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Iron modified MCM-41 materials characterised by methanol oxidation and sulphurisation reactions

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SiMCM-41, AlMCM-41, NbMCM-41 were applied as supports for iron species introduced by wetness impregnation and chemical vapour deposition (CVD) methods. Methanol oxidation and sulphurisation were used for the characterisation of catalytic properties. The support nature as well as the type of iron species have no effect on the selectivity of methanol oxidation. However, they bear a significant influence on both the activity and selectivity in the reaction between methanol and hydrogen sulphide. The wetness impregnation of NbMCM-41 and AlMCM-41 with Fe salt leads to the most effective catalysts in the sulphurisation of methanol.

KEY WORDS: SiMCM-41; AlMCM-41; NbMCM-41 supports for iron; impregnation; CVD; oxidation and sulphurisation of methanol.

1. Introduction

Iron is a well-known active species in many catalytic processes. A choice of a proper support for Fe plays a crucial role for the creation of highly effective iron containing catalysts. The important features of the matrices are, among others, high surface area and ability of the protection from the agglomeration of active metal oxide species. Due to that, M41S family of mesoporous molecular sieves discovered by Mobil Oil researchers [1] seems to be attractive supports for iron species.

A great advantage of such materials is not only a high surface area but also the possibility of easy introduction, into the mesoporous sieves structure heteroatoms (e.g. aluminium or niobium) which modify chemical properties of a created solid. An introduction of aluminium generates a weak acidity, whereas niobium is generally responsible for redox and Lewis acid properties of the catalysts. After iron introduction, depending on the nature of the matrix (i.e. its chemical composition), a different interaction between metal and a support can occur. As a result, various catalytic performances can be obtained.

Methanol oxidation is a reaction well adapted to characterise the redox and acidic active species on the catalyst surface. The structural information at the molecular level about the catalytic sites can be deduced from the catalytic behaviour of this reaction [e.g. 2–4]. A selective formation of methylal ($(CH_3O)_2CH_2$) can be assigned to a dual site including a redox dehydrogenating site and a Lewis acid centre, whereas the formaldehyde (CH_2O) formation requires only a redox dehydrogenating site. Methyl formate ($HCOOCH_3$) can be generated *via* oxidation reaction (redox centres) followed by the dehydration (on acidic sites). The surface basic sites are responsible for the $CO + CO_2$ formation. The selective formation of dimethyl ether (CH_3OCH_3) is assigned to the presence of strong acid sites. A great advantage of the use of methanol oxidation as a probe reaction is that it reveals only the catalytically active part and thus appears to be particularly useful to characterise supported catalysts. The most accurate characterisation could be obtained for the catalysts possessing a single kind of active sites. If the supports contain species which can also play a role of catalytic active centres it is useful to apply another test reaction additionally.

A good choice for the second test reaction seems to be methanol sulphurisation, i.e. the process in which alcohol interacts with the reducing agent (H_2S), contrary to the previously described process in which methanol was in the oxidising atmosphere.

The reaction between methanol and hydrogen sulphide has been studied on various oxides and sulphides [e.g. 5–9] and on zeolites [e.g. 10–13]. The main products are methanethiol (CH_3SH) and dimethyl sulphide (CH_3SCH_3). Also dimethyl ether can be formed as a side-product in the intermolecular dehydration process. It can also be an intermediate in the creation of dimethyl sulphide. The formation of dimethyl sulphide as well as methanethiol requires the presence of pairs Lewis acid–base centres. It is worthy to point out that the stronger basic sites are involved in the formation of methanethiol, whereas the stronger acid sites participate in the pro-

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duction of dimethyl sulphide. Thus the reaction between methanol and hydrogen sulphide allows the characterisation of acid–base pairs. Moreover, it distinguishes between the different strengths of acidic centres. It is noteworthy that hydrosulphurisation of methanol towards methanethiol is not only a well test reaction but it is also important for industrially thiol production (in the area of fine chemical production).

In this study we used both described reactions for the characterisation of catalytic activity of iron species located in three types of mesoporous matrices: SiMCM-41 (denoted MCM-41), AlSiMCM-41 (denoted AlMCM-41), and NbSiMCM-41 (denoted NbMCM-41).

