Raman studies of supported V, Cr and Sb oxides and their mechanical mixture with α-Bi$_2$Mo$_3$O$_{12}$

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Abstract

The interaction between V–Sb or V–Cr–Sb oxides and α-Bi$_2$Mo$_3$O$_{12}$ in mechanical mixtures during thermal treatments has been studied by laser Raman spectroscopy. Isolated V–Sb oxide and α-Bi$_2$Mo$_3$O$_{12}$ remain unchanged up to above 600°C. When mixed, V-related bands start to disappear and Bi–Mo-related bands widen already at 600°C indicating some kind of interaction between them. The presence of Cr$_2$O$_3$ in the mixture speed up this interaction, leading to the formation of a new Bi–Mo–V–O compound at temperatures below 600°C. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Raman spectroscopy; α-Bi$_2$Mo$_3$O$_{12}$; Vanadium oxide catalysts; Antimony oxide; Chromium oxide

1. Introduction

The direct transformation of propane to acrolein is still an industrially unsolved challenge. V–Sb oxides are known to activate propane to produce acrylonitrile in the presence of NH$_3$, but their selectivity for the oxidation to acrolein is very poor. One alternative could be the joint use of two catalysts, each one able to catalyze one step involved: propane to propylene, and propylene to acrolein. The α-Bi$_2$Mo$_3$O$_{12}$ is known as one of the best catalysts for the latter step [1].

The aim of this work is to study by FT-Raman the interaction between α-Bi$_2$Mo$_3$O$_{12}$ and the mixed oxides V–Sb–O (or V–Cr–Sb–O), prepared by different methods, upon thermal treatment in air. Although Raman studies have been done for both Bi–Mo [2,3] and V–Sb [4] oxides separately, no information is available on their interaction. Cr$_2$O$_3$ was explored as an additive to V–Sb–O because of its well-known performance for catalytic dehydrogenation.

2. Experimental

The mixed V–Sb and V–Cr–Sb oxides were prepared by two methods: (i) impregnation of γ-Al$_2$O$_3$ and calcination at 600°C (series I); and (ii) mechanical mixture of V$_2$O$_5$, Cr$_2$O$_3$, Sb$_2$O$_4$ and γ-Al$_2$O$_3$, prepared by suspension of finely

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Table 1
Composition of the mechanical mixture samples (wt.%)

Sample	V_2O_5	Cr_2O_3	Sb_2O_4	γ-Al_2O_3	α-$Bi_2Mo_3O_{12}$
I1	5	2.8	2.5	39.7	50
M1	5	2.8	2.5	39.7	50
M2	6.5	–	2.7	40.8	50
M3	14	–	14	58	14

ground powders of each oxide on n-pentane and evaporation of the solvent at 70°C (series M). The final samples were prepared by mechanically mixing these oxides with α-$Bi_2Mo_3O_{12}$ forming a suspension on *n*-pentane. The sample composition and notation are shown in Table 1. Thermal treatments of the samples under flow of air were carried out successively at temperatures between 300°C and 650°C and in a quartz reactor, connected to a vacuum unit. Total pressure was 500–700 Torr. Raman spectra were obtained at room temperature in the same reactor, after isolating it from the vacuum unit, with a Bruker RFS100 spectrometer equipped with a NdYAG laser source. Usually 1000–1500 scans were collected to obtain the spectrum with a resolution of 4 cm^{-1}, using a low laser power (20 to 130 mW) to avoid overheating of the sample.

