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Treatment and halogenation on low molybdenum silica: diffuse reflectance IR Fourier transform study (DRIFTS)

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Abstract

Low molybdenum silica (1.2 wt.% molybdenum) has been prepared by impregnation (pore filling method) from an aqueous $(NH_4)_6Mo_7O_{27}$ solution ($pH \approx 6$). The effect of temperature (373–673 K) was followed by diffuse reflectance IR Fourier transform spectroscopy (DRIFTS). The interaction between molybdenum species, MoO_4^{2-}, and silica surface (OH pairs) is recognized at 373 K through the appearance of a band at 905 cm^{-1} attributed to an Mo–O–Si linkage, that shifted, and decreased in intensity, with the increase in temperature to appear at 915 cm^{-1} at 673 K. Bands at 555 (ν_sMo–O–Mo) and 881 cm^{-1} (ν_{as}Mo–O–Mo) are correspondingly developed with temperture, and only at 673 K a band due to MoO_3 (998 cm^{-1}) is recognized. These observations are used to propose a firm correlation between the detached molydenum species upon the breaking of the Mo–O–Si bonds and MoO_3 formation. The spectral changes in the stretching frequency region of surface hydroxyls indicated that as the separation between adjacent hydroxyls (involved in interaction with MoO_4^{2-}) increases, the strength of the Mo–O–Si link decreases. The presence of Cl^- or F^- on the surface of silica was found to decrease the extent of interaction between the molybdenum species and silica through decreasing the probability of finding vicinal hydroxyls. The formation of polymolybdate phase identified on the surface of molybdenum-supported silica is also inhibited by halogenation.

1. Introduction

A considerable amount of research has been devoted to the synthesis and characterization of Mo/SiO_2 catalysts [1–4]. One common molybdenum starting material is ammonium heptamolybdate solutions of variable concentrations to achieve different molybdenum loadings (3–20%); some researchers went down to less than 1 wt.% [1,5].

However, in most cases in which different techniques were used, calcination at a temperature as high as 773 K was always adopted after loading. Conclusions seem to agree, depending on molybdenum content and technique used, about the detection of MoO_3 and polymolbdate phases exhibiting variables extents of interaction with silica surface.

The details of temperature effect on the interaction between molybdenum species and silica surface in the range ambient to 773 K are therefore masked by this one-step heating.

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In the present work, a low molybdenum-loaded (1.2 wt.%) silica is subjected to heating in the tmeperature range 373–673 K and the diffuse reflectance FTIR spectrum is recorded at each heating temperature. At this low molybdenum content, the situation is certainly less complicated than at high values of loading, and therefore a clearer picture can be visualized through a stepwise heating regime. On the other hand, it has been reported that the interaction between silica and molybdenum originated from AHM is relatively weak; therefore, an alternative approach based on producing labile ligands containing molybdenum, such as $MoCl_5$ and $Mo(\eta^3\text{-}C_3H_5)_4$ or adding co-promotor atoms to molybdenum, such as cobalt, nickel or copper, has been used in order to achieve uniform and reactive catalysts [6–9].

Another approach can profoundly alter the activity or selectivity by replacing the hydroxyl groups with another species, such as halides [10,11]. Therefore, halogenation (by Cl^- or F^-) before molybdenum loading has been conducted in order to visualize the effect of halides on polymolybdate formation. The attention was thus given in this case to the low frequency region (1400–400 cm^{-1}), where the polymolybdate species show their modes of vibration.

Diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) has been chosen to follow the minute differences expected at the examined molybdenum level (1.2 wt.%) due to its potentiality as a rapid and sensitive technique [12,13].

2. Experimental

The catalyst support, silica gel 60 (Merck), of surface area (BET) 450 $m^2\ g^{-1}$ total pore volume (N_2 adsorption) 0.82 $cm^3\ g^{-1}$ and particle diameter 0.040–0.063 mm, was used as-received.

1.2 wt.% Mo/SiO_2 catalyst was prepared by pore filling impregnation from an aqueous ammunoium heptamolybdate solution at pH 5.96, drying at 343 K for 6 h, and finally heating at 373, 473, 573 or 673 K in air for 6 h. The samples are designated S_I, S_{II}, S_{III}, and S_{IV}, respectively. Silica samples only heated at the above indicated temperatures are designated S_1, S_2, S_3 and S_4, respectively.

Halogenation before molybdenum loading was accomplished by dispersing the as-received silica in an aqueous solution of 0.4 M HCl (Scl) or 0.2 M NH_4F (Sf) at room temperature for 4 h, filtration, washing (three times) with distilled water and heating at 373 K. The molybdenum-loaded samples of this system were heated at 373 K and their designations are $S_I$cl and S_If.

