Laser Raman spectroscopy of MoO_3 and NiO–MoO_3 supported on gallia and gallium–aluminum mixed oxides

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The laser Raman spectra of MoO_3 and NiO–MoO_3 supported on gallia and gallium–aluminum mixed oxides are presented and correlated to the type of support and the hydrodesulfurization (HDS) activity of the catalysts. The results show that the support affects the species (orientation of catalyst) that are formed on its surface. For example, MoO_3 forms mainly HDS inactive tetrahedral species on gallia; on alumina surface, it forms the HDS active polymeric octahedral species. Also, bulk oxide is formed more readily on gallia than on alumina. On addition of NiO, as a promoter, to the MoO_3 catalyst supported on gallia, a band that can be assigned to HDS inactive species was also formed. The intensity of this band is low in the spectra of NiO–MoO_3 catalysts supported on alumina.

Keywords: catalysts, laser Raman spectroscopy (LRS), hydrodesulfurization (HDS), spectra, gallia, alumina, gallium–aluminum mixed oxides, active species, tetrahedral, octahedral

1. Introduction

Supported MoO_3 catalysts are of interest because of their application in various catalytic processes, e.g., cracking, hydrocracking, metathesis, oxidation, hydrogenation, polymerization, hydro-dehydrogenation and hydrodesulfurization (HDS) of hydrocarbons, petroleum products and coal. The need to increase yield and reduce deactivation, especially during hydroprocessing/hydrotreating, has led to the continuous search for ways of enhancing the properties of this catalyst system. Therefore, our research has focused on the development of supports that will help in improving the catalytic properties of this catalyst system.

Alumina has been the typical support for MoO_3 hydrotreating catalysts (promoted with NiO) because of some of its properties. These are large surface area, attrition resistance, strength and inherent Lewis acidity. However, it has the disadvantage of having a strong interaction with the active species on its surface when used as a support. This strong interaction influences the dispersion and nature of the active species on the surface. It also impedes the conversion of the metal oxides to the active sulfide phase. Another disadvantage is that alumina on its own does not show any Brønsted acidity, and its Lewis acidity does not take a significant part in catalytic reactions.

Because of the disadvantages, efforts have been directed into finding alternative supports for the active species. The support should have a surface area as high or higher than that of alumina and should exhibit less interaction with the additives, to increase the conversion of the metal oxides to the sulfides. It should also exhibit some Brønsted acidic characteristics, because it has been shown that the acid function of the carrier (support) influences the active sites [1].

One of our research objectives is to investigate the effect of using mixed oxides of gallium and aluminum (Ga–Al) as supports for MoO_3 and NiO–MoO_3. This is to see if these supports will display better activity, than alumina, for cracking, hydrocracking and hydrodesulfurization reactions. It has been shown that frequently there is synergism of activity when two oxides are mixed together and used as a catalyst support [2]. In addition, it is known that sometimes the mixture of two oxides produces a material with higher surface area than that of its constituents. This higher surface area may lead to better dispersion of the active species. Mixed oxides (especially silica–alumina) have been used as catalysts and catalyst supports in many reactions. However, gallia–alumina mixed oxides have been studied only very little. In particular, not much work has involved investigation of the HDS and hydrocracking activities of catalysts supported on them. Recently though, gallium has been shown to have valuable catalytic properties, including increased hydrogenation capability when added to zeolites [3–5]. In addition, when we prepared gallium–aluminum mixed oxides, they have larger surface area than alumina. Because of the suggested enhancement of activity for hydrogenation and the higher surface area, we thought that using this catalyst for cracking would lead to enhanced activity. Furthermore, we decided to investigate the hydrocracking and HDS actvity of MoO_3 and NiO–MoO_3 catalysts supported on the mixed oxides.

The results of our catalytic experiments show that MoO_3 and NiO–MoO_3 supported on gallia–alumina have good hydrocracking activity. However, the HDS activity decreases with increased gallium oxide content [6] despite the fact

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that the surface areas of the mixed oxides are higher than that of alumina. The aim of the present work is to understand the reasons for the observed catalytic activities (HDS) using Raman spectroscopy.

Raman spectroscopy has become a very powerful characterization technique for obtaining detailed information about the molecular structure of metal oxide catalysts on oxide supports. This is because each molecular state of a compound possesses a unique vibrational spectrum that is related to its structure. Raman spectroscopy is also ideally suited for *in situ* studies because there are no inherent limitations on the temperatures, pressures, or the presence of reaction gases that can be used during investigations. Numerous Raman spectroscopic studies of supported MoO_3 have been conducted and reported in the literature [7–25]. However, there is no Raman study of MoO_3 (with and without NiO promoter) supported on gallia and gallium–aluminum mixed oxides in the literature. One of the objectives of this paper is to contribute to the database of materials in this field. In addition, attempts will be made to correlate the Raman spectra to the hydrodesulfurization activity of the catalysts. Understanding the relationship between species present on the support surface and the catalytic activity may help in the design of catalysts with improved properties.

