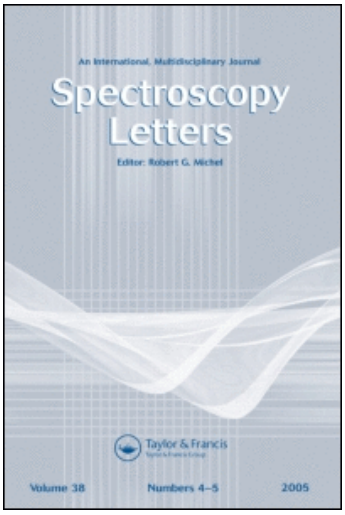


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# A LASER RAMAN STUDY OF MULTIPHASE Co-Bi-Mo OXIDE CATALYSTS

Keywords: Laser Raman spectroscopy, multiphase catalysts, Co-Bi-Mo oxides.

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## ABSTRACT

Cobalt and bismuth molybdates catalysts prepared by three different methods (coprecipitation, mechanical mixing and dispersion in n-pentane), have been studied by Laser Raman spectroscopy before and after testing the catalysts in the selective oxidation of isobutene to methacrolein. Raman bands ascribed to the component phases are observed in the spectra before test, while a phase transformation is detected after test.

## INTRODUCTION

Bismuth-molybdates are industrially important catalysts in reactions such as selective oxidation (i.e., propylene to acrolein) or ammoxidation (i.e., propylene to acrylonitrile).[1-3] Usually, these catalysts improve their catalytic performances upon addition of other elements, such as Co, Ni, etc., giving rise to multiphase catalysts.

The activity and selectivity of these catalysts in the reactions mentioned above have been related to cooperation effects (synergetic effects) between the phases existing in the catalysts. The origin of these effects has been attributed to different causes, such as surface monolayer formation, surface contamination by elements of one phase on the surface of the other phase, a remote control mechanism, formation of new phases by solid state reaction, etc.



Thus, in order to elucidate the nature of these synergetic effects, a detailed characterization of the catalysts before and after test should be performed, to ascertain the nature of the phases formed along the reaction. It has been demonstrated that, in many cases, the catalytic results can be explained by one of those processes,[3,4] but, in other cases, at least two processes are simultaneously involved.[5] In this way, Raman spectroscopy has proven to be a very effective tool in detecting the phases existing at different Bi-Mo compositions.[6]

Multiphase catalysts with different molar fractions of the component phases have been prepared following different methods. Pure cobalt molybdate and bismuth molybdates with Bi/Mo ratios of 2/1, 2/2, and 2/3 were prepared separately, while multiphase catalysts consisting of three molybdates were prepared either by coprecipitation of cobalt and bismuth salts, or mechanically mixing the single molybdate phases, or by dispersing them in n-pentane. Calcination of the catalysts was then performed in order to facilitate solid state reactions. In particular, some catalysts were not calcined in order to compare their catalytic activities with those calcined before the catalytic test. All catalysts were calcined at 723 K during the test in the selective

oxidation of isobutene to methacrolein.[5] Previous studies by X-ray diffraction[5,7] allowed us to ascertain the crystallographic phases existing in the catalysts prepared, and after the test; however, the technique is strongly dependent on the size of the crystallites, and so a spectroscopic study by Laser Raman technique is here provided, from the advantage of the high Raman scattering ability of these materials.

## EXPERIMENTAL

The starting materials were $Co(NO_3)_2.6H_2O$, $Bi(NO_3)_3.5H_2O$, and $(NH_4)_6Mo_7O_{24}.4H_2O$, all from Fluka (p.a.). Details of samples preparation are summarized in Table 1.



### Cobalt and bismuth molybdates (samples A, B, C, and D)

Cobalt molybdate (sample A) was prepared by co-precipitation[5] from 0.1 mol $Co(NO_3)_2.6H_2O$ and 0.1/7 mol ammonium heptamolybdate (hereafter AHM). After precipitation, the solid was filtered and calcined in air at 773 K for 2 h.

Bismuth molybdates (samples B, C, and D) with Bi/Mo atomic ratios of 2/1, 2/2, and 2/3 were prepared by co-precipitation[8] from $Bi(NO_3)_3.5H_2O$ and AHM at pH 7, adjusted with aqueous ammonia. Samples were calcined in a quartz reactor under static air atmosphere at 753 K for 6 h; a slow heating rate (1 K/min) from 298 to 753 K was used in order to ensure the complete decomposition of ammonium nitrate.

