}MoO₄). The different results of surface composition of the solids determined by XPS analysis are gathered in the Table 1.

4. CONCLUSIONS

Nanocrystalline Ni_{1-x}Co_xMoO₄ (x = 0, 0.5 and 1) powders have been successfully synthesized by a coprecipitation method. It led to the formation of crystalline phases at moderate temperature (550 °C). In the case of M = Ni or Co, a single phase of α -NiMoO₄ or β -CoMoO₄ is obtained, while in the mixed oxide Ni_{0.5}Co_{0.5}MoO₄, only the category α is observed. The higher specific area is obtained for NiMoO₄, this later present a surface rich on Ni species (XPS results). These catalysts will be tested in oxireforming of ethane to produce ethylene.

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