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Additional Information

**Partial oxidation of methane and methanol on FeO_x-, MoO_x- and FeMoO_x -SiO₂
catalysts prepared by sol-gel method: a comparative study**

by

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Abstract

FeOx-, MoOx and FeMoOx-SiO₂ materials prepared by a sol-gel procedure have been evaluated as catalysts for the partial oxidation of methane and methanol. The effect of decreasing the pH of the synthesis gel on the chemical nature of FeOx and MoOx species has been investigated. Characterization results show that low pH improves the dispersion of metal oxide species present in SiO₂ matrix. For FeOx/SiO₂ materials, the presence of dispersed FeOx species (rather than bulk Fe₂O₃) improves the selectivity to formaldehyde in the partial oxidation of methane and methanol. For FeMoOx/SiOx catalysts, dispersed species favor the selectivity to formaldehyde only for methane oxidation. In contrast, for bimetallic FeMoOx/SiOx system, a better dispersion does not improve the selectivity to the aldehyde in methanol oxidation. In spite of the fact that the activation temperature for methane oxidation is remarkably higher than that for methanol oxidation, catalytic results show that the most active and selective catalysts for the partial oxidation of methane are also the most effective materials for the partial oxidation of methanol.

Keywords: iron oxide; molybdenum oxide, methane; methanol; formaldehyde.

1. Introduction

Direct catalytic conversion of methane to methanol or formaldehyde has become a challenge in C1 hydrocarbon chemistry [1-5]. Many catalysts have been reported for the selective oxidation of CH₄ in both homogeneous and heterogeneous systems [2-4]. However, so far, no catalyst has demonstrated the combination of high conversion rate, selectivity, and stability that are required to make direct selective oxidation competitive against indirect oxidation via synthesis gas [2-5]. The main difficulty arises from the fact that the products of interest, i.e. methanol (CH₃OH) or formaldehyde (CH₂O), are more reactive than the methane molecule, and therefore susceptible to suffer consecutive oxidation to CO and CO_x under reaction conditions [2]. Among the materials used for direct oxidation of methane we can highlight catalysts with highly dispersed vanadium [6, 7], molybdenum [8-9] or iron [5, 10-13] species, but also Fe-containing mixed metal oxides, such as Fe-phosphates [11, 14,15] or Fe-molybdates [16], which are also considered as the most selective in the direct oxidation of methane to formaldehyde.

Heterogeneous iron-based catalysts have received attention for the selective oxidation of methane to formaldehyde using oxygen as an oxidant [5, 10-13]. In this way, it has been reported that doping silica with Fe³⁺ increases formaldehyde formation [5, 10]. On the other hand, FeO_x/SiO₂ catalysts prepared by the precipitation method are more effective to obtain formaldehyde than catalysts prepared by impregnation. This better performance is related to the presence of more dispersed iron species in the catalysts prepared by precipitation [10]. Likewise, it has been shown that Fe³⁺ cations or FePO₄ nanoaggregates introduced into mesoporous materials such as MCM-41 and SBA-15 are also effective for the selective oxidation of CH₄ to CH₂O [11,15]. Thus, it is suggested that the dispersion of iron sites is an essential factor to reach high selectivity towards oxygenated products such as CH₂O. However, there is no consensus on the structure of active iron

sites for the selective conversion of methane to formaldehyde. It has been proposed that Fe^{3+} mononuclear sites with tetrahedral coordination on silica are important for partial oxidation of alkanes [17], whereas two-dimensional FeOx oligonuclear sites could be related to the best catalytic performance for CH_2O formation [12,13]. However, isolated Fe^{3+} sites present lower catalytic activity than FeOx oligonuclear sites [12,13].

On the other hand, during the last three decades, catalysts with different physical and chemical properties have been studied for the selective transformation of methanol in order to produce useful chemicals like formaldehyde, acetic acid, and dimethyl ether. Thus, when a methanol molecule reacts with Brønsted acid centers, dimethyl ether is formed. On the other hand, when methanol reacts on redox sites (for example $\text{Mo}^{5+/6+}$, $\text{Fe}^{2+/3+}$, $\text{V}^{4+/5+}$) the main reaction product is formaldehyde and, to a lesser extent, other oxygenated products such as methyl formate and dimethoxymethane (obtained by partial oxidation of methanol) or carbon oxides (formed by total oxidation) [18-20].

Methanol can follow at least two reaction routes when used as a raw material in processes promoted by solid catalysts. The first one undergoes through oxidation reactions, which need molecular oxygen or oxygen supplied by the catalyst. The second path takes place through dehydration reactions, which do not need oxygen to occur. Except for the formation of dimethyl ether, which takes place by bimolecular dehydration of methanol, the remaining products need at least one oxidation step [18]. However, the formation of dimethyl ether is related to the ability of the catalyst to carry out dehydration processes, which is generally associated to the presence of acidic sites [18, 19]. Interestingly, the selective formaldehyde formation requires not strong acidic sites [18-25]. Three major situations can be distinguished in the process of catalytic oxidation of methanol which will influence product selectivity: i) strong acid sites will enhance the production of dimethyl ether, ii) strong basic sites will lead to the formation of carbon oxides and iii)

bifunctional materials (acidic and basic character, with active centers capable of yielding O^{2-} species) will lead to partial oxidation products, mainly formaldehyde [18].

One of the industrial methods to produce formaldehyde from methanol uses iron molybdate-based catalysts [22-25], developed after the first report of iron molybdate catalysts as a good option for the oxidation of methanol to formaldehyde in 1931 [24]. More recently, it has been suggested that in iron molybdate catalysts the presence of an excess of crystalline MoO_3 on the surface improves the catalytic performance during the methanol selective oxidation reaction [25].

In the present work, we want to check if catalysts which are selective to formaldehyde from methanol, hardly decomposing formaldehyde, can also maintain high selectivity from one of the most demanding molecules (methane), considering that in the methane to formaldehyde conversion, methanol is a reaction intermediate. Then, we show a comparative study of the partial oxidation of methane and methanol using FeO_x , MoO_x , and $FeMoO_x/SiO_2$ catalysts prepared by the sol-gel method. The catalysts were prepared by a sol-gel procedure following two different approaches: i) a standard sol-gel synthesis and; ii) a low pH sol-gel procedure. The results are discussed in terms of the dispersion of metal oxide species on silica, the interactions between the Fe and Mo sites and the chemical nature of the reactants.