2. Experimental

2.1. Gallia and gallium–aluminum mixed oxides

The Ga–Al catalysts were prepared by dissolving the required amount of $AlCl_3{\cdot}6H_2O$ in distilled water. The required amount of 0.086 or 0.86 M $GaCl_3$ solution was added to the $AlCl_3{\cdot}6H_2O$ solution and the mixture stirred vigorously. Ammonia solution was added to the mixture until pH 9 was reached. The mixture was then left overnight and the precipitate filtered off. The precipitate was washed with distilled water and ammonium acetate solution until free from chloride (tested with $AgNO_3$ solution). The washed precipitate was allowed to dry in air overnight and in the oven at 110 °C for another night. The sample was then calcined by drawing air through it at 500 °C for 4 h.

For example, the catalyst with 10 wt% gallium oxide is prepared by dissolving 42.62 g of $AlCl_3{\cdot}6H_2O$ in distilled water, and then adding 11.7 ml of 0.86 M $GaCl_3$ solution to the aluminum chloride solution. The mixture was then treated, as described above, to obtain the calcined catalyst support.

2.2. Addition of NiO, MoO_3

The metals were added to the supports by the incipient wetness method. The required amount of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ salt was dissolved in 0.85 ml of distilled water and added to 2 g of the support and the mixture then was mulled together for about 2 min. $NiNO_3{\cdot}6H_2O$ was also dissolved in 0.15 ml of distilled water and added to the above mixture. The mixture was mulled again for 3 min and then left to dry in air for 6 h after which it was transferred to an oven and dried overnight at 110 °C. The dried catalyst was then heated at 4 °C/min from 25 to 500 °C, and then calcined at 500 °C for 4 h.

2.3. Surface area

Surface area measurements were made using an ASDI RXM-100 surface characterization equipment, which obtains a multipoint adsorption isotherm. Approximately 20 mg of sample powder was degassed under vacuum (10^{-6} kPa) for about 15–20 min at 200–300 °C, before the adsorption of nitrogen.

2.4. Laser Raman spectroscopy (LRS)

Raman spectra were run on a Jarrell–Ash model 25–100 monochromator interfaced to a microcomputer. A Coherent Radiation model 590 argon-ion laser fitted with an Innova plasma tube was used to obtain exciting radiation having a wavelength of 514.5 nm, employing a laser current of 30 A.

The samples for LRS were prepared by making approximately 0.2 g of the powders into a self-supporting wafer (pellet). The pellet was then put into a glass cell specially designed for the experiment [26]. The cell was connected to a vacuum system and evacuated until the pressure was approximately 10^{-5} mm Hg. The cell was then filled with oxygen and the catalyst was heated to 500 °C by ramping at 4 °C/min and then kept at that temperature for 2 h. After cooling down to room temperature, the sample was evacuated once again and the cell sealed under vacuum.

The cell was then inserted into the sample compartment of the spectrometer and rotated at 300 rpm to avoid overheating one particular point on the sample. The sample was then analyzed by scanning between $\Delta\nu = 100$ and 1100 cm^{-1}.

2.5. Hydrodesulfurization (HDS)

The reactor used for the HDS studies has been described in a previous publication [27]. 0.15 g of catalyst was sulfided by passing 10% H_2S in H_2 over them while the reactor was held at 500 °C. The temperature of the reactor was reduced to 400 °C and thiophene was passed over the catalyst from a presaturator held at ∼15 °C. The products were analyzed by an on-line HP5890 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). Samples were taken and analyzed by the GC every 15 min and the reaction was stopped after the feed had passed over the catalyst for 4 h. Several catalysts were tested three times, the reproducibility of the thiophene HDS results was calculated to be ±3% of the stated value.

3. Results

3.1. Surface area and HDS

Some of the results of the HDS reactions carried out on these samples have been presented in [6]. It was seen that the HDS activity of a Ni–Mo catalyst supported on gallium–aluminum mixed oxides decreases with increasing gallium oxide content. This decrease is not a surface area effect, as the surface area of the mixed oxide support is greater than that of alumina (table 1).