### Multiphase molybdates (samples E - L)

These samples were prepared from cobalt and bismuth nitrates, or from single molybdates A, C and D, following three different methods: co-precipitation (samples E and I), mechanical mixtures (samples F and J) and dispersion in n-pentane (samples G, H, K and L). The first method consisted of mixing aqueous solutions of $Co(NO_3)_2.6H_2O$ and $Bi(NO_3)_3.5H_2O$[8] in the desired stoichiometric amounts (see Table 1), evaporation of water, drying and calcination of the solid. In the second method,[5] the mixtures were obtained by hand grinding the cobalt and bismuth molybdates in an agate mortar for 20 min, the solids being

Table 1. Preparation conditions of the samples studied

| Sample | Atomic ratio | | | Precursors[a] | Preparation[b] | Treatment[c] |
|---|---|---|---|---|---|---|
| | Co:Mo | Bi:Co | Co:Bi:Mo | | | |
| A | 1:1 | | | CoN+AHM | CP | 773/2 |
| B | | 2:1 | | BiN+AHM | CP | 753/6 |
| C | | 2:2 | | BiN+AHM | CP | 753/6[d] |
| D | | 2:3 | | BiN+AHM | CP | 753/6[d] |
| E | | | 9:1:10.5 | CoN+BiN+AHM | CP | 753/6[d] |
| F | | | 9:1:10.5 | 9A+0.5C | MM | 753/6[d] |
| G | | | 1:2:4 | 1A+1C | n-pentane | un-calcined |
| H | | | 1:2:4 | 1A+1C | n-pentane | 773/144 |
| I | | | 9:1:10 | 9A+0.5B | CP | 753/6[d] |
| J | | | 9:1:10 | 9A+0.5B | MM | 753/6[d] |
| K | | | 1:2:3 | 1A+1B | n-pentane | un-calcined |
| L | | | 1:2:3 | 1A+1B | n-pentane | 773/144 |

[a]CoN = cobalt nitrate; BiN = bismuth nitrate; AHM = ammonium heptamolybdate

[b]CP = co-precipitation; MM= mechanical mixture; n-pentane= dispersion in n-pentane.

[c]Calcination temperature (K)/time (h)

[d]heating rate = 1K/min

finally calcined at 753 K for 6 h. Dispersed mechanical mixtures were prepared by dispersing in n-pentane equal amounts of bismuth molybdates (2/2 or 2/3) and cobalt molybdate.[4] The solvent was evaporated and the solid dried at 353 K for 15 h. Two samples of these powder mixtures were not calcined, whereas other were calcined at 773 K for 6 days.

The multiphase catalysts were calcined at 753 and 773 K during 6 and 144 h; some catalysts were not calcined, in order to compare the effect of calcination on the catalytic activity.

The Raman spectra were collected on a computer-controlled Jobin Yvon spectrometer (model U1000). The 514.5 nm line from a Spectra Physics model argon-ion laser was used as the exciting source. The spectral shift-width was typically of 4 $cm^{-1}$ and laser source powers of approximately 20 mW, measured at the sample, were used.

## RESULTS

With regards to XRD monitoring of the crystallographic phases existing in the catalysts, the samples (calcined or uncalcined) show the diffraction maxima due to the phases depicted below, before the catalysis runs; Phases changes are observed only after the catalytic studies; i.e., no effect of calcination is observed on the phases existing in the catalysts.

The Raman spectra of bismuth molybdates (samples B, C, and D) before and after test are presented in Figure 1.

X-ray diffraction data for catalysts B, C, and D, prior to the catalytic test, have evidenced the crystallographic phases $\gamma$-$Bi_2MoO_6$, ($\alpha$+$\gamma$)-$Bi_2Mo_2O_9$, and $\alpha$-$Bi_2Mo_3O_{12}$.[5-8] Figure 1.a shows the Raman spectrum for sample D, with bands at 955, 925, 900, 858, 840, 815, 650 $cm^{-1}$ due exclusively to internal modes for Mo-O stretchings of the three crystallographically distinct $MoO_5$ units of the $\alpha$-$Bi_2Mo_3O_{12}$ phase[9] as it is assigned by Hardcastle et al.[10,11] by directly correlating the experimental wavenumbers with crystallographically determined Mo-O bond lengths. No band due to Bi-O stretchings in the 600-400 $cm^{-1}$ region is observed in the spectrum and bands below 400 $cm^{-1}$ must be assigned collectively as bending/wagging and external modes.