2. Experimental

2.1. Preparation of catalysts

Catalysts were prepared by the sol-gel method using tetraethyl orthosilicate (TEOS 98%), iron acetate (99%) and ammonium molybdate tetrahydrate (98%) as precursors of silicon,

iron and molybdenum, respectively. Oxalic acid (99%) was added as a chelating agent. All precursors were acquired from Sigma Aldrich.

Iron, molybdenum or iron-molybdenum oxide materials supported on silicon oxide were prepared with 0.5 or 1.5 wt % (Fe+Mo). In the case of bimetallic FeMoO_x catalysts, an Fe:Mo wt. ratio of 1:1 was used. Catalysts are named as 0.5Fe/Si, 1.5Fe/Si, 1.5FeMo/Si, 1.5Mo/Si.

For the synthesis of the catalysts, a defined mass of oxalic acid was dissolved in ethanol with vigorous stirring until a homogeneous solution was achieved. On the other hand, the amount of iron or molybdenum precursor needed to obtain catalysts with the appropriate loading (0.5 or 1.5 wt %) was dissolved in ethanol. In another vessel, the required TEOS mass was taken. These previous solutions were mixed, and water was finally added according to the TEOS/oxalic acid/water molar ratio of 1/1/4. Subsequently, the gelation process was carried out at 70 °C for 7 h while stirring at 300 rpm, the materials were dried at 105 °C for 12 h and calcined at 750 °C for 6 h.

In the same way, additional catalysts were also prepared by sol-gel but adjusting the final mixture at pH=1, by the addition of nitric acid. These samples will be named as 0.5Fe/Si-pH or 1.5FeMo/Si-pH. All of these materials were dried at 105 °C for 12 h and calcined at 750 °C for 6 h. In such a way, during the sol-gel process, using metallic alkoxides like tetraethyl orthosilicate, and organic salts like iron acetate (II), the pH of the medium plays an interesting role in directing the type of gel to be obtained. The hydrolysis reactions that are carried out by this method are nucleophilic substitutions and the rates of hydrolysis and condensation are different depending on the pH of the medium. When the medium is acidic, a polymer-type gel is obtained, while if the medium is basic, a colloidal gel is obtained [26].

Additionally, an alternative catalyst was also prepared by incipient wet impregnation to compare its catalytic performance with materials prepared by sol-gel. The support used was commercial silica (Aerosil-200®) with a surface area of 200 m²/g (\pm 25m²/g) whereas the iron and molybdenum precursors were the same used in sol-gel method. Silica was impregnated with ethanolic solutions of the metal precursors (1.5 wt% metal loading with a Fe/Mo ratio of 1:1). Subsequently, the materials were dried at 105 °C for 12 h and calcined at 750 °C for 6 h using a heating ramp of 1 °C/min. The sample is named as 1.5FeMo/Si-imp.

Table 1 shows some characteristics of the catalysts synthesized.

2.2. Characterization of catalysts

Powder X-Ray diffraction (XRD) patterns were collected in a PANalytical X'Pert PRO diffractometer equipped with an X'Celerator detector in a Bragg-Brentano geometry using K α_1 radiation of copper. Crystallite size has been estimated using the Scherrer equation.

Diffuse reflectance UV–vis (DR–UV–vis) spectra were recorded on a Cary 5 equipped with a Praying Mantis attachment from Harric.

Temperature-programed reduction with H₂ (H₂-TPR) experiments were carried out in a Micromeritics Autochem 2910 equipped with a TCD detector, using 0.05 g of freshly calcined catalyst and increasing the temperature from room temperature to 800 °C with a heating ramp of 10 °C min⁻¹, under 10% H₂/Ar (vol.%) and a constant flow rate of 50 mL min⁻¹.

TEM Analysis: Morphological, compositional and structural analysis of Fe/ and Fe-Mo/SiO₂ samples were performed by high resolution transmission electron microscopy

(HRTEM) with a field emission gun TECNAI G2 F20 microscope operated at 200 kV, having the capabilities of selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDX) in the facilities of the Servei Central de Suport a la Investigació Experimental (SCSIE) at the University of Valencia.

All samples were analyzed by EDX in TEM microscope and the distribution of iron and molybdenum in the silica matrix was determined by using EDX-mapping in nanoprobe mode. In order to prepare the TEM samples, the FeOx/SiO₂ and FeMoOx/SiO₂ powder samples were treated by sonicating in absolute ethanol for a few minutes and a drop of the resulting suspension was deposited onto a holey-carbon film supported on a copper grid, which was subsequently dried.

Analyses by X-ray photoelectron spectroscopy (XPS) were carried out in a SPECS spectrometer equipped with a Phoibos 150 MCD-9 detector. The samples were irradiated under vacuum (10^{-9} mbar) with a non-monochromatic Al K α (1486 eV) X-ray source, at an analyzer pass energy of 50 eV and an X-ray power of 100 W. Each spectrum was referenced to C 1s signal (284.5 eV) prior to their analysis using CASA XPS software.

2.3 Catalytic tests

Methanol oxidation

Catalytic experiments for partial oxidation of methanol were carried out in a fixed-bed quartz tubular flow reactor at atmospheric pressure, in the 200-550 °C temperature range, using 100 mg of catalyst diluted with silicon carbide (SiC) (catalyst: SiC in a 1:2 wt. ratio). Silicon carbide was used to dilute the catalysts in the catalytic bed in order to prevent the presence of hot spots. The feed consisted of a molar ratio MeOH/O₂/N₂ = 6/13/81, for a total flow of 50-100 mL min⁻¹. Once the desired reaction conditions have been reached (flow and reaction temperature) we left a stabilization time of 45 minutes

before undertaking the analyses. The analyses of reactants and products were carried out by gas chromatography using a thermal conductivity detector (TCD) and with two different chromatographic columns [27]: i) Molecular sieve 5 Å (3 m length) and ii) RT-U-bond (30 m, 0.53 mm ID).

Methane oxidation

Catalytic experiments for partial oxidation of methane were carried out in a fixed-bed quartz tubular flow reactor at atmospheric pressure. The temperature range was between 400-650 °C using 0.05-0.25 g of catalyst diluted with SiC (catalyst/SiC in a 1:2 wt. ratio). The feed consisted of a molar ratio $\text{CH}_4/\text{O}_2/\text{He} = 32/4.3/63.7$, for a total flow of 25-100 mL min^{-1} . For a comparative purpose some catalytic tests using $\text{CH}_4/\text{O}_2/\text{He} = 6/13/81$ molar ratio was also conducted. When the desired reaction conditions were reached (flow and reaction temperature) we left a stabilization time of 45 minutes before the analyses. The analyses of reactants and products were carried out by gas chromatography using a thermal conductivity detector (TCD) and with two different chromatographic columns: i) Molecular sieve 5 Å (3 m length) and ii) RT-U-bond (30m, 0.53 i.d.).