The thiophene HDS results for MoO_3 supported on gallia are shown in table 2. There was a slight increase in thiophene conversion as the MoO_3 content increases from 3 to 10 wt%. However, there was also a slight decrease in conversion as the loading of MoO_3 increases above this level. This decrease may be due to less dispersion of the catalyst on the support surface as loading increases. Overall, thiophene conversion seems to be relatively constant at around 6%.

The HDS results of the catalyst supported on the gallium–aluminum mixed oxides (15 wt% MoO_3), without NiO, are presented in table 3. Surprisingly, as the amount of gallium oxide present in the mixed oxide increases, the HDS activity decreases. Note, however, that the HDS conversion is not surface area dependent.

The thiophene HDS results for MoO_3 supported on gallium–aluminum mixed oxides promoted with 3 wt% NiO are also shown in table 3. As can be seen, the conversion of thiophene is increased significantly as NiO is added to most of the supports. This is consistent with expectation, as it is well known that the addition of NiO to supported MoO_3 leads to a significant increase in the HDS activity [28–31]. This is apparently due to the formation of the "Ni–Mo–O" species which is sulfided into the active "Ni–Mo–S" species. However, the conversion goes down as the gallium oxide content in the mixed oxide is increased. One important and unexpected observation is that the promotional effect of NiO decreases as the gallium oxide content in the mixed oxide is increased. For gallium oxide and mixed oxides containing high gallium oxide content, the addition of NiO leads to a decrease in HDS activity.

Table 1
Surface area of supports and supported catalysts.

Catalyst designation	Surface area (m^2/g)		
	Support only	With MoO_3[a]	With NiO–MoO_3[b]
Alumina	218	202	196
0.5Ga–Al[c]	242	234	221
3.0Ga–Al	263	244	229
10Ga–Al	281	248	236
20Ga–Al	263	237	223
50Ga–Al	252	185	172
Gallia	48	40	34

[a] 15 wt% MoO_3.
[b] 3 wt% NiO and 15 wt% MoO_3.
[c] Ga–Al: gallium–aluminum mixed oxides. The number in the designation is the (wt%) of gallium oxide in the support.

Table 2
Thiophene HDS conversion for catalyst supported on gallia.

MoO_3 (%)	Surface area	Thiophene HDS conversion[a] (%)
3	47	6.7
5	46	6.7
10	44	7.1
13	42	6.5
15	40	6.1

[a] These values are calculated for thiophene after 4 h on-stream.

3.2. Raman spectra of MoO_3 supported on Ga_2O_3

The Raman spectra of increasing loadings of MoO_3 supported on gallium oxide are shown in figure 1. At 3 wt%

Table 3
Thiophene HDS conversion for catalyst supported on gallium–aluminum mixed oxides.

Catalyst	Thiophene HDS conversion[a] (%)	
	MoO_3[b]	NiO–MoO_3[c]
Alumina	11	37
0.5Ga–Al	12	29
3.0Ga–Al	10	26
10Ga–Al	9.8	19
20Ga–Al	9.7	12
50Ga–Al	9.5	9.1
Gallia	6.1	3.2

[a] These values are calculated for thiophene after 4 h on-stream.
[b] Supported 15 wt% MoO_3 without a promoter.
[c] Supported 15 wt% MoO_3, promoted with 3 wt% NiO.

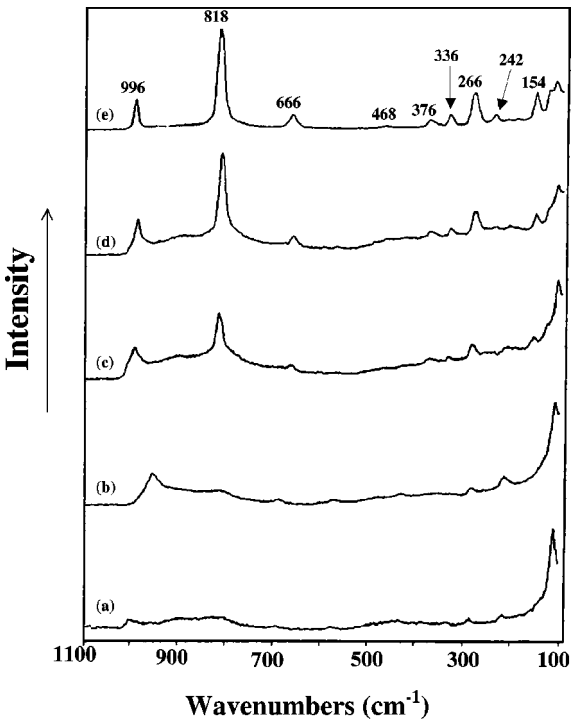

Figure 1. Laser Raman spectra of (a) 3, (b) 5, (c) 8, (d) 13 and (e) 15 wt% MoO_3 supported on gallium oxide.