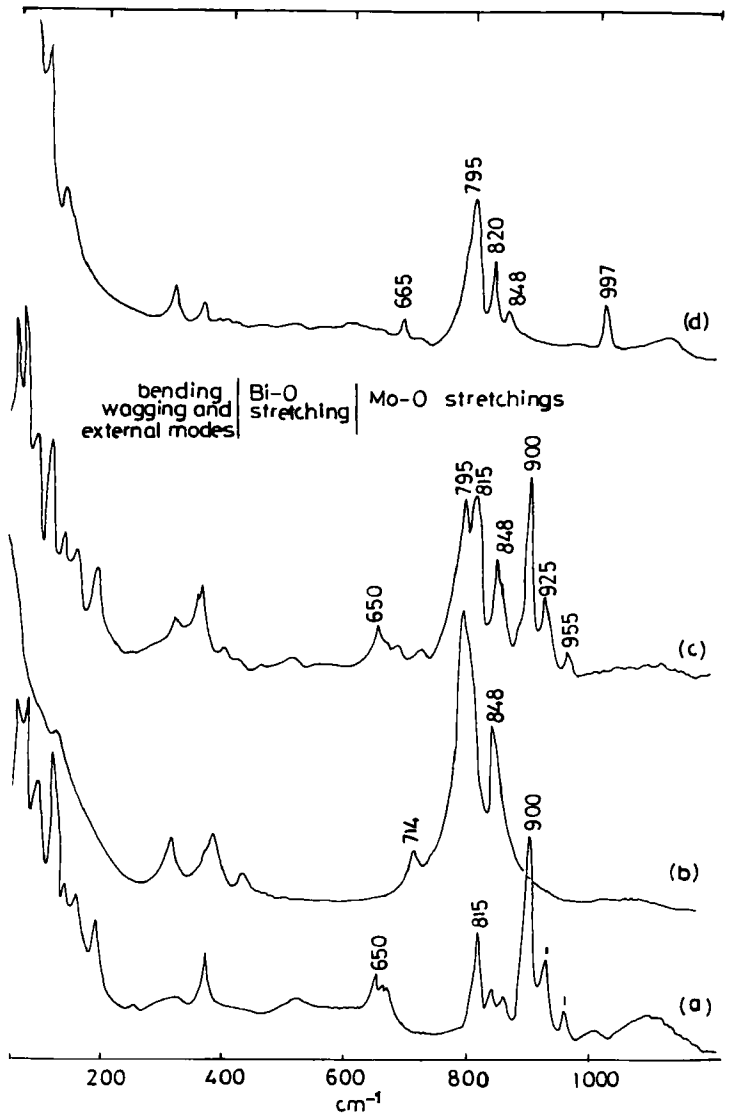


FIG. 1.-Laser Raman spectra of catalysts: (a) D before test; (b) C before test; (c) C before test; and (d) C after test.

The Raman spectrum of sample B, crystallographically identified as the $\gamma$-$Bi_2MoO_6$ phase, is shown in Figure 1.b. The structure of this phase has been studied by X-ray diffraction[12] and consists of alternating layers of $BiO_2^{2+}$ and corner sharing, distorted [$MoO_6$] octahedra. Only one type of [$MoO_6$] octahedron is present in this structure, and the bands at 848, 795 and 714 $cm^{-1}$ have been assigned to Mo-O stretchings of the [$MoO_6$] octahedron.[11]

The spectrum of sample C is shown in Figure 1.c; bands assigned to both, $\alpha$-$Bi_2Mo_3O_{12}$ and $\gamma$-$Bi_2MoO_6$ phases are observed, indicating that the composition of this 2:2 sample is biphasic (($\alpha$+$\gamma$)-$Bi_2Mo_2O_9$), as it has been also demonstrated by X-ray diffraction measurements.[5]



After the test, however, the XRD results for samples C and D evidenced the presence of $\gamma$-$Bi_2MoO_6$ (koechlinite) and $MoO_2$ (tungarinovite), the diffraction peaks due to $\alpha$-$Bi_2Mo_3O_{12}$ being abstent in the diagram recorded after the test. In addition, traces of $MoO_3$ and $Bi_{2x}Mo_{1-x}O_3$-type phase were also detected. Correspondingly, the Raman spectra recorded for samples C and D aftere the test are also different to those for the untested samples, Fig. 1.d. Bands corresponding to $\gamma$-$Bi_2MoO_6$ (848, 795 $cm^{-1}$) and $MoO_3$ (997, 820 and 665 $cm^{-1}$ due to terminal Mo-O bond, Mo-O-Mo and $Mo_3O$ stretchings, respectively[13]) are, however recorded, being $\alpha$-$Bi_2Mo_3O_{12}$ bands absent after test.