2. Experimental

2.1. Preparation of the catalysts

The parent materials were MCM-41, AlMCM-41 and NbMCM-41 prepared in the following way: ethanol and aqueous ammonia were added to the surfactant solution – cetyltrimethylammonium chloride (Aldrich) in water. The solution was stirred for 10 min and tetraethoxysilane – TEOS (Aldrich) was added followed by aluminium sulphate (Polskie Odczynniki Chemiczne – Gliwice) or niobium(V) oxalate (CBMM, Brazil) – depending on the desired product. The ratios of Si/Al or Si/Nb in the gel were assumed as 32. After stirring for 2 h at the room temperature the resulting precipitate was recovered by filtration, washed with distilled water and dried in air at the room temperature. The template was removed by the calcination at 823 K for 8 h.

The Fe modification was carried out in three manners: wetness impregnation with aqueous or methanol solution of iron salt and chemical vapour deposition (CVD) techniques.

1. Wetness impregnation with aqueous solution of $Fe(NO_3)_3$

The outgased mesoporous material (353 K, 1 h in evaporator) was filled in with the appropriate amount (a volume of the solution ideally equal to the pore volume of the support) of an aqueous solution of iron(III) nitrate(V) (Aldrich) and located in an evaporator flask, where the catalyst was rotated and heated at 353 K for 45 min. Various concentration of Fe^{3+} in the solution was applied due to the desired iron loading (3 or 1 wt% – the last amount was applied only in the case of siliceous MCM-41 material). The impregnated powder was dried at 393 K for 12 h and then calcined at 823 K for 4 h in the oven.

2. Wetness impregnation from methanol solution of $Fe(NO_3)_3$

The procedure was almost the same as described above. The difference was in the use of methanol solution of iron(III) nitrate(V) (Aldrich) instead of aqueous one. This technique was applied only for siliceous MCM-41 molecular sieve.

3. Chemical vapour deposition (CVD)

The third type of catalysts was obtained by the CVD method using $FeCl_3$ (Merck) as a precursor of Fe species. The CVD reaction was carried out in the apparatus built according to the literature data [14]. The mesoporous molecular sieve was placed in a vertical quartz reactor and dried at 673 K for 2 h under a dry helium stream. Then the reactor was cooled down to 603 K. The helium steam was passed through the heated container filled with solid $FeCl_3$. Then the system was kept for 3 h at 603 K. The reaction product was cooled to room temperature. Finally, the catalyst was dried and calcined at 823 K in air flow for 4 h.

2.2. Nitrogen adsorption/desorption

The N_2 adsorption/desorption isotherms were obtained in a Micromeritics ASAP equipment, model 2010. The samples (200 mg) were pre-treated *in situ* under the vacuum at 573 K for 3 h. The surface area was calculated by the BET method. The pore size distributions (PSD), the pore sizes (the maximum of the PSD), and the mesopore volumes were determined from the adsorption isotherms.

2.3. X-ray diffraction (XRD) studies

XRD patterns were recorded by TUR 42 diffractometer with CuK radiation ($\lambda = 0.154$ nm).

2.4. Methanol sulphurisation

The reaction was carried out in a fixed-bed flow reactor. A catalyst with the weight of 0.02 g and size fraction of $0.5 < Ø < 1$ mm was placed into the reactor. The samples were activated in helium flow (40 cm^3 min^{-1}) at 723 K for 2 h. Next the temperature was reduced to 623 K. The reactant gas mixture of $CH_3OH/H_2S/He$, molar ratio of methanol to hydrogen sulphide of 1:2, was used with a total flow rate of 40 cm^3 min^{-1}. The reactor effluent was analysed using an online gas chromatograph (SRI 8610 GAS) with the FID and FPD detectors. Hydrogen was used as a carrier gas. Substrates and products were separated on 2 m column filled with GS-Q. The column was heated as follows: at 318 K for 18 min, then 8 K/min up to 508 K.

2.5. Methanol oxidation

The reaction was performed in a fixed-bed flow reactor. A catalyst with the weight of 0.02 g, size fraction of $0.5 < Ø < 1$ mm was placed into the reactor. The samples were activated in helium flow (40 cm^3 min^{-1}) at 723 K for 2 h. Next the temperature decreased to 573 K. The reactant gas mixture of CH_3OH and O_2, diluted by He, was used with a total flow rate of 40 cm^3 min^{-1}. The reactor effluent was analysed using an online gas chromatograph (SRI 8610 GAS) with the FID and TCD detectors. Hydrogen was used as a carrier gas. Substrates and products were separated on 2 m column filled with GS-Q. The column was heated as follows: at 308 K for 40 min, then 10 K/min up to 508 K.

