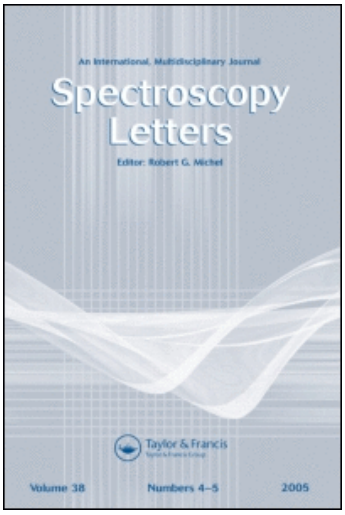

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X-Ray Photoelectron and Raman Spectroscopies, Comparative Studies of Supported Molybdenum Cobalt and Cobalt Molybdenum Catalysts

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X-RAY PHOTOELECTRON AND RAMAN SPECTROSCOPIES. COMPARATIVE STUDIES OF SUPPORTED MOLYBDENUM COBALT AND COBALT MOLYBDENUM CATALYSTS

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ABSTRACT

Laser Raman Spectroscopy is used to study catalysts : Co, Mo or Co-Mo supported on alumina. Well defined salts spectra are compared to those of these solids, which permits to establish superficial structures of cobalt, molybdenum or both.

For molybdenum catalysts, we found two structures depending upon the concentration :

- isolated MoO_4^{2-} molecular ions at low concentration < 4%
- polymolybdate phase at higher concentration

For cobalt catalysts two structures are also observed :

- tetrahedrally surrounded Co^{2+} ions at low concentration
- Co_3O_4 clusters at higher concentrations.

For cobalt-molybdenum (8%) catalysts three cases occur :

- no effect is observable at very low concentration of cobalt (0.5%)
- a well defined compound appears fcr Co/Mo atomic ratio 0.25
- when the cobalt concentration increases a third structure is observed but not identified.

All these results are compared to X Ray photoelectron spectroscopic studies and are in good agreement with them.

INTRODUCTION

UV, IR, visible spectroscopic techniques have been used to deal with the phases identification and cationic or anionic sites determination on the surface of hydrodesulfurization catalysts -cobalt and molybdenum supported on alumina-. In spite of the great number of works, a lot of questions remain unsolved and especially that of active superficial site is discussable since the superficial structures are not well defined and depend on preparation methods. An effort has been made in that field and the results were controlled by thermogravimetry (1) and X Ray photoelectron spectroscopy (2, 3).

The aim of this work is then to show what Raman spectroscopy can bring to the study of these compounds and to point out the complementary aspect of the two techniques : Raman and X Ray spectroscopies.

EXPERIMENTAL PART

a) Preparation of the samples

The Pechiney γ Alumina we used (specific area : 100 m^2/g) does not exhibit any Raman Spectrum with our experimental methods.

Mo/Al_2O_3 and Co/Al_2O_3 catalysts were prepared by impregnating γ alumina with a solution of ammonium paramolybdate or cobalt nitrate, air dried and calcinated under oxygen at 773 K.

$Co\text{-}Mo/Al_2O_3$ catalysts were prepared by impregnating γ Al_2O_3 with a mixed solution of $(NH_4)_6\ Mo_7O_{24}$, $Co(No_3)_2$ in well defined ratio, air dried and calcinated under oxygen at 773 K.

The contents of supported elements are expressed in percentage in weight of molybdenum or cobalt.

$CoMoO_4$ was obtained by heating the commercial compound $CoMoO_4,\ 4\ H_2O$ under oxygen at 873 K during 16 hours. Sodium dimolybdate was prepared by heating a stoechiometric mixture of Na_2MoO_4 and MoO_3 at 880 K. The aluminium cobaltite was synthetized by Delmon and All. (4). Co_3O_4, $ZnCo_2O_4$ were prepared by calcinating cobalt carbonate or a mixture of cobalt and zinc carbonate as already described (5).

All other used compounds were commercial products.

b) Raman spectra

Raman spectra were recorded on a Raman Laser microprobe Mole (6). The sample was punctually illuminated (spot size of one micron in diameter). The scattered light was analyzed by an optical microscope coupled with a double holographic grating monochromator and the detector was a photomultiplier followed by a DC amplifier and a chart recorder.

This system using a high numerical aperture collection optic permits to record Raman spectra using a low power of the laser Beam at the sample.

Moreover because of good contact between the particles and the support a good protection against thermal degradation is obtained.