MoO_3 loading, peaks of low intensities are seen at 1003, 890(b), 814(b), 668, 576, 448, 284 and 214 cm^{-1}. (These peaks are difficult to see in the spectra in figure 1 at low loadings, but may be seen in the expanded scale spectra.) As the loading is increased, the peaks become sharper and more intense. As the loading is increased above 8 wt% the spectra show a band at 995 cm^{-1} which seems to be the new position of the band which was at 1003 cm^{-1} in the sample with 3 wt% MoO_3. There is no further shift of this band at loadings of MoO_3 greater than 8 wt%. However, the band becomes sharper as MoO_3 loading is increased.

Others bands are found at 817, 666, 378, 336, 288, 244 and 212 cm^{-1}. The most noticeable feature at high loading is the increase in the intensity of the bands at 817, 666 and 288 cm^{-1} with increasing MoO_3 loading. These bands have been assigned to the vibrations of bulk MoO_3.

The spectrum of the sample with 5 wt% MoO_3 loading seems different from the other spectra in this series. For example, the presence of the band at 954 cm^{-1} is unusual since this peak is not present in any of the other spectra. This peak, at 954 cm^{-1}, has been assigned to the stretching vibration of the terminal Mo=O bond of a polymerized ($Mo_7O_{24}^{6-}$ or $Mo_8O_{26}^{4-}$) octahedral species under ambient condition [24]. Therefore, this suggests that the sample must have been exposed to moisture during preparation.

3.3. Raman spectra of $NiO–MoO_3$ supported on Ga_2O_3

The spectra of 3 wt% NiO and increasing amounts of MoO_3 supported on gallium oxide are shown in figure 2. At 3 wt% MoO_3 a low intensity band is found at 952 cm^{-1} which increases in intensity as the MoO_3 content increases. A broad band is also present at 800 cm^{-1} at 3 wt% MoO_3 which shifts to a higher wavenumber with increased loading, and finally, appears at 820 cm^{-1} for the catalysts with loadings over 10 wt% MoO_3.

A very big and broad band is found at 450 cm^{-1} for the catalyst with 3 wt% MoO_3 loading, which seems to be due to the presence of bulk NiO since the position and shape is similar to that observed by Chan and Wachs [7] in the spectrum of NiO supported on alumina. This peak is conspicuously absent as the loading of MoO_3 is increased above this value.

A weaker broad band is also present at ~898 cm^{-1} in all the spectra; it shows an increase in intensity with increased MoO_3 loading. This band may be due to a vibration of a Ni compound since it is absent in the spectra of MoO_3 supported on gallia. As the loading of MoO_3 is increased above 3 wt% a new band appears at 994 cm^{-1} which shows an increase in intensity with loading. Other bands are also present in the spectra of the catalysts containing more than 10 wt% MoO_3 at 820, 664, 336, 288 and 240 cm^{-1}.

This series of catalysts is different from the one without nickel in some respects. First, the bands due to bulk MoO_3, even though they appear at the same loadings as the catalysts without nickel, are of a much lower intensity for the same MoO_3 loading. Also, there is the appearance of a new band around 956 cm^{-1} that is absent in the spectra of the unpromoted catalysts. The bands at 336 and 994 cm^{-1} only appear at high MoO_3 loadings in the series containing nickel, whereas they are both present at lower loadings in the series without nickel.

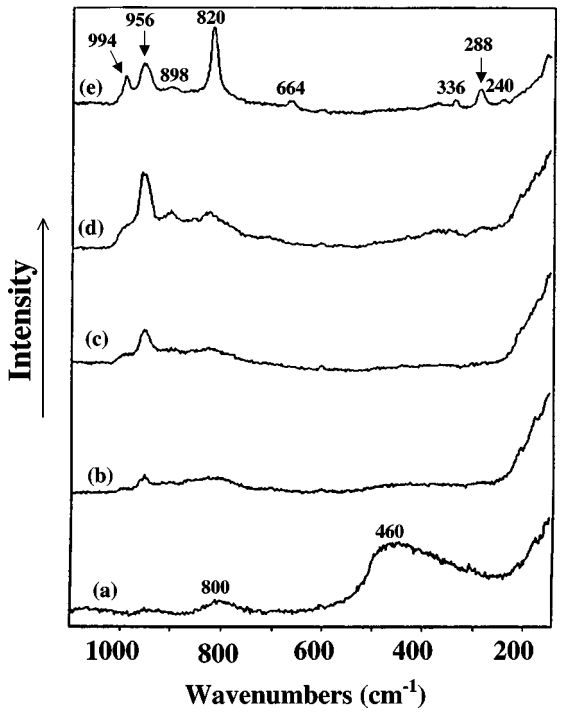

Figure 2. Laser Raman spectra of 3 wt% NiO and (a) 3, (b) 5, (c) 8, (d) 10 and (e) 13 wt% MoO_3 supported on gallium oxide.