Figure 2 shows the spectrum of sample A before test, identified as $\beta$-$CoMoO_4$ by XRD, with bands at 852, 777, and 344 and 309 $cm^{-1}$ which can be ascribed to the stretching and bending modes of $MoO_4^{2-}$ species. No change was observed in the spectrum after the test.

The Raman spectra of multiphase catalysts before test ($\alpha$-$Bi_2Mo_3O_{12}$+ $\beta$-$CoMoO_4$ and ($\alpha$+$\gamma$)$Bi_2Mo_2O_9$+ $\beta$-$CoMoO_4$)), are presented in Figure 3.

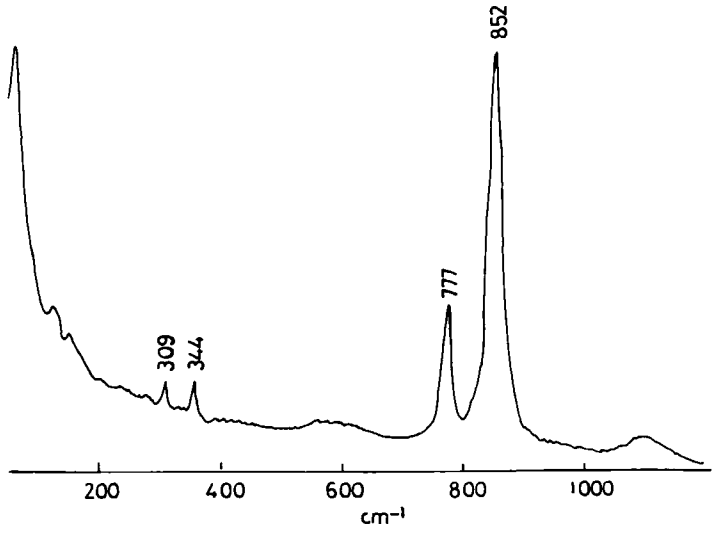


FIG. 2.-Laser Raman spectrum of catalyst A before and after the test (no change was observed).



Samples E-H show similar spectra (Fig 3.a) with bands at 955, 925, 900, 815, 650 and 851 and 777 $cm^{-1}$ that are ascribed to Mo-O stretchings in $\alpha$-$Bi_2Mo_3O_{12}$ and $\beta$-$CoMoO_4$, respectively. In a similar way, the Raman spectra of samples I -L (Fig. 3.b) present bands at 955, 925, 900, 815, 650 and 795 $cm^{-1}$, assigned to $\alpha$-$Bi_2Mo_3O_{12}$ and $\gamma$-$Bi_2MoO_6$, respectively, and two bands at 851 and 777 $cm^{-1}$ ascribed to $\beta$-$CoMoO_4$.

Different spectra for both series of samples E-H and I-L are observed after test (see Figure 4.a and b, respectively). Only bands due to $MoO_3$ and $\beta$-$CoMoO_4$ are observed in the spectra of E-H samples, while bands due to $\gamma$-$Bi_2MoO_6$ are depicted, in addition to $MoO_3$ and $\beta$-$CoMoO_4$, in the spectra of I-L samples.

## DISCUSSION

Before test, the Raman spectra of samples C and D showed bands due to $\alpha$-$Bi_2Mo_3O_{12}$, $\gamma$-$Bi_2MoO_6$ and $\alpha$-$Bi_2Mo_3O_{12}$, respectively. After

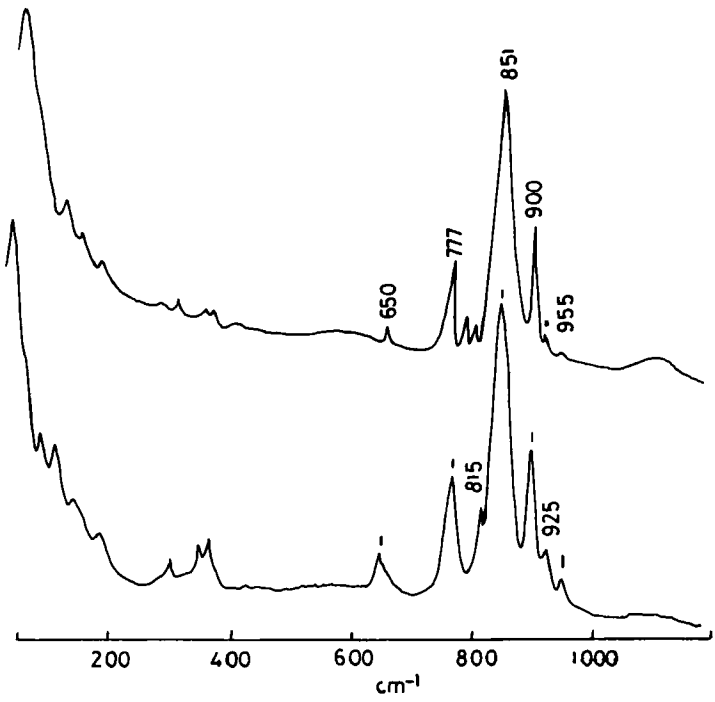


FIG. 3.-Laser Raman spectra of multiphase catalysts before test: (a) catalysts E-H; (b) catalysts I-L.