The 5145 Å and the 4579 Å line from a "Lexel model 95" Ar^+ Laser was used as the exciting source. The power at the sample was approximately 3 mW.

Eventually, using a global illumination of this sample (150 to 300 μ in diameter), a map giving the repartition of the different species on the support can be obtained using a characteristic Raman line. In this case the spatial resolution is approximatively one micron.

The frequencies reported in table I, II, III are accurated to ± 3 cm^{-1}.

RESULTS AND DISCUSSION

a) Previous results obtained by X Ray photoelectron spectroscopy (ESCA)

In this paragraph, we are going to recall briefly the conclusions we came to after the ESCA studies of these compounds (2, 3).

- Mo/Al_2O_3
  - . Mo^{+6} ions only are present
  - . Alumina is covered by a monolayer up to a 8% molybdenum content (5.10^{18} at.Mo/m^2), but it is impossible to locate these ions which can be either in octahedral and tetrahedral superficial sites of alumina.
- Co/Al_2O_3
  - . Alumina is covered by a monolayer up to 3% cobalt content (3.10^{18} at.Co/m^2) which corresponds to a saturation of tetrahedral supeficial sites of alumina by Co^{2+} ions.
  - . Co_3O_4 clusters appear for higher contents.
- $Co\text{-}Mo/Al_2O_3$
  - . CO^{2+} ions are surrounded by Mo^{+6} ions up to a ratio Mo/Co = 4 This phase was detected by ESCA as well as by thermogravimetric measurements under reducing conditions. With a few hypothesis not completely confirmed by ESCA, a model (3) could be proposed for the distribution of ions on the alumina surface (Co^{2+} ions are then in tetrahedral sites and Mo^{+6} in octahedral sites).

b) Results obtained by Raman Spectroscopy

- Mo/Al_2O_3 (fig.1, table I)

The similarity between $CaMoO_4$ spectrum (1.a) - Molybdenum is in a tetrahedral environment-and spectrum (1.b) confirms the results obtained by Brown and All (7). For very

TABLE I

Raman frequencies (cm^{-1}) of Mo/Al_2O_3 and reference samples
(sh : shoulder B : Broad)

1%	2%	4%	6%	8%	10%	$CaMoO_4$
						75
						111
						142
202	202					192
						206
			220	220	219	
						255
322	324					319
		332				
		356	355	361	361	
					377 sh	
390	393					390
401 sh						403
			570	572	566	
794	794					794
			sh	sh	sh	
			B	B	B	
851	850					851
884	881	882				884
					903 sh	
	940 B	955	954	953	953	

low molybdenum concentrations, Mo^{+6} ions occupy isolated tetrahedral superficial sites of alumina. Before saturating all the tetrahedral sites, for example for a 2% molybdenum content ($1.25.10^{18}$ at.Mo/m^2) a broad line appears at 940cm^{-1} which gets more important for higher ratios.

For a 4% content, the surface is heterogeneous, we can see the spectrum of molybdenum in tetrahedral environment (fig. 1.e) and a line at 950 cm^{-1} characteristic of a new arrangement (fig. 1.d). The relative proportion of each arrangement depends on the analyzed surface area.

For a 8% content, a broad non resolved and asymmetric line is observed at 954 cm^{-1} and also two weak lines at 560 cm^{-1} and at 220 cm^{-1}. The line at 560 cm^{-1} can be assigned to an arrangement containing several Mo atoms as suggested by Vivier and all (8) and Kiss, Holy (9). So this line could be assigned to a stretching vibration ν_{as} of a $(Mo)_2O$ group and the line at 220 cm^{-1} to a deformation one. The ν_S line should be situated around 800 cm^{-1} in the non resolved shoulder. The line at 954 cm^{-1} and also the shoulder at 903 cm^{-1} correspond to a $\nu_{Mo\text{-}O_{(t)}}$ and $\nu_{Mo\text{-}O_{2(t)}}$ stretching vibration where $O_{(t)}$ is a terminal oxygen (10).

The $Na_2Mo_2O_7$ compound with bridged molybdate octahedra and tetrahedra (11) shows a similar better resolved spectrum between 800 and 950 cm^{-1} and a broad line at 550 cm^{-1}. So we can postulate a two dimensional polymeric non regular arrangement of bridged molybdate octahedra and tetrahedra on the top of alumina in accordance with our ESCA results and IR studies of Giordano (12).

- Co/Al_2O_3 (fig.2, table II).

Co_3O_4, $CoAl_2O_4$, $ZnCo_2O_4$ are normal II, III spinels.