3.4. Raman spectra of MoO_3 supported on Ga–Al series

The Raman spectra of 15% MoO_3 supported on alumina and gallium–aluminum mixed oxides are shown in figure 3. The most noticeable feature in all the spectra is the peak at 1002 cm^{-1}. The intensity of this peak goes down as the gallium content in the support is increased, showing that the concentration of the species that gives rise to this vibration is decreasing with increase in gallium oxide content. As the gallium content is increased to 50 wt%, the 1002 cm^{-1} band seems to disappear and instead a new band now appears at 994 cm^{-1}.

Another band is present at 870 cm^{-1}, which also shows a decrease in intensity with increasing gallium oxide content. However, the decrease in the intensity of this band is not as pronounced as that of the band at 1002 cm^{-1}. A band is also present at 950 cm^{-1} which is absent in the spectrum of MoO_3 supported on alumina, but present in that supported on the mixed oxides. The intensity of this band goes up with gallium oxide content. It should be noted however, that this band is absent in the spectra of MoO_3 on pure gallium oxide (figure 1(e)). This therefore shows that the species that is responsible for this peak is present only when there are mixed oxides.

Bands are present in the low wavenumber region of the alumina spectrum at 376, 292 and 210 cm^{-1}. These bands

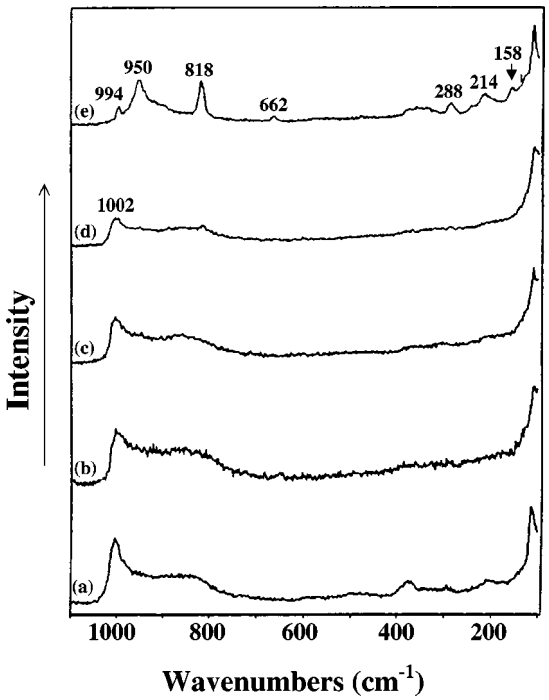

Figure 3. Laser Raman spectra of 15 wt% MoO_3 supported on gallium–aluminum mixed oxides: (a) 0, (b) 0.5, (c) 3.0, (d) 10 and (e) 50 wt% gallium oxide content in the support.

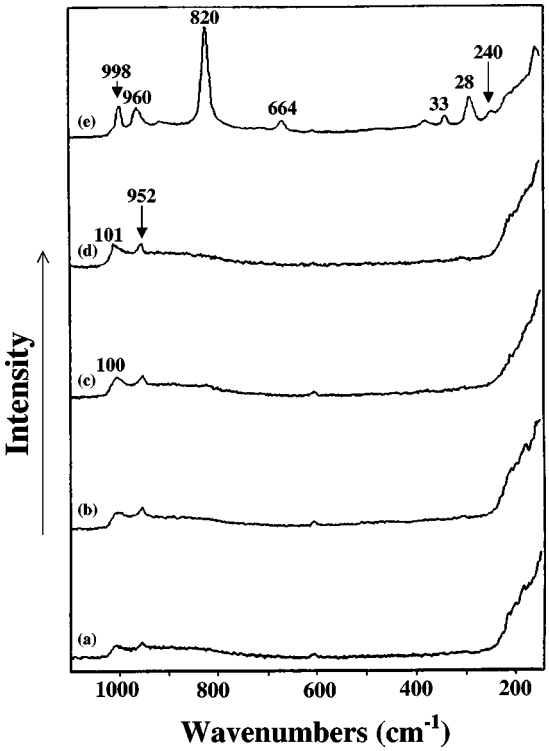

Figure 4. Laser Raman spectra of 3 wt% NiO and 15 wt% MoO_3 supported on gallium–aluminum mixed oxides: (a) 0, (b) 3, (c) 10, (d) 20 and (e) 100 wt% gallium oxide content in the support.

are, however, noticeably absent in the spectra of MoO_3 supported on the gallium–aluminum mixed oxides and on gallia. As the gallium oxide content is increased above 5 wt%, new bands are found at 816, 662, 255, 214 and 155 cm^{-1}. These bands show an increase in intensity as gallium oxide content is increased.