The diffuse reflectance spectra were recorded at room temperature on a Nicolet 20 SX Fourier transform IR spectrometer (4000–400 cm^{-1}) as KBr pellets. Spectra were acquired at a mirror velocity of 0.8 $cm\ s^{-1}$ at a nominal resolution of 4 cm^{-1} after averaging 100 scans, and represented in the Kubelka-Munk format.

3. Results and discussion

3.1. Parent silica

The surface of sample S_1 seems to accommodate at least three defined types of OH groups (Fig. 1); free (non-interacting; 3741 cm^{-1}); highly perturbed through hydrogen bonding, probably forming an extending domain (very broad band in the range 3600–3200 cm^{-1}); and surface silanols perturbed only by lateral interaction with each other (3662 cm^{-1}) [14,15]. Those of the second type are greatly decreased through condensation in pairs at 473 K; this condensation prevented some hydroxyls from hydrogen-bonding. Therefore, an increase in the intensity of the band with a slight shift to higher frequency, due to free isolated OH groups, is seen (sample S_2). A free isolated hydroxyl can also result from the condensation of surface hydroxyls in pairs from an odd numbered group.

Groupings of hydrogen-bonded silanols should end with free hydroxyls; these differ from the isolated free ones. The occurrence of such terminal hydroxyls could, however, be neglected only if very large groupings occurred, and it becomes likely if OH dimers are considered [15]. The increase in extent of dehydroxylation at 573 K (sample S_3) can be recognized through the evaluation of the two bands at 3718 and 3540 cm^{-1}, which are assigned respectively to the free and bound component of an isolated couple of hydrogen-bonded silanols [15–17]. Heating at 673 K (S_4) resulted in the increase and predominance of free isolated OH groups with the persistence of few OH groups which are pertured via hydrogen-bonding to different extents (Fig. 1).

In the low frequency region, the dehydroxylation can be inferred through a consecutive decrease in the intensity of the band at 970 cm^{-1}, attributed to the Si–O stretching vibration of surface silanols [18].

3.2. Molybdenum-loaded silica

The DRIFT spectra of Mo/SiO_2 samples are shown in Fig. 2. Heating at 373 K (sample S_I) resulted, in the low frequency region, in the appearance of new bands at 555 (ill-defined), 905 and 942 cm^{-1}; meanwhile, the SiO–OH band (970 cm^{-1}) appeared as a diffuse shoulder. The increase in heating temperature resulted in multiple spectral changes, thus the intensity of the band at 555 cm^{-1} increased and that at 905 cm^{-1} decreased in proportion to temperature, the latter showing a shift to higher frequency with temperature, where it appeared at 915 cm^{-1} at 673 K. The 942 cm^{-1} band exhibited a continuous shift to higher frequency and become more defined at 970 cm^{-1} in sample S_{IV}. A band began to appear at 881 cm^{-1} in sample S_{II} (473 K) and became more visible in sample S_{IV}, accompanied in the latter case of appearance of a small well-defined band at 998 cm^1.

In the high frequency region, the spectrum of sample S_I showed a band of free isolated OH (3743 cm^{-1}) and a structureless region due to hydrogen-bonded groups (3600–3200 cm^{-1}). At 473 K (sample S_{II}), a slight gain in the intensity of the band at 3743 cm^{-1} was produced, with the emergence of a band at 3664 cm^{-1} due to laterally interacting groups. The latter band showed a definite decrease upon increasing the temperature to 573 K (S_{III}), accompanied by the development of a band at 3540 cm^{-1} which became

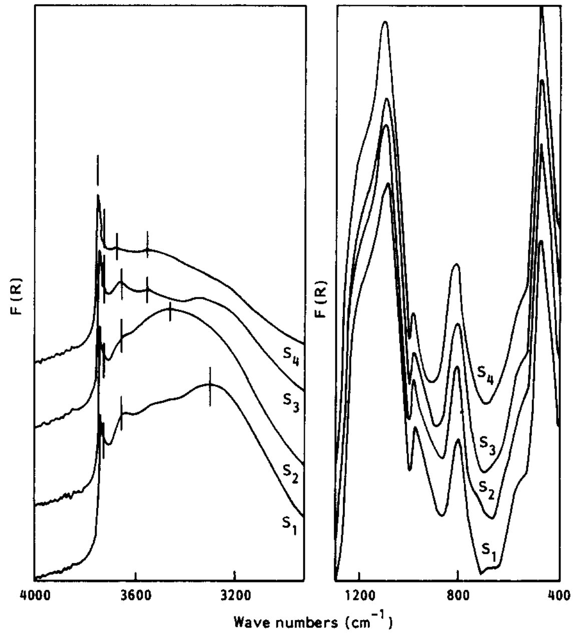

Fig. 1. DRIFT spectra of parent silica heated at 373, 473, 573 and 673 K.