3. Results and discussion

The Raman spectra of the samples I1 and M1 are shown in Fig. 1 after thermal treatment in air at different calcination temperatures (T_c). The spectrum of the sample I1 after calcination at $T_c = 400$°C only shows bands typical for α-$Bi_2Mo_3O_{12}$ (120, 194, 368, 512, 649, 816 and 902 cm^{-1}). The spectrum of M1 sample at $T_c = 400$°C is composed of a mixture of the bands of α-$Bi_2Mo_3O_{12}$, V_2O_5 (144, 285, 702 and 994 cm^{-1}), Cr_2O_3 (551 cm^{-1}) and Sb_2O_4 (197 and 405 cm^{-1}). Calcination of these samples at $T_c > 400$°C, for I1, and $T_c > 500$°C, for M1, leads to the disappearance of the bands corresponding to α-$Bi_2Mo_3O_{12}$. Noteworthingly, the spectra of pure α-$Bi_2Mo_3O_{12}$ after calcination at 600°C (not shown) did not show this effect (only the small band at 994 cm^{-1} disappeared), and the spectrum (not shown) of the mixture of V, Sb, Cr and Al oxides used to make sample M2 showed no change after calcination at 650°C. These results indicate that an interaction between V–Sb–Cr–O and Bi–Mo–O phases takes place already at these moderate temperatures, and that this interaction decreases the thermal stabilility of the Bi–Mo–O phase.
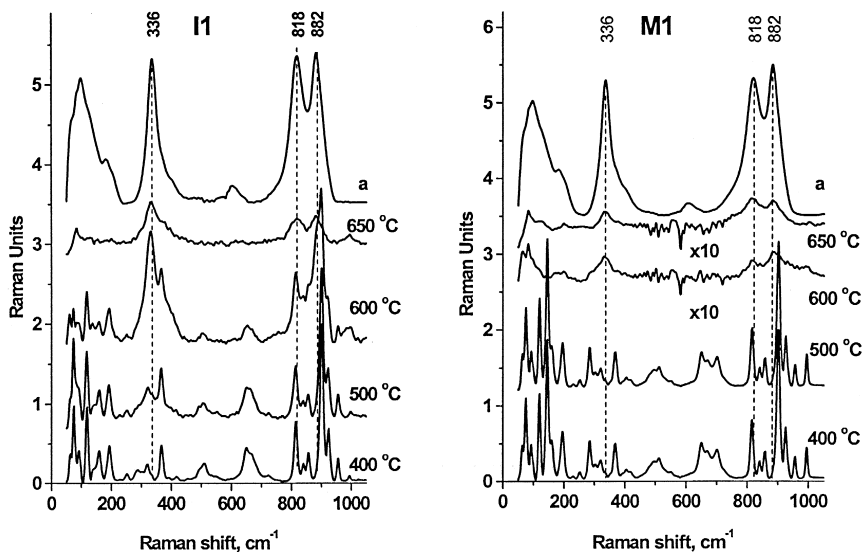

Fig. 1. Thermal evolution of mixtures I1 (left) and M1 (right) and spectrum of $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ (a).

The spectra of the samples I1 after $T_c = 600$ and of M1 after 650°C are very similar with new broad bands at 83, 332, 820, 881 and 996 cm^{-1}. The most interesting bands are those at 332, 820 and 881 cm^{-1}. Literature reports data about bands in these frequency regions for Mo, Cr and Bi–Mo oxides. Quincy et al. [5] reported bands at 338 and 820 cm^{-1} for Mo/TiO_2 at Mo concentration above 7.5 wt.% and attributed this to formation of MoO_3. Bhakoo et al. [6] and Hardcastle and Wachs [7] observed the band at 880 cm^{-1} for Bi–Mo–O and assigned it to the formation of Bi-rich phases ($Bi_6Mo_6O_{15}$, $Bi_{38}Mo_7O_{78}$). Hu et al. [8] observed bands at 820 cm^{-1} for MoO_3/SiO_2 and at 820 and 880 cm^{-1} for MoO_3/ZrO_2, but these bands were absent for MoO_3/Al_2O_3. Hardcastle and Wachs [9] reported a band at 880 cm^{-1} for 0.5% CrO_3/Al_2O_3 after calcination at 500°C, and assigned it to the symmetric stretching mode of Cr–O. It should be noted that all these components could be formed upon calcination of our samples.