3. Results and discussion

3.1. *Characterisation of the prepared materials*

Tables 1 and 2 present the fundamental data concerning the catalysts used in this study. All the mesoporous molecular sieves, modified with iron species, posses high surface areas typical of MCM-41 type materials, lower in the case of materials prepared *via* CVD. The latter also exhibits lower values of pore volumes and diameters. One can explain this phenomenon by filling of pores with iron oxide species as it was proposed in [15]. In fact only for these samples the separate iron oxide phase was detected using XRD measurements [16]. It suggests that iron oxides in CVD catalysts have a higher concentration or smaller dispersion than those in the materials prepared *via* the wetness impregnation method. However, at least for AlMCM-41 matrix, the spectroscopic studies published in [17] clearly showed that iron species are well dispersed in CVD catalysts. Therefore, one can postulate a high concentration of iron oxide species in these materials. It is worthy of notice that in the catalysts prepared *via* CVD another iron species ($Fe^{3+}—O—Fe^{2+}$) exists (table 2). Moreover, the samples based on AlMCM-41 matrix exhibit the aluminium extra framework species (table 2), which should be considered in the discussion of the catalytic activity of the prepared materials.

Taking into account textural/structural data (table 1) one can conclude that the nature of mesoporous molecular sieves, i.e. their chemical composition (Si, Si + Al or Si + Nb) do not play a crucial role in the structure properties of the Fe modified samples. The modification technique determines the iron species located on the mesoporous support.

Table 1
The texture/structure characterisation of iron containing catalysts

Catalyst*	Fe, wt%	BET surface area, $m^2\ g^{-1}$	Pore volume, $cm^3\ g^{-1}$	Pore diameter, nm
Fe/MCM-41 1%	1	–	–	–
Fe/MCM-41 3%	3	1160	0.78	3.33
Fe/MCM-41 3% Me	3	–	–	–
Fe/NbMCM-41 3%	3	1090	0.88	3.33
Fe/NbMCM-41 CVD	2.9	990	0.62	3.07
Fe/AlMCM-41 3%	3	1090	0.86	3.33
Fe/AlMCM-41 CVD	4.2	970	0.66	3.09

*In the symbols of catalysts slash indicates the impregnation; slash and CVD – the chemical vapour deposition; slash and Me – the impregnation in methanol solution.

Table 2
The characterisation of species on the catalyst surface

Catalyst	Preparation technique	Species
Fe/MCM-41 1% Fe/MCM-41 3% Fe/MCM-41 3% Me Fe/NbMCM-41 3% Fe/AlMCM-41 3%	Impregnation	Iron oxide species in extra framework position [16]; and in the case of AlMCM-41 Al-extra framework species [17]
Fe/NbMCM-41 CVD Fe/AlMCM-41 CVD	Chemical vapour deposition	$Fe^{3+}—O—Fe^{2+}$ clusters [17]; Fe-extra framework oxide species [16]; and in the case of AlMCM-41 Al-extra framework species [17]

3.2. *Methanol oxidation*

The question arises to what extent the nature of iron species located in the extra framework positions of all MCM-41 matrices applied in this work and its interaction with the support influence the selectivity of the catalytic process. Methanol oxidation was chosen as a test reaction. This process characterises both redox and acidic properties of the active centres. Iron species can play a role of both redox site and Lewis acid center. The results presented in table 3 indicate the domination of redox properties of all samples applied (also those without iron – AlMCM-41 and NbMCM-41), which appears in the production of formaldehyde (HCHO). The presence of 3 wt% of iron in the mesoporous matrix increases slightly the activity (methanol conversion) but does not significantly change the reaction selectivity. However, it does not take place in the case of a lower iron loading (1 wt%) or in the case of iron introduced from methanol solution.

In the case of Fe/MCM-41 3% material a selectivity towards formaldehyde is 99.7% and moreover, traces of dimethyl ether are detected. When the iron loading is reduced three times (for Fe/MCM-41 1%), a considerable amount of methyl formate is observed (27 % of selectivity). X-ray diffraction measurements did not

Table 3
Conversion of methanol and selectivity (related to the methanol conversion) after 300 min time on stream in the reaction between CH_3OH and O_2