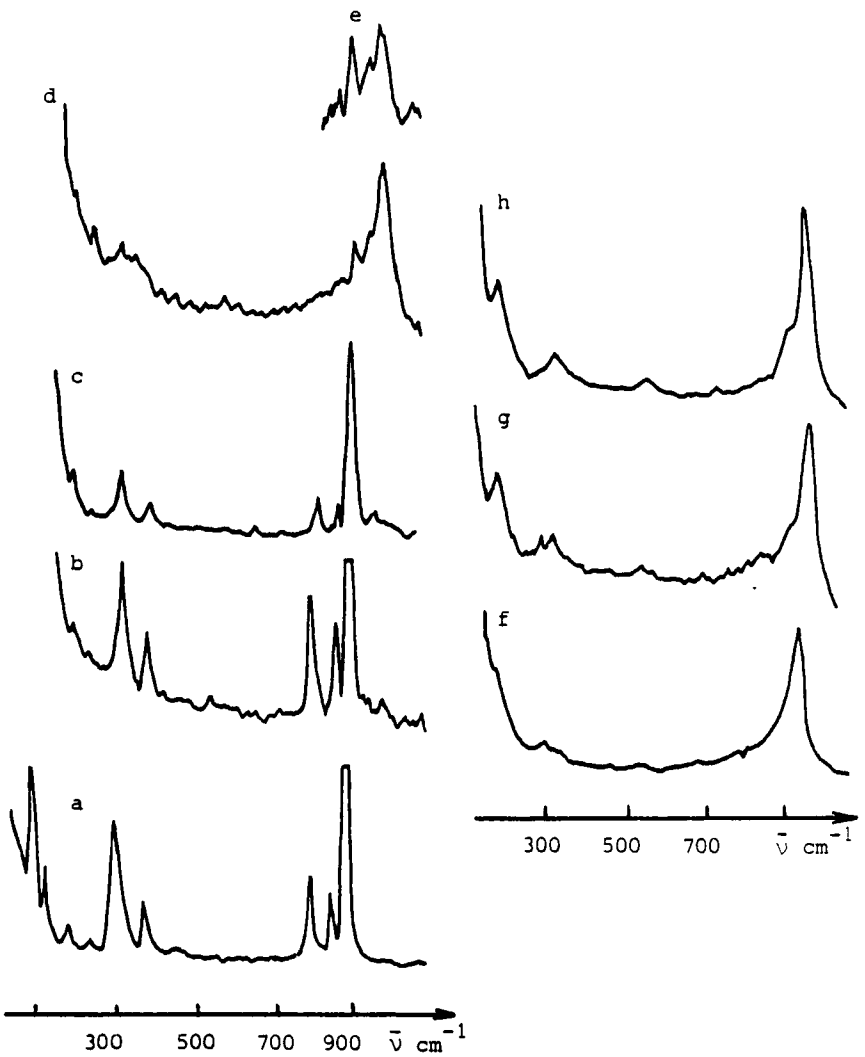

FIG. 1

Raman spectra of Mo/Al_2O_3 catalysts

a) $CaMoO_4$, fentes 3 cm^{-1} ; b) 1%, f.3cm^{-1} ; c) 2%, f.3cm^{-1}
d) 4%, f. 6 cm^{-1} ; e) 4%, f.6cm^{-1} ; f) 6%, f.8cm^{-1}
g) 8%, f. 8 cm^{-1} ; h) 10%, f.7cm^{-1}

TABLE II

Raman frequencies (cm^{-1}) of Co/Al_2O_3 catalysts
(w : weak ; sh : shoulder)

Co/Al_2O_3			Co_3O_4	$CoAl_2O_4$	$ZnCo_2O_4$
1%	2%	6%			
		470	468		
484	484	480			480
				490	
		515	510	515	515
		521			
527	527	612 (w)		609 (w)	616 (w)
		676	674		672 (sh)
690	689	689		689	696
				711 (sh)	

We can see that the Raman spectra of these compounds are very similar, so it is very difficult to attribute the observed lines to specific vibrations. This is also the case for IR Spectroscopy (13, 14). Nevertheless these compounds may be considered as references in our study.

For low cobalt coverages (1 and 2%) we observe a spectrum similar to the $CoAl_2O_4$ one, particularly for the 705 cm^{-1} intense narrow line, but the 609 cm^{-1} broad line and the 771 cm^{-1} shoulder are absent and the low frequencies doublet ($\sim$ 500 cm^{-1}) are shifted. These remarks coupled with the ESCA results are in accordance with tetrahedrally surrounded Co^{2+} ions on the top of alumina and not in γAl_2O_3 lattice.