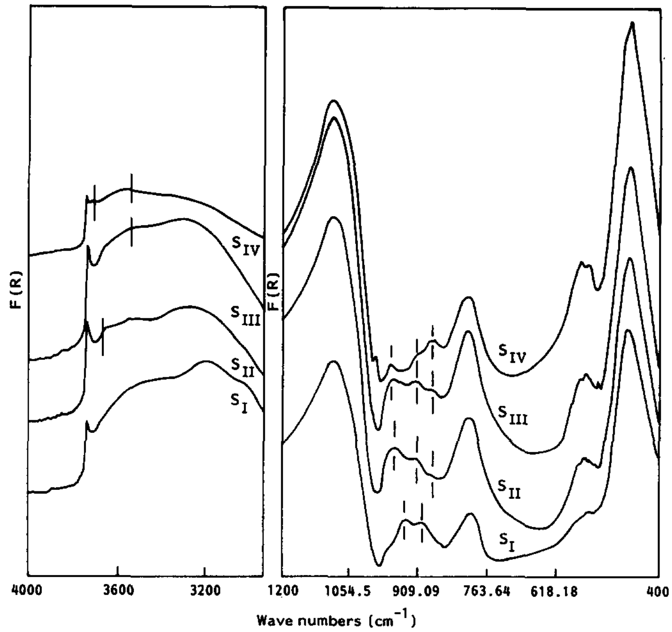

Fig. 2. DRIFT spectra of 1.2 wt.% Mo/SiO$_2$ catalyst heated at 373, 473, 573 and 673 K.

more observable at 673 K (S_{IV}) with the simultaneous appearance of a band at 3718 cm^{-1}.

The aqueous molybdate solution contains the following equilibrium [19]:

$$Mo_7O_{24}^{6-} + 4H_2O \rightleftharpoons 7\,MoO_4^{2-} + 8H^+$$

The involvement of surface hydroxyls in interaction with molybdenum species, MoO_4^{2-}, is manifested by the disappearance of the band of 970 cm^{-1} upon laoding. This band is shown to disappear upon interaction with reactive hydrogen sequestering agents [20]; however, the interaction seems to affect all kinds of surface hydroxyls, as can be seen from the lower intensity of the band due to free isolated OH groups compared with the unloaded sample. This interaction resulted in Mo–O–Si bonds, which are responsible for the band at 905 cm^{-1} in the spectrum of sample S_I. The occurence of this band at a lower frequency than that reported [21] may be due to interaction of water, whose effect is decreased with the increase in temperature (915 cm^{-1}, sample S_{IV}). Nevertheless, the decrease in the intensity of this band with temperature implies that most of the Mo–O–Si bonding is weak, and only the strongest persists up to 673 K (sample S_{IV}). The breaking of such bonds would results in an open siloxane [4] that, in view of the reversibility of surface dehydroxylation–rehydroxylation up to 673 K [22], would lead to reformation of surface hydroxyls in their place. It has to be mentioned that upon loading and heating, those vicinal hydroxyls which did not participate with molybdenum species have to be depleted through condensation and closed siloxane bridges left in their places. Therefore, the nature of the regenerated hydroxyls is a direct consequence of the nature of the groups primarily involved in interaction with molybdenum species. In other words, if an interacted pair of OH groups were originally widely seperated, but still able to interact as a pair, their regenerated counterparts are of the same nature.

The strength of interaction between molybdenum species and surface OH groups depends on the separation between the latter—as the separation increases the resulting bonding is weak. This explains the appearance of the band at 3664 cm^{-1} upon heating at 476 K (sample S_{II}), where the OH groups responsible for this band are not too near to each other [14,15], therefore their bonding with molybdenum species is easily broken upon heating at 473 K. With the increase in temperature, further bond breaking has occurred at interaction sites involving OH groups which were originally more adjacent to each other. The regenerated OH groups in this case are able to hydrogen-bond with each other, and being reformed at higher temperatures, i.e. on the surface accommodating a low number of hydroxyls, their perturbation via hydrogen bonding with other hydroxyls is low. Consequently, they act as an isolated couple of silanols and this results in the appearance of the two bands at 3718 and 3540 cm^{-1} in sample S_{IV} (673 K). The defined character of the band at 3718 cm^{-1} implies that a considerable number of such couples has been formed [23]; therefore, the decrease in the intensity of the band due to free isolated OH groups (3743 cm^{-1}) in sample S_{IV} can be attributed to their perturbation due to the increased formation of the above-mentioned couples. At the examined low level of molybdenum, most of the interaction had apparently taken part in narrow pores, where the probability of finding a pair of suitably OH groups in high. The proposed regeneration of OH groups had thus occurred mainly in these narrow pores, where the extent of perturbation of the free isolated OH groups is high.