Catalyst	Conversion of CH_3OH, %	Selectivity, %			
		$HCOOCH_3$	$(CH_3)_2O$	CH_4	
Fe/MCM-41 3%	98	99.7	–	0.3	–
Fe/MCM-41 1%	94	73	27	–	–
Fe/MCM-41 3% Me	64	–	100	–	–
NbMCM-41	95	100	–	–	–
Fe/NbMCM-41 3%	98	99.8	–	0.2	–
AlMCM-41	96	98		2	
Fe/AlMCM-41 3%	100	97.2	–	0.6	0.2

show a new different iron oxide phase which could be responsible for the selectivity change. A similar phenomenon was observed by Wachs *et al.* [3] who examined the oxidation of methanol on niobium containing silica. The selectivity towards methyl formate increases for the catalysts with a lower metal loading. This behaviour is explained by the presence of methoxy (CH_3O^-) groups on the catalyst surface. The lower iron loading is, the higher amount of methoxy groups occurs. At the low Fe loading a free surface of the support is accessible for both reagents, methanol and oxygen. The formation of methoxy group was assigned to the inferior activity of such catalysts. It requires the presence of pairs Lewis acid–base sites on the catalyst surface. In this work one can also observe a decrease of methanol conversion parallel to the growth of methyl formate selectivity in the following order: Fe/MCM-41 3% (conv. 98%; methyl formate selectivity 0) < Fe/MCM-41 1% (conv. 94%; methyl formate selectivity 27%) < Fe/MCM-41 3% Me (conv. 64%; methyl formate selectivity 100%). A significant role of the surface methoxy groups in the formation of methyl formate is supported by the activity and selectivity of the catalyst prepared from methanol solution of iron(III) nitrate(V). For the above mentioned material it was methyl formate which was the only product of methanol oxidation process. It is clear that the impregnation from methanol solution of iron salt does not only lead to the incorporation of iron species but also makes possible the surface methoxy groups formation.

It is common knowledge that surface methoxy groups are an intermediate in the formation of formaldehyde [4, 18]. It is important to stress that in the formation of methoxy species Lewis acid centres are involved. It is a reason for the high activity in the production of formaldehyde, shown by the pure matrices (NbMCM-41 and AlMCM-41). Both supports posses Lewis acid centre; NbMCM-41 in the form of framework Nb^+ species [19] and in AlMCM-41 extra framework aluminium species (table 2). The participation of Lewis acid sites in the methanol oxidation also explains why the various reducibility of iron species dependent on the nature of matrix as well as on the method of iron incorporation [16, 20, 21] do not influence the activity in methanol oxidation towards formaldehyde.

The above discussion of the results of methanol oxidation clearly shows that this reaction does not allow us to distinquish between the role of iron species and the Lewis acid sites originating from the supports. Therefore, this reaction does not characterise precisely the form of Fe on the catalyst surface. For that purpose the second test reaction sulphurisation of methanol was applied.

3.3. *Methanol sulphurisation*

The conversion of methanol and distribution of the reaction products are presented in table 4. So as to examine the influence of chemical composition of mesoporous sieves on the catalytic performance the reaction was also carried out using the pristine catalysts before iron introduction.

Taking into account data gathered in table 4 one can unequivocally certify the role of MCM-41 chemical composition, both in activity and selectivity of the reaction between methanol and hydrogen sulphide. This phenomenon is visible if one compares the properties of the materials before and after iron incorporation. The aluminosilicate material before the modification exhibits the highest activity (45%) whereas the pure silicate sample is totally non-active. Considering the conversion of methanol, the following sequence of the supports activity can be drawn: AlMCM-41 > NbMCM-41 ≫ MCM-41. Not only does the activity differ but also the selectivity significantly depends on the chemical composition of the pristine solid. It can be explained by the presence of different acid–base centres on the catalyst surface. The creation of methanethiol and dimethyl ether takes place with the participation of Lewis acid–base centres [9, 13, 22]. Concerning the aluminosilicate mesoporous molecular sieve such a pair can be formed by $Al^{\delta+}$ cation from extra framework position (Lewis acid site) and an oxygen from the framework, e.g. coordinated to aluminium in the framework. In the case of NbMCM-41 sample the Lewis acid site is represented by $Nb^{\delta+}$ cation in the framework or in the extra framework position and Lewis basic site by $NbO^{\delta-}$, which existence in niobiosilicate mesoporous molecular sieves has been previously found [23]. If one considers that the formation of methanethiol requires stronger Lewis basic sites compared to that involved in the production of dimethyl ether (this phenomenon is caused by the necessity of S–H cleavage in the creation of thiol) a stronger basicity of $NbO^{\delta-}$ species *vs.* $O^{\delta-}$ from the aluminosilicate framework could be postulated. The performance of $NbO^{\delta-}$ sites manifests in the selectivity to methanethiol, which is above 90%. The domination of acidity is expressed by the highest dimethyl ether formation on AlMCM-41 sample, whereas NbMCM-41