3. RESULTS

3.1. Catalyst Characterization

Although the catalysts were prepared by sol-gel method, a modification of the synthesis conditions was undertaken on diluted FeOx and FeMoOx catalysts (by maintaining the final pH at 1 by the addition of a solution of nitric acid). We must indicate that the addition of nitric acid, within the limits of the buffer formed in solution, makes possible to keep a pH close to 1. By using this procedure, it is possible to have a slow gel formation, which

could lead to a better metal dispersion on the silica matrix. These catalysts, named as 0.5Fe/Si-pH and 1.5FeMo/Si-pH.

Figure 1 shows the XRD patterns of silica containing MoO_x, FeO_x and FeMoO_x catalysts. 1.5Mo/Si standard catalyst displays a similar XRD profile (Fig. 1, pattern c) than SiO₂ support, showing a broad signal centered at ca. 24°, related to the connectivity between SiO₄ tetrahedra in the amorphous silica matrix. No diffraction lines corresponding to molybdenum oxide were observed. This indicates that molybdenum is likely located on SiO₂ as isolated MoO_x species or, if present as MoO₃ entities, they display very low crystallinity.

To compare iron species, we calcined iron precursor (iron acetate II) at the same temperature (750 °C) of the catalysts, showing peaks at ca 33.01, 35.52, 49.45, 54.16, 62.62 y 64.19 related with hematite species JCPDS: 33-0664 [28-30]. In this way, standard 1.5Fe/Si and 1.5FeMo/Si catalysts show intense peaks corresponding to iron oxide Fe₂O₃-hematite, with an average crystallite size of ca. 20 nm (Fig. 1, patterns a, and b). XRD profile of standard bimetallic 1.5FeMo/Si catalyst also displays diffraction peaks of hematite (Fig. 1, pattern b), although showing lower intensity and a broader profile than 1.5Fe/Si catalyst. This suggests an improved dispersion of the iron sites on the silica when Mo is incorporated. The analysis of the FWHM of hematite lines indicates the presence of Fe₂O₃ domains in 1.5FeMo/Si of ca. 12 nm, which is lower than that observed in 1.5Fe/Si samples.

In materials with iron and molybdenum (1.5FeMo/Si, 1.5FeMo/Si-pH and 1.5FeMoSi-imp) we expected peaks for iron molybdate at ca: 13.83, 15.29, 19.41, 20.34, 21.71, 22.63, 22.95, and 24.90 [31]. However, no peaks corresponding to crystalline Fe₂(MoO₄)₃ were observed due to the oxides are very dispersed on the silica or the crystal size is so small

that they cannot be identified by X-ray diffraction since the detection limit is around 3-4 nm.

Figure 1. XRD patterns of iron and iron-molybdenum catalysts. For a comparative purpose the XRD pattern of pure Fe₂O₃ (hematite, prepared by calcination of iron acetate at 75°C for 2h) is also included. Catalysts: 1.5Fe/Si (a), 1.5FeMo/Si (b), 1.5Mo/Si (c), 0.5Fe/Si-pH (d), 1.5FeMo/Si-pH (e), 1.5FeMoSi-imp (f).

The control of the pH during the synthesis of FeOx and FeMoOx based catalysts led to the disappearance of Fe₂O₃ XRD peaks (Fig. 1, patterns d and e). This way, the acid treatment during the sol-gel process seems to improve the dispersion of the iron sites on SiO₂. In addition, 1.5FeMo/Si-imp catalysts synthesized by a conventional wet impregnation method also shows a good metal dispersion, since no clear peaks could be identified (Fig. 1, pattern f).

As the XRD does not provide information about non-crystalline species, the samples were analyzed by means of DR-UV-Vis spectroscopy (Figure 2). This way, different aggregation or coordination degrees of iron or molybdenum oxide species can be suggested. Unfortunately, there is some extent of overlapping among bands corresponding to Fe or Mo species which prevents an accurate interpretation of the spectra. However, interesting information can be extracted, especially if catalysts with the same composition and different preparation method are compared.

At least four different zones can be distinguished in the spectra [31-35]. Signals appearing at low wavelengths (Fig. 2, Zone I) are indicative of the presence of highly isolated species, such as tetrahedral Fe³⁺ or Mo⁶⁺ units. Bands at higher wavelengths (Fig. 2, Zone

II), are typically assigned to octahedral or dimeric Fe^{3+} or Mo^{6+} units, while signals over 300 nm (Fig. 2 Zone III), are assigned to polymeric Fe^{3+} or Mo^{6+} species and to small Fe_2O_3 clusters. Finally, bands over 450 nm (Fig. 2, Zone IV) are related to the presence of Fe_2O_3 or MoO_3 with low interaction with silica matrix.

Molybdenum species are highly dispersed in 1.5Mo/Si catalyst as the bands are mainly located within Zones I and II (Fig. 2, spectra c), suggesting the presence of isolated tetrahedral and octahedral MoO_x species. In the case of standard 1.5Fe/Si catalyst, several shoulders in the 450-600 nm range are observed. The high intensity of the shoulders at Zones III and IV, confirms the presence of Fe_2O_3 crystals with different level of interaction with the support. The standard bimetallic 1.5FeMo/Si catalyst also shows shoulders at high wavelengths (Fig. 2, spectra c, Zone IV), indicating the formation of iron and or molybdenum oxide crystallites. The relative intensity of bands in Zone IV in UV-VIS spectra suggests a higher proportion of Fe_2O_3 crystallites in the monometallic 1.5Fe/Si catalyst than in bimetallic 1.5FeMo/Si catalyst.

Figure 2. DR-UV-vis spectra of iron and iron-molybdenum catalysts. Catalysts: 1.5Fe/Si (a); 1.5FeMo/Si (b); 1.5Mo/Si (c); 0.5Fe/Si-pH (d); 1.5FeMo/Si-pH (e); and 1.5FeMo/Si-imp (f).