3.5. Raman spectra of NiO–MoO_3 supported on Ga–Al

The spectra of NiO (3 wt%)-promoted MoO_3 (15 wt%) supported on alumina and gallium–aluminum mixed oxides are shown in figure 4. As seen for the unpromoted oxide, all the spectra have a broad band at $\sim$1002 cm^{-1} that shifts to a higher wavenumber with increased gallium oxide content. This band becomes sharper and the intensity seems to increase with increasing gallium oxide content.

A broad band is present between 800 and 920 cm^{-1} in the spectra of the mixed oxides. As the gallium oxide content is increased the intensity of this band decreases. A band at 952 cm^{-1} is present in the spectra of alumina, gallia and all the mixed oxides. The intensity of this band seems to be constant for all the mixed oxides but is very high for pure gallium oxide support. At very high gallium oxide content, bands are present at 820, 664, 336, 288 and 240 cm^{-1}.

4. Discussion

4.1. Raman spectra of MoO_3 supported on Ga_2O_3

The 996 cm^{-1} band is found at all loadings (except 5%) of MoO_3, while the 250 cm^{-1} band is found only at very high loadings. As proposed by Vuurman et al. [8,9], these two bands may not be due to the vibrations of the same species. This result is not in agreement, however, with most of the other studies which show that these two vibrations originate from the same species. Vuurman et al. [8] suggested that the band at 996 cm^{-1} is due to the stretching vibration of the Mo=O bond of a mono-oxo molybdenum species, which according to them, cannot be easily characterized as due to tetrahedral or octahedral species. They however suggested a distorted octahedral species. The presence of this band at all loadings shows that it is a vibration that is common to bulk and dispersed species. This may explain the assignment of the band in this region to the vibration of bulk MoO_3 by Brown et al. [10].

The band at 336 cm^{-1} which Vuurman et al. [8,9] said is also due to the vibration of mono-oxo molybdenum species (tetrahedral or octahedral) is absent at low loadings in the spectra of MoO_3 on gallia. However, this band is present when MoO_3 loadings over 5 wt% are used. Earlier, Vuurman et al. [23] had suggested that the 336 and 995 cm^{-1} vibrations originated from the same source, as they always appear together in their spectra. The result here confirms this assignment since the two bands are present together in the spectra.

The presence of a broad band around 890 cm^{-1} has been shown to be due to the Mo–O–Mo vibration of a polymeric species, which could be tetrahedrally or octahedrally coordinated. The disappearance of this band as the MoO_3

loading is increased to 15 wt% suggests that this species is covered by bulk or crystalline MoO_3 at high loadings. Brown et al. [10] have proposed that it is possible for crystalline MoO_3 to physically cover other species on the surface.

4.2. Raman spectra of NiO–MoO_3 supported on Ga_2O_3

The presence of the broad band centered around 460 cm^{-1}, which has been assigned to the vibration of NiO, shows that bulk NiO is present on the support surface at low loadings. As the MoO_3 loading is increased above 3 wt%, the intensity of this peak is reduced and it disappears at loadings over 5 wt%. This may indicate that NiO does not enter the subsurface layer of gallia but stays on the surface as bulk compound or combines with the support to form a nickel–gallia compound.

The peak at 956 cm^{-1} has been assigned to two species in the literature. Several authors have suggested that this vibration is due to the Mo=O stretching vibration of a polymeric species, while Janibello and Mitchell [11] suggested that it is due to the Mo=O stretching vibration of surface bound tetrahedral species (MoO_4^-). Since this band is not present in the spectra of MoO_3 supported on gallia, it is also possible that it is the vibration of a nickel gallate species. However, the species that gives rise to this band cannot be a nickel gallate species since this band is present in the spectrum of a catalyst containing no nickel (see figure 3). In addition, the species cannot be polymeric since it is known that polymeric species are the active species for HDS reaction and the presence of this peak leads to reduced HDS activity. Therefore, the only possible assignment for this band is that it is due to the vibration of surface bound tetrahedral species as suggested by Janibello and Mitchell [11]. The increase in the intensity of this band as the MoO_3 loading is increased is consistent with the decrease in the HDS activity and the promotion effect of Ni of this series of catalysts, since tetrahedral MoO_3 is known to be inactive for HDS.