test the formation of new phases, $\gamma$-$Bi_2MoO_6$ and $MoO_3$ is detected in both catalysts. If the spectrum of $\beta$-$CoMoO_4$, is compared to those of bismuth molybdates (in the same region), it is rather simple, indicating a higher symmetry around the Mo site.

The Raman spectra of the multiphasic catalysts, prepared by coprecipitation, mechanical mixing or dispersion in n-pentane did not indicate the formation of a new phase after calcination. The Raman spectra corresponded to those cobalt and bismuth molybdates and they were identical to those observed for the non-calcined catalysts. After test, the Raman spectra indicated a transformation of of $\alpha$-$Bi_2Mo_3O_{12}$

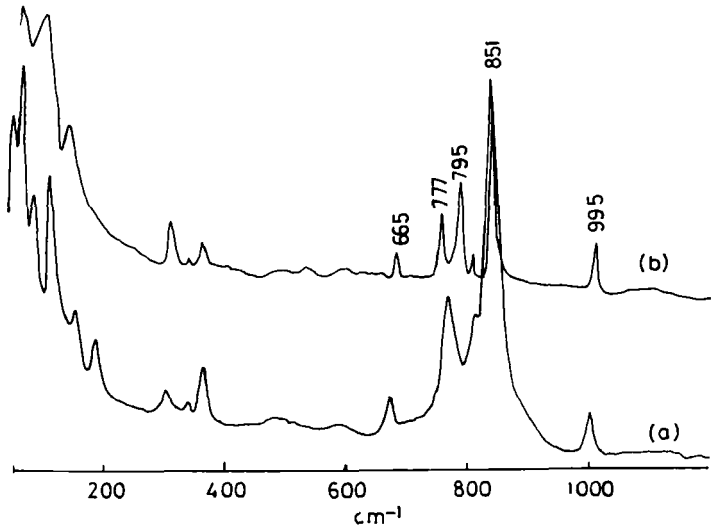


FIG. 4.-Laser Raman spectra of multiphase catalysts after the test: (a) catalysts E-H; (b) catalysts I-L.



into $\gamma$-$Bi_2MoO_6$ and $MoO_3$.The absence of bands due to $\gamma$-$Bi_2MoO_6$ in catalysts E-H after test, must be due to the fact that the bands ascribed to $MoO_3$ and $\beta$-$CoMoO_4$ mask those of $\gamma$-$Bi_2MoO_6$.

The observation of bulk $MoO_3$ in the Raman spectra of catalysts after test, confirms our previous results[5] obtained by X-ray measurements which indicated a transformation of of $\alpha$-$Bi_2Mo_3O_{12}$ into $\gamma$-$Bi_2MoO_6$ and $MoO_2$, being $MoO_3$ detected as traces. Thus, the transformation occurring during the test could be expressed as $\alpha$-$Bi_2Mo_3O_{12} \rightarrow \gamma$-$Bi_2MoO_6 + 2MoO_3$, with a subsequent reduction of $MoO_3$ to $MoO_2$.

The detection of bulk $MoO_3$ by Raman measurements is due to the strong Raman scattering power of this transition metal oxide.

## CONCLUSIONS

The Raman spectra of multiphase catalysts, prepared either by coprecipitation, mechanical mixing or dispersion in n-pentane, show bands ascribed to the internal and external modes of the molybdates phases existing in these catalysts before test ($\beta$-$CoMoO_4$, $\alpha$-$Bi_2Mo_3O_{12}$ and ($\alpha$+$\gamma$)-$Bi_2Mo_2O_9$). No effect of calcination is observed on these phases.

Phase changes are observed in the Raman spectra, only after the catalytic studies, $\alpha$-$Bi_2Mo_3O_{12}$ being transformed into $\gamma$-$Bi_2MoO_6$ and $MoO_3$.

Raman spectroscopy can detect the phases formed after test more precisely than X-ray diffraction measurements, probably due to the strong scattering power of the species present in the catalysts after catalytic reaction.



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