It is noteworthy to mention that acid treatment during the synthesis leads to a decrease in the relative intensity of UV-VIS bands at higher wavenumbers for 1.5Fe/Si-pH and 1.5FeMo/Si-pH samples (Fig.2, spectra d and f respectively). This means that decreasing the pH of the synthesis gel, the dispersion of metal oxide species on SiO_2 improves.

Finally, supported 1.5FeMo/Si-imp catalyst, prepared by impregnation, presents a UV-VIS spectrum similar to that of 1.5FeMo/Si-pH (Fig. 2, spectrum f). However, it displays a low intensity shoulder at ca. 550 nm (Zone IV), indicating lower dispersion of metal oxide species on the surface, i.e. a higher concentration of bulk MoO₃ or Fe₂O₃.

As commented previously, the transformation of methanol and methane into formaldehyde is related to the presence of surface redox pairs, able to supply oxygen species via Mars-Van Krevelen mechanism. Therefore, reducibility studies are of paramount importance to understand the catalytic behavior of these materials in both methanol and methane transformation.

Temperature programmed reduction (TPR-H₂) profiles are displayed in Figure 3. TPR-H₂ profile of 1.5Mo/Si catalyst shows a broad reduction signal with an onset temperature of ca. 250 °C, and two maxima centered at 410 and 499 °C (Fig. 3, c). These peaks must be related to the reduction of the Mo⁶⁺-dispersed species detected. Reduction profile of the standard 1.5Fe/Si catalyst (Fig. 3, a) is not very clean since, according to the DR-UV-VIS results, it shows the coexistence of several iron species with different chemical nature. However, it presents the highest proportion of Fe₂O₃ crystallites as observed by XRD. Then, TPR-H₂ profile of 1.5Fe/Si is characterized by the presence of three peaks at 348, 457 and 623 °C, which can be associated to Fe₂O₃ → Fe₃O₄ (348 °C), Fe₃O₄ → FeO (457 °C) and FeO → Fe (623 °C) (Fig. 3, a) [36-38]

In the case of the 0.5Fe/Si-pH sample (Fig. 3, d), two main reduction signals are observed, one at 420 and another one at 623 °C, with two shoulders at ca. 300 and ca. 500 °C. In this case, the maximum in hydrogen uptake shifts to lower temperatures, indicating a higher reducibility with respect to the standard 1.5Fe/Si catalyst.

Considering bimetallic 1.5FeMo/Si, 1.5FeMo/Si-pH and 1.5FeMo/Si-imp samples (Fig. 3, b, d and f) the reduction process can be attributed at lower temperatures (between 400 - 450°C) to the reduction of α -Fe₂O₃ to Fe₃O₄ [39] and MoO₃ to MoO₂ [40]. On the other hand, at higher temperatures (above 600 °C) the reduction of Fe²⁺ (FeO to Fe) and Mo⁴⁺ (MoO₂ to Mo) can also take place. In this way, the influence of the synthesis method on the reducing capacity of the catalysts is also observed (Fig. 3, b, d and f). Thus, for the catalyst prepared by the sol-gel method without modifying the pH (1.5FeMo/Si) it is observed that the highest hydrogen consumption occurs at 499 °C, similarly as for the catalyst synthesized by impregnation (1.5FeMo/Si-imp). On the other hand, the highest hydrogen consumption for the catalyst synthesized by the sol-gel method modifying the pH (1.5FeMo/Si-pH) takes place at 410 °C. This again confirms the influence of the acidic medium during synthesis. Then, at low pH there are more dispersed metal species and low clustering. This is observed for the lowest peak intensity at lowest temperature (410 °C) in the catalyst synthesized by modifying the pH (Fig. 3, d).

On the other hand, the traditional sol-gel method leads to: i) occlusion of the species inside the matrix of the support and ii) formation of metal aggregates. In this way, for the catalyst (1.5FeMo/Si) a large peak is evident at higher temperatures (499 °C). This confirms the two observations suggested above; occlusion of the metallic species and formation of aggregates, generating a shift towards higher reduction temperatures (Fig. 3, b). Finally, the catalyst prepared by the impregnation method (1.5FeMo/Si-imp) also shows a peak of maximum consumption at 499 °C, related to the formation of aggregates of metallic species on the support surface (Fig. 3, f).

Figure 3. TPR-H₂ results of iron and iron-molybdenum catalysts. Catalysts: 1.5Fe/Si (a); 1.5FeMo/Si (b); 1.5Mo/Si (c); 0.5Fe/Si-pH (d); 1.5FeMo/Si-pH (e); and 1.5FeMo/Si-imp (f).

In order to shed some light on the morphology and dispersion of supported metal oxide species, selected samples were analyzed by TEM. Figure 4 shows low magnification TEM micrographs of 0.5Fe/Si and 0.5Fe/Si-pH catalysts. As it can be observed, the sample synthesized in acid media (0.5Fe/Si-pH, Fig. 4A) presents well dispersed nanoparticles, displaying low density and low crystallinity.

Figure 4. Low magnification TEM micrographs of 0.5Fe/Si-pH (A) and 0.5Fe/Si (B) and EDX-mapping of Fe and Si of a region of 0.5Fe/Si sample.

Two types of particles were observed in 0.5Fe/Si-pH catalyst: i) small grain size nanoparticles (less than 1.5 nm); and ii) iron oxide particles ranging from 2 to 10 nm. A similar distribution was observed in 0.5Fe/Si catalyst, although in this case the nanoparticle size was bigger than 10-15 nm.

The distribution of iron oxide species on SiO₂ was further confirmed by EDX analysis. EDX-mapping shows that, overall Fe species is well dispersed on the silica when the catalyst is synthesized in acid media (0.5Fe/Si-pH).

Figure 5 presents TEM micrograph and the corresponding EDX map of supported FeMoO_x catalyst prepared at low pH (1.5FeMo/Si-pH). In this particular case, TEM

analysis does not show any agglomeration of metal oxide species, i.e. the sample is composed of well-dispersed nanoparticles (less than 1.5 nm) with low crystallinity.

Figure 5. Low magnification TEM micrographs of and its corresponding EDX-mapping of Si, Fe and Mo in 1,5FeMo/Si-pH catalyst.

In fact, EDX maps show that Fe and Mo are well dispersed within the same position on SiO₂, i.e. no segregation of Fe or Mo was observed in this material. This suggests an effective interaction between Fe and Mo metal oxide species in this catalyst.