For higher coverages (6%) the observed spectrum can be interpreted as a sum of CoO_4 tetrahedra and Co_3O_4 cluster lines (Table II). This is also in good agreement with the ESCA.

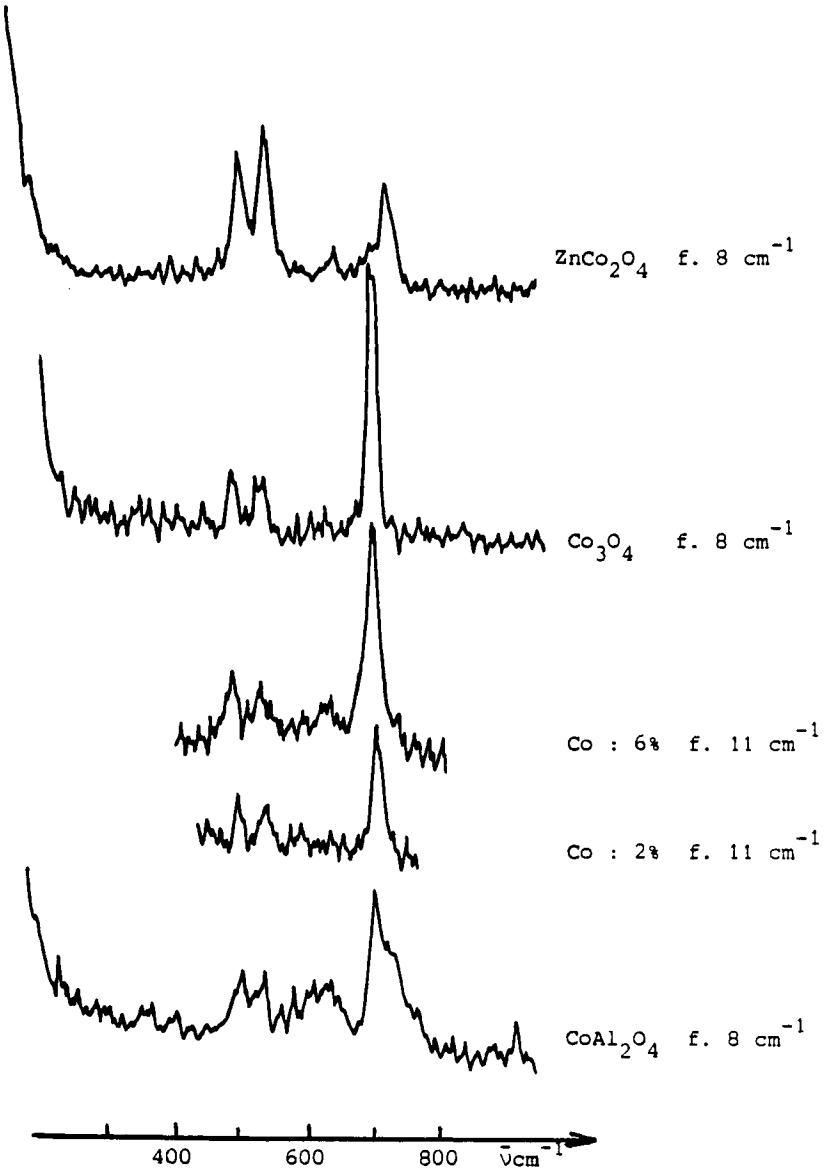

FIG. 2

Raman spectra of Co/Al_2O_3 catalysts

- Co-Mo/Al_2O_3 (fig.3, table III).

This section deals with the effects of introducing cobalt into Mo/Al_2O_3 catalysts. So we have chosen samples having a constant molybdenum concentration (8%) and an increasing cobalt content.

For a 0.5% cobalt content, there is no modification compared to the Mo/Al_2O_3 Raman spectrum, but for higher cobalt concentration (1.2 and 2%) we observe an intense spectrum suggesting a well defined compound. Some similarities appear between this spectrum and that of the a $CoMoO_4$ compound where the molybdenum is tetrahedrally surrounded (15) ; especially the 942 cm^{-1} line

TABLE III

Raman frequencies (cm^{-1}) of Co-Mo-catalysts
(w : weak ; sh : shoulder ; B : Broad)

Mo : 8 %				Mo = 6.5% : Co = 1 %	a $CoMoO_4$
0.5 %	1.225 %	2 %	3 %		
	180 (w)	180 (w)		180 (w)	
		220		220	
	275 (w)				274 (w)
	335	333	342 (B)		334
349				345	
	369	369		366	367
374 (sh)					
565		568		565 (w)	
	819	822	816	816	819
844 (sh)					
	880	880	876	(sh)	880
914 (sh)					
	938	942	936 (B)	942	937
	948 (sh)				
955		953		953	

could be assigned to a $Mo-O_{(t)}$ vibration. However the weak lines at 950 cm^{-1}, 568 cm^{-1} and 220 cm^{-1} attest the presence of polymeric molybdate.