A band around 900 cm^{-1} has been suggested as due to the vibration of an aluminum molybdate, $Al_2(MoO_4)_3$, species [10,14]. The band around 898 cm^{-1} can therefore be assigned to the vibration of a gallium molybdate, $Ga_2(MoO_4)_3$, species. The intensity of this band also grows with increased MoO_3 loading and so may be related to the band at 952 cm^{-1}. The only suggestion for this band in the literature is that it is due to the vibration of a tetrahedral species on the surface [11–22]. Even though it is known that isolated tetrahedral species (MoO_4^-) are found at low loadings, the tetrahedral species that gives rise to this vibration may be a polymeric one. It was suggested previously [32] that polymeric species containing tetrahedral MoO_3 are known. The presence of NiO on the catalyst surface must have influenced the formation of the HDS inactive tetrahedral species (polymeric and surface bound) since they are not present in the spectra of the unpromoted catalysts.

4.3. Raman spectra of MoO_3 supported on Ga–Al

The peak at 1002 cm^{-1} is assigned, in the literature, to the stretching vibration of terminal Mo=O bond. However, most of the reports did not indicate whether the peak originates from a tetrahedral, octahedral, isolated or polymerized species. Although there is no consensus on the assignment of this band in the literature, correlating the band with the hydrodesulfurization results may help in its assignment. As seen in figure 3, this band shows a decrease in intensity with increasing gallium oxide content. Since the increase in the intensity of the band follows the same trend as the HDS activity (table 3), it is possible that this species is responsible for the activity of the catalyst. It has been suggested that the polymeric octahedral species present on the surface of the support is responsible for the activity of MoO_3 catalysts for sulfur removal [33]. Therefore, this peak at 1002 cm^{-1} can be assigned as the stretching vibration of distorted octahedral species. As the gallium content in the support is increased, the band at 1002 cm^{-1} disappears and a new band appears at 994 cm^{-1} (see figure 3(e)), which has been assigned to the vibration of a mono-oxo molybdenum species. This therefore shows that the species formed on the surface is dependent on the type of support.

The presence of the band at 870 cm^{-1}, which has also been assigned to the terminal Mo=O vibration of a polymeric species, on alumina and the mixed oxides shows the importance of this species to the catalytic activity of the catalyst. As the gallium oxide content is increased, the intensity of this band decreases and the catalytic activity of the catalysts also decreases.

The presence of a band at 950 cm^{-1} in the spectra of MoO supported on the mixed oxides shows that the presence of gallia influences the formation of polymeric tetrahedral species as explained above. The presence of this band in the absence of NiO aids in the assignment of the band (also found in all the spectra containing NiO) to the vibration of a tetrahedral species. The absence of this band in pure gallium and in pure alumina shows that the distortion of the surface, by the presence of two oxides, is responsible for the formation of this species.

The presence of bands attributable to bulk MoO_3 at high gallium content shows that as the gallium oxide content is increased, more bulk compound is being formed.

4.4. Raman spectra of NiO–MoO_3 supported on Ga–Al

The presence of the band at 952 cm^{-1} in all the spectra in this series shows that the presence of NiO enhances the formation of a tetrahedral species. It should be noted that this band did not appear in the spectra of the unpromoted catalysts until the gallium content is about 10 wt% and even then the intensity is much lower than that observed for the promoted catalyst.

A weak band is present in the spectra of MoO_3 supported on gallia and on mixed oxides with gallium content over 10 wt% at 898 cm^{-1} (seen in the enlarged spectra).

This band has been assigned to the vibration of a surface tetrahedral species. This shows that the presence of gallia and NiO enhances the formation of this species, which has been shown to be unreactive in HDS. This may therefore explain the decrease in the promotional effect of NiO on the catalysts as the gallium oxide content is increased.

The band at 1002 cm^{-1}, assigned to the vibration of an M=O vibration of a polymeric species, shifts to a higher wavenumber as the gallium oxide content is increased. The implication of this is not yet known. The increase in the intensity, and the increased sharpness of this band as the gallium oxide content is increased may be due to the increase in the amount of the species present and also to increase in the degree of polymerization of the catalyst.

4.5. Comparison between gallia and alumina

The Raman spectra of increasing loadings of MoO_3 supported on alumina are not presented in this study because they have been presented in the literature. However, the spectra of 15 wt% MoO_3 and 3 wt% NiO–15 wt% MoO_3 supported on alumina are presented (see figures 3 and 4).