1.5FeMo/Si catalyst, synthesized by the standard sol-gel method, was also analyzed by TEM (Fig. S1, supporting information). Unlike the sample synthesized at low pH, two different areas are observed in this sample. The first one shows similarities with 1.5FeMo/Si-pH sample, displaying a homogeneous distribution of Mo and Fe on the SiO₂ matrix. The second area is composed by iron oxide nanoparticles with size ranging from 5 to 50 nm (Figure S1), in coexistence with low amounts of Mo. In addition, SAED pattern confirms the crystalline nature of these particles, which can be indexed to Fe₂O₃-hematite structure (Fig. S1A).

To get further insights into the effect of the acid treatment on the nature of supported metal oxide species, selected materials were analyzed by XPS (Figure 6 and Table 1). Table 1 presents the surface concentration of cationic species and Mo/(Mo+Fe) atomic ratios for supported FeO_x and FeMo_x catalysts. When analyzing the surface composition of supported FeMoO_x materials, enrichment in Mo with respect to the theoretical composition is observed for both acid treated and non-acid treated samples. This effect has already been observed in Fe-Mo-O system, and could be assigned to the segregation of MoO₃, although the formation of surface iron molybdate phases is also possible [34].

Figure 6A displays Fe 2*p* core-level XPS spectra of SiO₂-supported FeOx and FeMoOx catalysts synthesized by the sol-gel method. All the materials show 2*p*_{3/2} and 2*p*_{1/2} peaks at B.E. values of ca. 711.5 and 725.1 eV, respectively, which can be ascribed to the presence of Fe³⁺ species (Fig. 6A) [41]. Although the spectra show a very broad profile (due to low metallic content in the samples), broader Fe 2*p* peaks are observed when the catalysts are synthesized in acid media (Fig. 6A, spectra b and d), suggesting a higher dispersion of Fe³⁺ species when the synthesis is carried out at low pH.

The nature of Mo surface sites in Mo-containing catalysts was also analyzed by XPS. Figure 6B shows Mo 3*d* core-level XPS spectra of SiO₂-supported FeMoOx catalysts synthesized by the sol-gel method. Both spectra can be fitted to two single peaks, displaying their Mo 3*d*_{5/2} components at B.E. of ca. 232.6 and 235.8 eV. The peak centered at 232.6 eV can be assigned to the presence of Mo⁶⁺ surface sites either in MoO₃ or Fe₂(MoO₄)₃ [42], while the signal observed at higher B.E. values (235.8 eV) can be ascribed to the presence of monomeric/polymeric MoO_x species [36]. Interestingly, the relative intensity of the high binding energy signal increases when the catalysts are prepared in acid media (Fig. 6B, spectra c and d). This indicates that, as it was observed for Fe³⁺ sites, a low pH during the synthesis also improves Mo⁶⁺ dispersion on SiO₂.

Figure 6. Fe 2*p* (A) and Mo 3*d* (B) core-level XPS spectra of SiO₂-supported FeOx and FeMoO_x synthesized by the sol-gel method. a) 0.5Fe/Si; b) 0.5Fe/Si-pH; c) 1.5FeMo/Si-pH; d) 1.5FeMo/Si-pH. Red spectra represent samples prepared in acid media.

According to this, the dispersion of metal oxide species on SiO₂ in bimetallic FeMoOx catalysts is improved when the synthesis is carried out at low pH. Interestingly (as

observed by UV-VIS), bimetallic FeMoO_x catalyst prepared by a simple impregnation method (1.5FeMo/Si-imp) presents a better dispersion than the catalyst prepared by the standard sol-gel method (1.5FeMo/Si). This low dispersion on standard 1.5FeMo/Si catalyst should be due to the inappropriate pH during the synthesis, which leads to the aggregation of metal oxide species. Overall, the dispersion of metals on the surface of bimetallic catalysts follows the trend: 1.5FeMo/Si-pH > 1.5FeMo/Si-imp > 1.5FeMo/Si.

3.1. Catalytic results for Methanol oxidation

Supported iron, molybdenum and mixed iron/molybdenum oxide catalysts prepared by the sol-gel method have been tested in the oxidation of methanol (Table 2). The catalytic results show that formaldehyde and carbon oxides were the main reaction products, although low amounts of dimethyl ether, methyl formate and dimethoxymethane were also observed.

Fe-free 1.5Mo/Si catalyst shows low capacity for methanol activation and low selectivity to formaldehyde, displaying a relatively high formation of dimethyl ether. Monometallic 0.5Fe/Si and 1.5Fe/Si catalysts also show a low tendency to form formaldehyde in a selective way. However, the methanol conversion achieved is one order of magnitude higher than that of monometallic 1.5Mo/Si sample. Interestingly, 1.5FeMo/Si sample displays the highest activity and selectivity to formaldehyde, indicating a synergetic effect between molybdenum and iron oxide species.

On the other hand, the control of the pH (low pH values) during the preparation method has demonstrated to be of paramount importance. Then, a drastic increase of methanol conversion (from 51 to 82%) and selectivity to formaldehyde (from 38% to 71%) is observed for 0.5FeMo/Si-pH, with respect to standard 0.5Fe/Si and 1.5Fe/Si catalysts.

Conversely, pH control led to a slight decrease in both formaldehyde formation and catalytic activity in the case of 1.5FeMo/Si-pH catalyst, comparing with standard 1.5FeMo/Si material (Table 2). For comparative purpose, another FeMoOx catalyst was prepared by a simple impregnation method (1.5FeMo/Si-imp, see Experimental section), and evaluated in methanol transformation. In this particular case, the catalyst displays a similar selectivity to formaldehyde than the standard 1.5FeMo/Si catalyst, but showing a higher catalytic activity (Table 2).

Overall, the acid treatment seems to have different effects depending on the catalyst composition. The lowest activity and selectivity to formaldehyde in methanol transformation has been observed with monometallic 0.5Fe/Si, 1.5Fe/Si and 1.5Mo/Si catalysts. However, when 0.5Fe/Si catalyst is synthesized at low pH (0.5Fe/Si-pH), a drastic increase in both activity and selectivity to formaldehyde is observed. Conversely, the acid treatment has a deleterious effect in the case of supported FeMoOx catalyst (1.5FeMo/Si-pH), decreasing both the activity and the selectivity to formaldehyde.