For a 3% cobalt coverage the spectrum is modified and a new phase appears which is very difficult to identify.

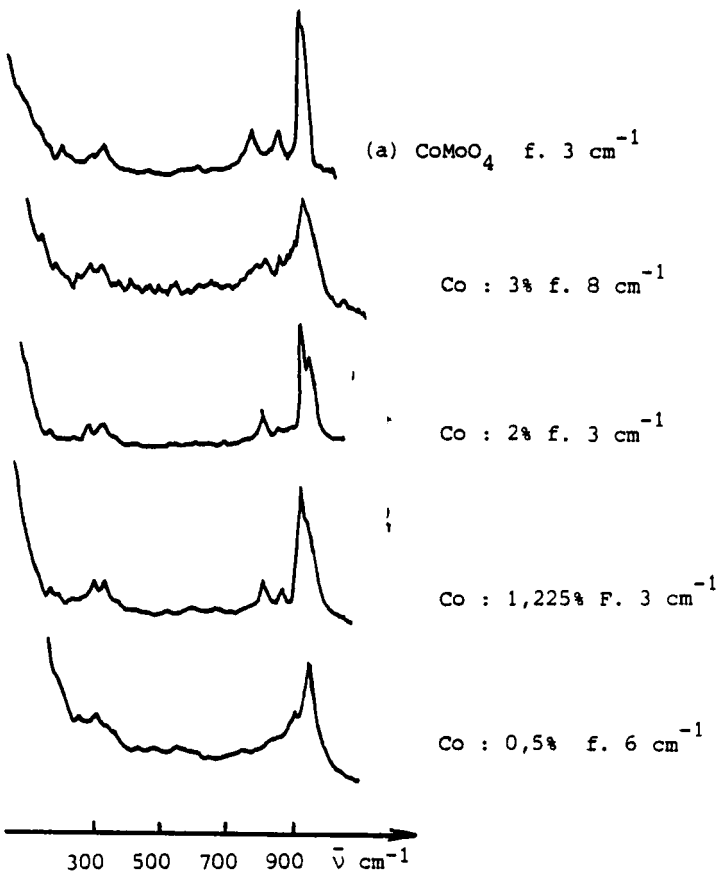

FIG. 3

Raman spectra of $CO.Mo/Al_2O_3$ catalysts (Mo:8%)

In all these spectra we never observed any lines of cobalt oxides or aluminium cobaltite.

These results are in accordance with a well defined phase similar to (a) $CoMoO_4$, but they show that molybdenum tetrahedra exist whereas in our first postulated model all molybdenum ions were octahedrally surrounded. However it seems difficult to modify this model completely since information about cobalt sites is absent in Raman spectroscopy and $Co2p_{1/2}$ binding energy measured by ESCA is intermediate between that of Co^{2+} ions in tetrahedral coordination and that of Co^{2+} ions octahedral coordination.

CONCLUSION

Raman spectroscopy is very sensitive to the structural and superficial properties of solids and the interpretation of spectra is often difficult. So it is necessary to complement with data given by other techniques.

In a previous work (2, 3), X Ray photoelectron spectroscopy was used for the characterization of hydrodesulfurization catalysts. Raman spectra of these catalysts and of several well defined solids permitted to confirm some results and to precise cobalt or molybdenum environments. Some new data about interactions between different sites could also be observed.

AUTHORS' NOTE

We received recently a preprint "Raman Spectroscopic Study of Co-Mo/γAl_2O_3" by J. Medema and C. Van Stam, V.H.J. De Beer, A.J.A. Konings and D.C. Koningsberger to be published in Journal of Catalysis. This work differ from ours by the following experimental points :

- Alumina Specific Area
- Calcination temperature
- Co-Mo/Al_2O_3 catalysts preparations
- Cobalt, molybdenum concentrations
- Power of the Laser Beam
- Low frequencies up to 200 cm^{-1} can be observed in our case

So some of our results are quite in accordance with theirs, others are complementary but a few of them differ.

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