It has been proposed [4] that the species that leaves the surface upon breaking of Mo–O–Si bonds is the precursor of MoO_3 detected on the surface. The simultaneous and consecutive increase in the bands at 881 and 555 cm^{-1} due to respectively the asymmetric [24] and symmetric [6] stretching of Mo–O–Mo that corresponds to the decrease in the band due to Mo–O–Si (905–915 cm^{-1}), and the appearance at 673 K of the band at 998 cm^{-1} due to the stetching vibration of terminal Mo–O in MoO_3 [25] can be understood in that sense. The strongly bound molybdenum species that resisted heating up to 673 K and resulted in the barely visible band at 915 cm^{-1} (S_{IV}) formed, through condensation, a polymolybdate phase that caused the appearance of the band at 970 cm^{-1} due to Mo=O stretching [21]. The earlier appearance of this band at 942 cm^{-1} in the case of sample S_I may be related to the action of water [26], whose effect is reduced upon increasing the temperature (S_{IV}).

3.3. Halogenated silica

The DRIFT spectra of samples Scl and Sf in the region 1400–400 cm^{-1} (Fig. 3) show that halogenation has decreased hydroxylation extent of silica, whereby a decrease in the intensity of the band at 970 cm^{-1} (Si–OH) has taken place. Also, it can be seen that halogenation has resulted in the appearance of a band at 907 cm^{-1}, which was absent in

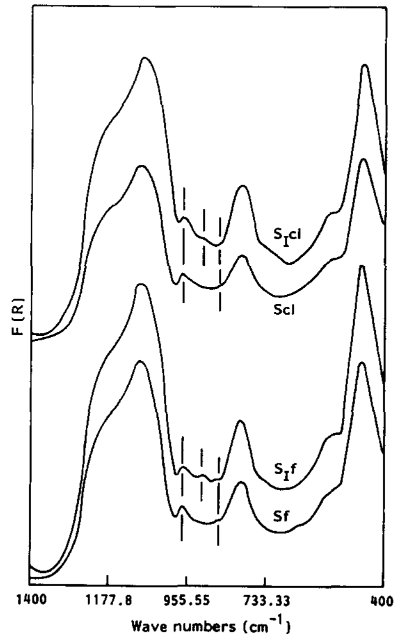

Fig. 3. DRIFT spectra of prehalogenated S_I samples.

the case of the unhalogenated sample (S_I). A band at 908 cm^{-1} was previously reported to appear if silica was degassed at temperatures greater than 673 K, and was assigned to a localized reactive siloxane bridge [27]. That this band appeared only after heating to 673 K may indicate that such a siloxane has been formed through condensation between two OH groups located not near to each other, as OH groups too near to each other can interact at lower temperatures. Tentatively, we may explain the appearance of the band at 907 cm^{-1} in the case of halogenated samples under study (those heated at 373 K only) on the basis that halogenation has decreased the population of adjacent hydroxyls, therefore the condensation upon heating involves OH groups which are at a wider separation and results in siloxane bridges of similar nature to those formed at 673 K. Although it may be possible that halogenation may decrease the extent of physically absorbed water, it is questionable to consider surface dehydroxylation at 373 K. Whether this speculation is true or not, a decrease in hydroxylation upon halogenation can eventually be ascertained.

A decrease of the extent of interaction between molybdenum species and silica surface upon halogenation can be inferred from the prominence of the band due to Si–OH (970 cm^{-1}) in the spectra of samples $S_I$cl and S_If (Fig. 3). The decrease in hydroxylation upon halogenation is thus the cause of this result, which is also manifested by the absence of the band at 942 cm^{-1} due to polymolybdate that appeared in the case of sample S_I (Fig. 2). As the formation of this phase is considered to result from condensation between molybdenum species attached to the silica surface [4], the decrease in the number of these species thus leads to less likely formation of polymolybdate. Another possibility is that halogenation has decreased the probability of vicinal molybdenum species attached to the surface, and consequently decreased the extent of condensation, through which polymolybdate formation takes place. However, the interaction between molybdenum species and silica was not completely inhibited, since a band at 921 cm^{-1} due to Mo–O–Si is seen in the spectra of both $S_I$cl and S_If samples. The appearance of this band at its usual frequency can be interpreted as halogenation decreasing the extent of interference of water that was noted in the case of the unhalogenated samples (S_I, Fig. 2).

Chloride ion seems to hinder the interaction between molybdenum species and silica slightly more than fluoride, since the band at 921 cm^{-1} in sample S_If appeared more itense than that in sample $S_I$cl. It appears that the surface site adjacent to a hydroxychloride is of lower accessibility than the one adjacent to a hydroxyfluoride due to the larger size of Cl^-.

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