3.2. Catalytic results for Methane oxidation

Monometallic and bimetallic catalysts were also tested in methane oxidation (Table 3). Initially, the catalytic tests were carried out at the same conditions than methanol transformation (reaction temperature 450 °C, catalyst weight 0.1 g, total flow 50 mL min⁻¹ and feed ratio CH₄/O₂/He: 6/13/81 molar). In all cases, no conversion was observed because not even traces of reaction products were detected. In order to achieve appreciable activity, the reaction temperature had to be increased until 600-650 °C. Unfortunately, under these conditions formaldehyde was obtained as minority, CO and CO₂ being the main reaction products. According to this, the experiments were

undertaken at lower oxygen concentration and higher methane-to-oxygen ratio ($C_1/O_2/He$: 32/4.3/63.7 molar ratio, see Figure 1), with the aim of mitigating COx formation.

Unlike methanol oxidation, only three reaction products, formaldehyde (CH_2O), CO and CO_2 , were observed in methane oxidation tests. Methanol was not detected in any of the experiments conducted. Table 3 shows the catalytic performance of SiO_2 -supported FeOx and FeMoOx catalysts in the oxidation of methane at 650 °C. Standard 1.5Mo/Si catalyst presents very low reactivity and low selectivity to formaldehyde, whereas 1.5Fe/Si shows a catalytic activity 5 times higher. Interestingly, the standard bimetallic 1.5FeMo/Si catalyst maintains similar selectivity to formaldehyde, but at higher methane conversion. Nevertheless, to properly compare the selectivity to formaldehyde, the conversion must be fixed, since a drastic decrease in formaldehyde selectivity is observed when the methane conversion increases. Thus, if the selectivity to formaldehyde at isoconversion (2%) is compared, bimetallic 1.5FeMo/Si catalyst presents much higher values than monometallic 0.5Fe/Si and 1.5Fe/Si catalysts.

The acid treatment during the preparation procedure resulted, compared to the standard catalysts, in an increase of both methane conversion and selectivity to formaldehyde. Regarding formaldehyde formation, the most selective catalyst was 0.5Fe/Si-pH, followed by bimetallic 1.5FeMo/Si-pH. At 2% methane conversion 0.5Fe/Si-pH catalyst presents a relatively high selectivity to formaldehyde of ca. 34%.

The bimetallic catalyst prepared by impregnation (1.5FeMo/Si-imp) showed an intermediate catalytic behavior in both catalytic activity and selectivity to formaldehyde between those prepared by sol-gel method with or without acidification.

3. Discussion

According to the catalytic results (Tables 2 and 3) the reactivity of methane is remarkably lower than that of methanol. Then, using the same reaction conditions (catalysts, contact times and feed) we have found that catalysts achieving a 60 % conversion in methanol transformation at 450 °C (Table 2), only reach methane conversions lower than 5 % at 650 °C (Table 3). Therefore, an accurate comparison is not easy to conduct. For example, the adsorption of methane on supported iron or molybdenum oxide at 450 °C is almost negligible, whereas methanol strongly adsorbs on metallic sites. Apart from that, the C-H bond energy is considerably higher in the case of methane and therefore it is more difficult to activate.

The main problem to obtain partial oxidation products from alkanes, such as formaldehyde from methane, is the fact that the molecules of the desired product are remarkably more reactive than the reactant. This way, if methane can be activated, formaldehyde will be more easily decomposed, yielding carbon oxides. Figures 7 and 8 show the evolution of the selectivity to formaldehyde with methane or methanol conversion for some representative catalysts. The experiments were carried out by changing the contact time and maintaining the same feed ratio and reaction temperature.

Figure 7. Variation of the selectivity to formaldehyde vs methane conversion at 650 °C. Catalysts: (■) 0.5Fe/Si-pH, (▲) 1.5FeMo/Si, (●) 1.5FeMo/Si-pH. Experimental conditions in text, Methane:O₂:He = 32/4.3/63.7 molar ratio.

As it can be observed the selectivity to formaldehyde sharply drops with the methane conversion (Fig. 7). Thus, for the most selective catalysts (i.e. 0.5Fe/Si-pH), at 650 °C the selectivity to formaldehyde is 50 % at 1% methane conversion. However, it drastically

drops when increasing methane conversion up to 5% (down to ca. 23 % selectivity to formaldehyde). Conversely, using the same set of catalysts in methanol oxidation at 450 °C, a relatively high selectivity to formaldehyde is achieved (62-75 %), which is maintained constant even at high methanol conversion (70-80 %) (Fig. 8).

Figure 8. Variation of the selectivity to formaldehyde vs methanol conversion at 450 °C. Experimental conditions in text, i.e. Methanol:O₂:He = 6/13/81 molar ratio. For comparison it has been also inserted the catalytic results for methane oxidation (as in Fig. 7).

Then, under these conditions, the contact of formaldehyde with the iron/molybdenum oxide sites does not lead to overoxidation. On the other hand, a drastic decomposition of formaldehyde into carbon oxides is observed when the same active sites are in contact with formaldehyde at 650 °C, like in the case of methane oxidation. Therefore, the extreme differences observed in the yields to formaldehyde from methane (1.3% in the best case) and methanol (ca. 55%) seem to be due to the different reaction temperature required for the activation of methane and methanol.

Despite the different reaction conditions used, a certain correlation of the catalytic parameters has been observed in the oxidation of methane and methanol (Figures 9 and 10). Then, for both reactions the least active catalyst is 1.5Mo/Si, followed by the standard Fe/Si catalysts. The most active samples are the bimetallic FeMoO_x catalysts and 0.5Fe/Si-pH, synthesized in acid media.

Figure 9. Variation of activity for methane conversion vs activity for methanol conversion. Note: Catalytic activity in methane transformation in mol_{CH₄} kg_{cat}⁻¹ h⁻¹ and in

methanol transformation in $\text{mol}_{\text{CH}_3\text{OH}} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$. Reaction conditions as in Tables 2 and 3. Symbols: (■) Mo/Si; (■) Fe/Si; (■) FeMo/Si samples.

A similar trend has been observed regarding the selectivity to formaldehyde. Thus, supported FeMoOx catalysts (catalysts prepared by sol-gel method and by impregnation) and 0.5Fe/Si-pH are the most selective materials.