Table 4

The conversion of methanol and products distribution (related to the methanol conversion) after 300 min time on stream in the reaction between CH_3OH and H_2S

Catalyst	Methanol conv., %	Product distribution, %			
		$(CH_3)_2O$	CH_3SH	$(CH_3)_2S$	COS
MCM-41	0	–	–	–	–
AlMCM-41	45	76.0	13.0	11.0	Traces
NbMCM-41	17	7.5	90.2	2.3	–
Fe/MCM-41 3%	3	–	100	–	–
Fe/AlMCM-41 3%	45	26.6	51.5	21.8	Traces
Fe/NbMCM-41 3%	37	1.5	91.0	2.6	4.9
Fe/AlMCM-41 CVD	48	40.6	36.0	22.0	3.4
Fe/NbMCM-41 CVD	17	13.0	77.0	4.0	6.0

exhibits acidic–basic properties in which basicity is strong enough to catalyse the reaction pathway towards methanethiol.

As it was demonstrated above, the product distribution is strongly affected by the nature (the chemical composition) of the molecular sieve. After the modification of the parent materials one can notice that the location of iron species in the neighbourhood of niobium species leads to a high selectivity to methanethiol. However, depending on the modification procedure, which determines the kind of iron species formed (table 2), the methanethiol selectivity is the same (Fe/NbMCM-41 3%) or lower (Fe/NbMCM-41 CVD) than that on the pristine support (NbMCM-41). It is noteworthy that on the CVD catalyst the activity does not change after Fe introduction and Fe species are present not only in the form of Fe-oxide but also as Fe^{3+}—O—Fe^{2+}. The latter should exhibit the higher acidity *vs.* basicity and due to that the selectivity to dimethyl ether increases, whereas that to methanethiol decreases. Fe-oxides in the extra framework positions, which are the only iron form on Fe/NbMCM-41 3% material, enhances the activity and hardly changes the selectivity. It is because iron-oxide species creates Lewis acid–base pairs comparable with that from niobium species in the support.

In the case of AlMCM-41 modified samples the significant amounts of dimethyl ether and dimethyl sulphide were found in the reaction products (table 4). The introduction of iron does not increase the activity (methanol conversion) but meaningfully changes the selectivity (enhances both the methanethiol and dimethyl sulphide formation and decreases the dimethyl ether selectivity). It could suggest that iron-oxide species play a key role as Lewis acid–base pairs in the chemisorption of hydrogen sulphide. Contrary to Fe-modified Al-MCM-41 materials the incorporation of iron into niobiosilicate mesoporous molecular sieve does not significantly change the product selectivity but noticeably increases the catalytic activity (as discussed above). This difference is due to the various nature of active species on both supports, NbMCM-41 and AlMCM-41.

The influence of iron modification technique on the selectivity in the reaction between CH_3OH and H_2S is visible for AlMCM-41 based materials (table 4, figure 1). Before the introduction of iron, i.e. on the pristine support, dimethyl ether is the main product (76% after 300 min time on stream). In the presence of Lewis acid centres dimethyl ether can react with hydrogen sulphide to form dimethyl sulphide [13]. However, the formation of dimethyl sulphide can also occur *via* different reaction pathways. It can be formed in the direct reaction between two methoxy groups (generated by the dissociative adsorption of methanol) and hydrogen sulphide [10]. Figure 1 shows the selectivity to both, dimethyl ether and dimethyl sulphide, rather stable in time on stream, which allows the suggesting that dimethyl ether is not an intermediate in the creation of sulphide. Moreover, the selectivity towards Me_2O slightly increases indicating the modification of the catalyst surface during the reaction. Such a modification is probably due to the H_2S dissociation towards H^+, which generates Brønsted acidity on the catalyst surface involved in Me_2O formation. This effect is better pronounced if Fe is introduced onto AlMCM-41 and it is accompanied by a slightly decrease of thiol selectivity. One cannot exclude the reaction between methanethiol and alcohol towards dimethyl ether and hydrogen sulphide. Thus, the substitution of oxygen in dimethyl ether by sulphur from hydrogen sulphide postulated for zeolites [13] seems not to take place on the catalysts used in this work.