The major difference between these two supports is in the position of the band around 1000 cm^{-1}. This band is present at 1002 cm^{-1} in the spectrum of MoO_3 on alumina and around 995 cm^{-1} on gallia. These two vibrations have been assigned to different species: the 1002 cm^{-1} band to the vibration of a polymeric species, while the 995 cm^{-1} band is assigned to the vibration of a distorted tetrahedral molybdenum.

Another difference is the absence of the broad band at 870 cm^{-1} in the spectrum of gallia, which is present in the spectrum of alumina. This band is also assigned to the vibration of a polymeric molybdenum species that is known to be active for HDS.

The bands due to bulk MoO_3 do not appear in the spectra with 15 wt% loading on alumina, but this band is present at very low loadings on gallia. This may be partly due to the very different surface area of the supports, or it may be due to a very different interaction between MoO_3 and the supports.

The addition of nickel leads to the formation of different species on gallia and alumina, as discussed in section 4.6.

4.6. Effect of NiO addition

The addition of Ni to MoO_3 supported on gallia leads to the formation of a band that is assigned to a surface tetrahedral species (956 cm^{-1}). This species is HDS inactive and may explain the reduction in HDS activity of MoO_3 supported on gallia, despite the fact that the presence of Ni leads to a late appearance (i.e., only at higher loadings) of the bands due to bulk MoO_3. The band around 995 cm^{-1} in the unpromoted sample is absent (or of low intensity when present) at low loadings of MoO_3. This shows that Ni affects the species that is formed on the surface.

The addition of NiO to MoO_3 supported on alumina leads to the reduction in the intensity of the bands at 870 and 1002 cm^{-1}, which are assigned to the vibration of the polymeric species which, when sulfided, are thought to be the active species for HDS. The decrease in the intensity of these bands may be because of an interaction between the polymeric species and the added nickel to form the "Ni–Mo–O" species. This species does not seem to give rise to any Raman active vibration, and the large decrease in the intensity of the 870 and 1002 cm^{-1} bands explains the large increase in the HDS activity on the addition of nickel.

Even though the presence of Ni leads to the appearance of the band assigned to inactive tetrahedral MoO_3, the intensity of this band is so low that the effect on the HDS activity is minimal.

5. Conclusion

The Raman spectra of MoO_3 and NiO–MoO_3 supported on gallia and mixed oxides of gallium and aluminum are presented. They show that the support affects the species that are formed on the surface. One difference is that MoO_3 forms mainly tetrahedral species on gallia, while it forms a polymeric octahedral species on alumina surface. Bulk oxide is also formed more readily on gallia than on alumina, appearing at a much lower MoO_3 loading on gallia. These differences probably are responsible for the very different catalytic behavior.

Another important point is that the addition of nickel leads to the formation of a band which can be assigned to HDS inactive species (surface bound tetrahedral species) on gallia. This behavior may be responsible for the low HDS activity of these catalysts since this peak is the most prominent one in the spectra of NiO–MoO_3 on gallia. In contrast, the addition of nickel to MoO_3 supported on alumina shows a reduction in the intensity of the band assigned to the vibration of the polymeric species. No other Raman bands are seen, and it is being suggested that the polymeric species, which are also present in the absence of Ni, reacts with Ni to form the "Ni–Mo–O" species which is apparently weak or inactive in the Raman spectrum. This would explain the large promotion of HDS activity seen when alumina and mixed oxides containing a large amount of alumina are used as the catalyst support.

The Raman spectra of MoO_3 supported on the mixed oxides resembles that obtained when alumina is the support in that bands at 1002 and 870 cm^{-1} are present. However, as the gallium content in the support is increased the intensity of these bands decreases. Bands in the low-temperature region in the spectrum of MoO_3 supported on alumina (380 and 298 cm^{-1}) are missing from the spectra of the mixed oxides. The decrease in the intensity of these bands may be correlated with the decrease in the HDS activity of the sulfided catalysts, as these bands are known to originate from a species which when sulfided is the active species on the catalyst surface.

The addition of NiO as a promoter leads to a significant reduction in the intensity of the bands at 1002 and 870 cm^{-1}

(present in the spectra of the unpromoted catalysts) for the catalyst supported on all the mixed oxides. The implication of this reduction in intensity to the catalytic activity (HDS) is explained above for the alumina-supported catalysts. The presence of a new band at 952 cm^{-1} in the spectra of Ni–Mo supported on the mixed oxides is suggested to be due to the vibration of a tetrahedral species which is unreactive for HDS.

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