For methane oxidation the selectivity to formaldehyde at isoconversion conditions varies according to the order: 0.5Fe/Si-pH > 1.5FeMo/Si-pH > 1.5FeMo/Si-imp > 1.5FeMo/Si > 0.5Fe/Si > 1.5Fe/Si > 1.5Mo/Si. It seems that, at the reaction temperature studied, iron oxide species are more selective than molybdenum oxide species and, among Fe^{3+} species, the higher the dispersion, the higher the selectivity to formaldehyde. The same correlation between selectivity to formaldehyde and metal oxide dispersion has been observed for supported FeMoOx samples (1.5Fe/Si-pH > 1.5FeMo/Si-imp > 1.5FeMo/Si).

In methanol oxidation iron species seem to be the most selective ones, although the presence of molybdenum plays a positive role. This is in agreement with the fact that the industrial catalysts for the selective oxidation of methane contain Fe and Mo [24,34].

Figure 10. Relationship between the selectivity to formaldehyde (achieved from methane, at 650 °C and a methane conversion of 2%) with the selectivity to formaldehyde (achieved from methanol, at 450 °C and a methanol conversion of 50%). Reaction conditions as in Tables 2 and 3. Symbols: (■) Mo/Si, (■) Fe/Si, (■) FeMo/Si samples.

It is well known that, in methanol oxidation, the simultaneous presence of iron and molybdenum is required to obtain optimal results from a commercial viewpoint [43-45]. However, the role of each component is still under discussion. It seems that the surface of industrial selective catalysts consists of molybdenum oxide [43, 44] whereas the presence of Fe in the surface is negative because of the tendency of iron oxide to form carbon oxides [45]. However, molybdenum oxide alone is not a suitable catalyst. Although initially MoO₃ can be highly selective to formaldehyde, it presents a low reactivity due to its low re-oxidation capacity below 500 °C. Then, the presence of iron oxide is required, more than as an active site, but as a continuous supplier of oxygen to the selective Mo sites. Then, the preferred location of iron sites seems to be the sub-surface, avoiding a direct contact with the reactant. XPS analyses conducted on supported FeMoOx catalysts are in agreement with this assumption, showing Mo surface enrichment in all cases.

According to our results, dispersed iron species have resulted to be highly selective in methanol transformation. In addition, supported FeMoOx catalysts have also led to optimal catalytic performance, probably due to the fact that the materials contain both Fe³⁺ and Mo⁶⁺ sites, where iron supplies oxygen and improves re-oxidation of Mo sites. A possible explanation to this observation would be that a low pH during the synthesis favors the dispersion of MoOx species at the expense of Mo⁶⁺ sites similar to those found in MoO₃ or Fe₂(MoO₄)₃ (as deduced from XPS analyses). These non-dispersed surface sites have been reported to be highly selective in the partial oxidation of methanol to formaldehyde.

In the present work, a sol-gel method has been used to achieve a higher dispersion of metal oxides on the silica matrix. This high dispersion has been achieved when the pH was controlled during the synthesis. Our results indicate that the most selective sites to

produce formaldehyde from methane are dispersed Fe^{3+} species. This agrees with most of studies in methane oxidation in which the presence of Fe_2O_3 crystallites must be avoided [8]. However, the exact nature of the most selective species does not remain clear. Isolated tetrahedral Fe^{3+} species on silica have been proposed as the active Fe sites [46], although other authors propose that 2D oligomeric FeO_x are more selective than isolated species [14]. Molybdenum supported catalysts have been also reported to be capable of transforming methane into formaldehyde. A high dispersion of molybdenum on the support leads to good catalytic performance [47,48], although some authors have proposed that MoO_x species are more selective to formaldehyde than isolated MoO_x species [49]. Overall, the sol-gel method employed in the present article together with the use of nitric acid to decrease the pH of the synthesis gel, lead to FeO_x or FeMoO_x catalysts with high dispersed metal oxide species on SiO_2 . Non-acid treated samples present lower dispersion of the metals on the support, as it is corroborated by several characterization techniques (XRD, TEM and DR-UV-Vis.), which show the presence of bulk Fe_2O_3 crystallites with low interaction with the support. The better dispersion induced by the acid treatment leads to an increase in formaldehyde formation during methane oxidation.

Regarding methanol oxidation on monometallic FeO_x catalysts, the selectivity to formaldehyde is favored when the synthesis is carried out in acid media, due to an enhanced dispersion of metal oxide species on SiO_2 . However, this effect is not observed in supported FeMoO_x catalysts.

Finally, it is worth mentioning that a parallelism in the catalytic activity and the selectivity to formaldehyde between methane and methanol oxidation has been observed. However, methane requires remarkably higher reaction temperatures to achieve comparable conversions to those obtained with methanol. Due to this, formaldehyde hardly

decomposes from methanol at 400-450 °C, while it readily decomposes from methane at 650 °C.

4. Conclusions

The control of the pH in the preparation by sol-gel method of catalysts of iron and iron-molybdenum with silica highly improves the dispersion of the metals on SiO₂. This better dispersion leads to an important increase in the formaldehyde formation from methane. However, metal oxide dispersion in silica matrix is not that important for the partial oxidation of methanol to formaldehyde. Thus, in the case of methanol oxidation the highest selectivity to formaldehyde was achieved with acid-treated FeO_x/SiO₂ catalysts, but also with bimetallic FeMoO_x/SiO_x catalyst synthesized by standard sol-gel procedure or by impregnation. The catalytic results obtained in methane and methanol oxidation show a certain correlation for both catalytic activity and selectivity to formaldehyde in spite of their different reactivity.

The different stability of formaldehyde on the same active sites for both reactions (low from methane and high from methanol oxidation) is likely due to the different reaction temperatures required for the activation of methane and methanol. Then at 450°C formaldehyde is quite stable whereas at 650 °C readily decomposes into carbon oxides.

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Table 1. Characteristics of the catalysts synthesized.

Catalyst	Acid	Fe	Mo	S _{BET}	Fe+Mo/(Fe+Mo+Si)	Mo/(Fe+Mo) at.	
	Treatment	wt.%	wt.%	(m ² /g) ^a	at. ratio (XPS)	Bulk	Surface (XPS)
0.5Fe/Si	No	0.5	0	491	0.25	-	-
1.5Fe/Si	No	1.5	0	nd	nd	-	-
1.5Mo/Si	No	0	1.5	nd	nd	-	-
1.5FeMo/Si	No	0.75	0.75	437	0.71	0.37	0.66
0.5Fe/Si-pH	Yes	0.5	0	nd	0.21	-	-
1.5FeMo/Si-pH	Yes	0.75	0.75	540	0.78	0.37	0.67
1.5FeMo/Si-imp	-	0.75	0.75	nd	nd	0.37	nd

a) nd= not determined.