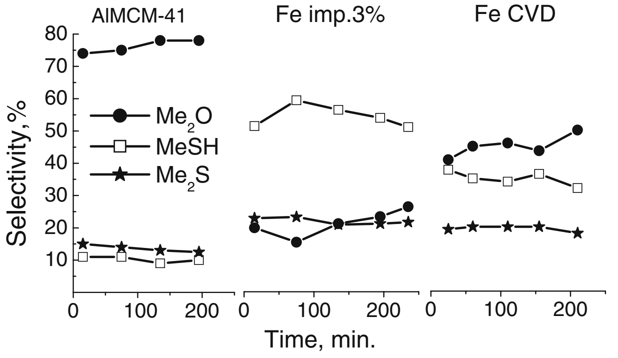

Figure 1. Selectivity (related to the methanol conversion) in the reaction between CH_3OH and H_2S for AlMCM-41 based materials.

Interestingly, the product distribution differs depending on the Fe modification procedure applied. The wetness impregnation leading to the location of iron oxides in the extra framework sites (table 2) increases much more basicity of the catalysts than the CVD technique. The latter causes the formation ofFe^{3+}—O—Fe^{2+} besides iron oxides. As a result the selectivity to thiol enhances more significantly on Fe/AlMCM-41 3% than on Fe/AlMCM-41 CVD material. Generally, it is clear that the introduction of iron species increases the reaction between chemisorbed methanol and hydrogen sulphide and inhibits the activity of the support (AlMCM-41) in the intermolecular dehydration of methanol towards dimethyl ether. This effect is more pronounced when iron is introduced *via* wetness impregnation procedure.

The role of the Fe modification procedure in the effectiveness of sulphurisation process is well illustrated by the comparison of methanol and hydrogen sulphide conversion plotted in figure 2. A bigger difference between the conversion of both reagents indicates the domination of the dehydration of alcohol over the sulphurisation reaction. It is evidenced that on Fe/Al-MCM-41 3% catalyst both curves are on the same level, whereas the highest difference is noted when the reaction is performed on a pure support. That indicates the

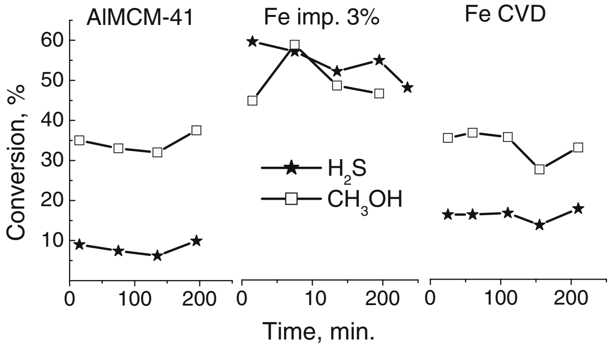

Figure 2. Conversion of methanol and hydrogen sulphide in the reaction carried out on AlMCM-41 based catalysts.

highest effectiveness of the extra framework iron oxide species in the reaction between methanol and hydrogen sulphide.

It is worthy of notice that the activity of iron containing silicate MCM-41 (ca. 3% of methanol conversion) is very poor in spite of a high concentration of iron oxide species on its surface. It indicates that iron oxide species cannot always act as pairs of Lewis acid–base centres active in the hydrosulphurisation of methanol. It depends on the support nature (chemical composition). The role of the support is the chemical interaction with the iron–oxide species making the Fe–O bond weaker and the interaction with the reagents stronger, and/or the support is a source of Lewis basic centres. Both features are characteristic of AlMCM-41 and NbMCM-41 but not of MCM-41 materials.

Moreover, it should be pointed out that among the reaction products the traces of COS are observed. The possibility of COS creation during the reaction between methanol and hydrogen sulphide was described elsewhere [13].

4. Conclusions

In both catalytic reactions studied within this work methoxy species are intermediates in the formation of final products. Moreover, both reactions involve the presence of Lewis acid–base pairs. However, the nature of the second reagent, oxygen or hydrogen sulphide, strongly influences the activity and selectivity of the reaction. Oxygen can be chemisorbed on the defects of the support and can create active species (Lewis basic sites) even on silicate MCM-41 materials. This is most probably a reason why under the conditions used in this work one cannot observe the role of the support and Fe species in the methanol oxidation. It is not a case of the reaction with hydrogen sulphide. The dissociative adsorption of both methanol and hydrogen sulphide requires the presence of Lewis acid–base pairs absent on MCM-41 samples. The various product distribution on iron-modified NbMCM-41 and AlMCM-41 catalysts is determined by the participation of active centres of the support and the nature of iron active species. The latter is conditional upon the modification procedure. The wetness impregnation of NbMCM-41 and AlMCM-41 with Fe salt leads to the most effective catalysts for the formation of sulphur organic products.

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