To ascertain the formation of CrO_3 and to show the influence of Cr_2O_3 on the samples I1 and M1 during calcination, we prepared the samples M2 and M3 without Cr_2O_3 and with various contents of the other oxides. Their Raman spectra are shown in Fig. 2. For these samples, no Raman spectral change was observed after $T_c = 500°C$ and the spectra are addition of the pure spectra corresponding to V_2O_5, Sb_2O_4 and α-$Bi_2Mo_3O_{12}$. Sample M2 has the same content of α-$Bi_2Mo_3O_{12}$ as I1 and M1. A comparison of their spectra in Fig. 1 (I1 and M1) and Fig. 2 (M2) shows that the α-$Bi_2Mo_3O_{12}$ phase is stable for $T_c = 650°C$ in the absence of Cr_2O_3. Only one new band 330 cm^{-1} appears after calcination at this temperature, while bands of α-$Bi_2Mo_3O_{12}$ do not disappear. On the contrary, upon calcination of the sample M3 (which has equal content of V_2O_5, Sb_2O_4 and α-$Bi_2Mo_3O_{12}$) at 600–650°C, bands assigned to V_2O_5 and α-$Bi_2Mo_3O_{12}$ disappeared and only bands remained related to Sb_2O_4 (197 and 405 cm^{-1}) as well as broad, weak bands 340 and 818 cm^{-1}.

The difference between the M2, M3 and I1, M1 samples may be induced by absence of Cr_2O_3 in the M2, M3 samples. Thus, a possible interpretation of the spectra of samples I1 and M1 after calcination at high T_c could be due to the formation of CrO_3 and MoO_3 phases. CrO_3 might cause the band at 880 cm^{-1} and MoO_3
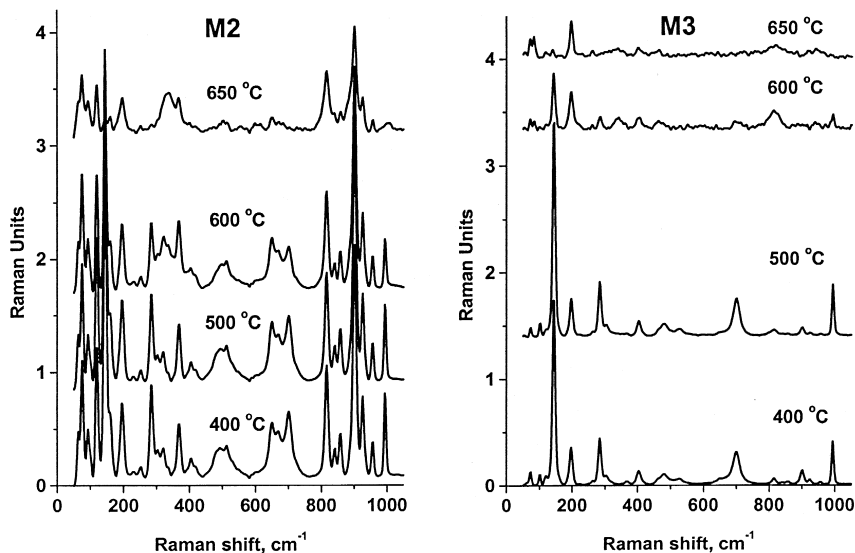

Fig. 2. Thermal evolution of mixtures M2 (left) and M3 (right).

those at 820 and 320 cm^{-1}. However, this interpretation will not explain why the band at 350 cm^{-1}, assigned to a bending mode of CrO_3, is absent, and why the bands of the α-$Bi_2Mo_3O_{12}$ phase (which did not vary even at $T_c = 600°C$ in the absence of V–Cr–Sb oxides) disappear in the M1 sample spectra.

Another possible interpretation of the variations of the I1 and M1 spectra at high T_c could be a strong interaction between α-$Bi_2Mo_3O_{12}$ and V–Cr–Sb oxides, leading to the formation of a mixed Bi–V–Mo oxide. For comparison, Raman spectra of a crystalline $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ phase (spectrum a) synthesized either by coprecipitation (at left) or by the citrate method (at right), which are almost identical, are included in Fig. 1. It may be seen that the spectra for I1 and M1 samples after high T_c show a similar pattern, although with much lower intensities. This supports the formation of a new $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ phase of low crystallinity. This phase has been found to be active and selective in the oxidation of propane to acrolein [10].

4. Conclusions

Based on the results above, one may conclude that the presence of Cr_2O_3 in the mixture of V–Sb oxide with α-$Bi_2Mo_3O_{12}$ leads to: (i) a decrease the thermal stability of α-$Bi_2Mo_3O_{12}$, in calcination at high temperature,

(ii) an interaction between these phases with formation of a new phase $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$, poorly crystallized. Further work is presently being done to study the evolution of these mixed oxides systems under propane ODH reaction conditions.

Acknowledgements

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