Table 2. Methanol oxidation at 450 °C on Fe and/or Mo catalysts^a

Catalyst	Methanol conversion (%)	Selectivity (%) ^b				Activity ^c	STY _{CH₂O} ^d	Selectivity to CH ₂ O at X=50%
		CH ₂ O	CH ₃ OCH ₃	CO	CO ₂			
0.5Fe/Si	45	26	4	30	40	33.0	8.6	26
1.5Fe/Si	51	38	2	31	29	37.4	14.2	38
1.5Mo/Si	4.2	43	11	28	12	3.08	1.32	35
1.5FeMo/Si	65	74	3	21	2	47.6	35.2	75
0.5Fe/Si-pH	82	71	1	25	2	60.0	42.6	76
1.5FeMo/Si-pH	56	66	3	28	3	41.0	27.1	66
1.5FeMo/Si-imp	84	77	1	17	5	61.5	47.4	77

^a Reaction conditions: CH₃OH:O₂:He = 6/13/81 molar ratio, 450 °C, catalyst weight = 0.1 g, Total flow = 50 mL min⁻¹; ^b Other products observed are dimethoxymethane and methyl formate as minorities; ^c Activity in mol_{CH₃OH} kg_{cat}⁻¹ h⁻¹ and STY in mol_{CH₂O} kg_{cat}⁻¹ h⁻¹.

Table 3. Methane oxidation at 650 °C on Fe and/or Mo catalysts^a.

Catalyst	Methane conversion (%)	Selectivity (%) ^b			Catalytic activity ^c	STY _{CH₂O} ^c	Selectivity to CH ₂ O (at X= 2%)
		CH ₂ O	CO	CO ₂			
Blank run	< 0.1	0	0	100	-		-
0.5Fe/Si	1.0	22.5	47.0	30.5	3.91	0.88	12
1.5Fe/Si	1.5	10.2	54.1	35.7	5.86	0.60	8
1.5Mo/Si	0.3	10.5	55.0	34.6	1.17	0.12	4
1.5FeMo/Si	2.4	11.0	56.4	32.6	9.38	1.03	15
0.5Fe/Si-pH	2.7	29.8	41.5	28.7	10.5	3.14	34
1.5FeMo/Si-pH	3.3	15.1	50.8	34.1	12.9	1.76	25
1.5FeMo/Si-imp	2.8	12.5	55.3	32.2	10.9	1.36	20
0.5Fe/Si-pH ^d	4.8	5.2	55.2	39.6	37.3	0.36	n.a

^a Reaction conditions: C₁:O₂:He = 32/4.3/63.7 molar ratio, catalyst weight = 0.1 g, Total flow = 50 ml min⁻¹; ^b No other products have been detected; ^c Catalytic activity in mol_{CH₄} kg_{cat}⁻¹ h⁻¹ and space-time yield, STY, in mol_{CH₂O} kg_{cat}⁻¹ h⁻¹; ^d

Reaction conditions: C₁:O₂:He = 6/13/81 molar ratio, catalyst weight = 0.05 g, Total flow = 50 ml min⁻¹.

Caption to figures

Figure 1. XRD patterns of iron and iron-molybdenum catalysts. For a comparative purpose the XRD pattern of pure Fe₂O₃ (hematite, prepared by calcination of iron acetate at 75°C for 2h) is also included. Catalysts: 1.5Fe/Si (a), 1.5FeMo/Si (b), 1.5Mo/Si (c), 0.5Fe/Si-pH (d), 1.5FeMo/Si-pH (e), 1.5FeMoSi-imp (f).

Figure 2. DR-UV-vis spectra of iron and iron-molybdenum catalysts. Catalysts: 1.5Fe/Si (a); 1.5FeMo/Si (b); 1.5Mo/Si (c); 0.5Fe/Si-pH (d); 1.5FeMo/Si-pH (e); and 1.5FeMo/Si-imp (f).

Figure 3. TPR-H₂ results of iron and iron-molybdenum catalysts. Catalysts: 1.5Fe/Si (a); 1.5FeMo/Si (b); 1.5Mo/Si (c); 0.5Fe/Si-pH (d); 1.5FeMo/Si-pH (e); and 1.5FeMo/Si-imp (f).

Figure 4. Low magnification TEM micrographs of 0.5Fe/Si-pH (A) and 0.5Fe/Si (B) and EDX-mapping of Fe and Si of a region of Fe/Si samples.

Figure 5. Low magnification TEM micrographs of and its corresponding EDX-mapping of Si, Fe and Mo in 1,5FeMo/Si-pH catalyst.

Figure 6. Fe 2p (A) and Mo 3d (B) core-level XPS spectra of SiO₂-supported FeOx and FeMoOx, synthesized by the sol-gel method. a) 0.5Fe/Si; b) 0.5Fe/Si-pH; c) 1.5FeMo/Si-pH; d) 1.5FeMo/Si-pH. Red spectra represent samples prepared in acid media.

Figure 7. Variation of the selectivity to formaldehyde vs methane conversion at 650 °C. Catalysts: (■) 0.5Fe/Si-pH, (▲) 1.5FeMo/Si, (●) 1.5FeMo/Si-pH. Experimental conditions in text, Methane:O₂:He = 32/4.3/63.7 molar ratio.

Figure 8. Variation of the selectivity to formaldehyde vs methanol conversion at 450 °C. Experimental conditions in text, i.e. Methanol:O₂:He = 6/13/81 molar ratio. For comparison it has been also inserted the catalytic results for methane oxidation (as in Fig. 7).

Figure 9. Variation of activity for methane conversion vs activity for methanol conversion. Note: Catalytic activity in methane transformation in mol_{CH₄} kg_{cat}⁻¹ h⁻¹ and in methanol transformation in mol_{CH₃OH} kg_{cat}⁻¹ h⁻¹. Reaction conditions as in Tables 2 and 3. Symbols: (■) Mo/Si, (■) Fe/Si, (■) FeMo/Si samples.

Figure 10. Relationship between the selectivity to formaldehyde (achieved from methane, at 650 °C and a methane conversion of 2%) with the selectivity to formaldehyde (achieved from methanol, at 450 °C and a methanol conversion of 50%). Reaction conditions as in Tables 2 and 3. Symbols: (■) Mo/Si, (■) Fe/Si, (■) FeMo/Si samples.

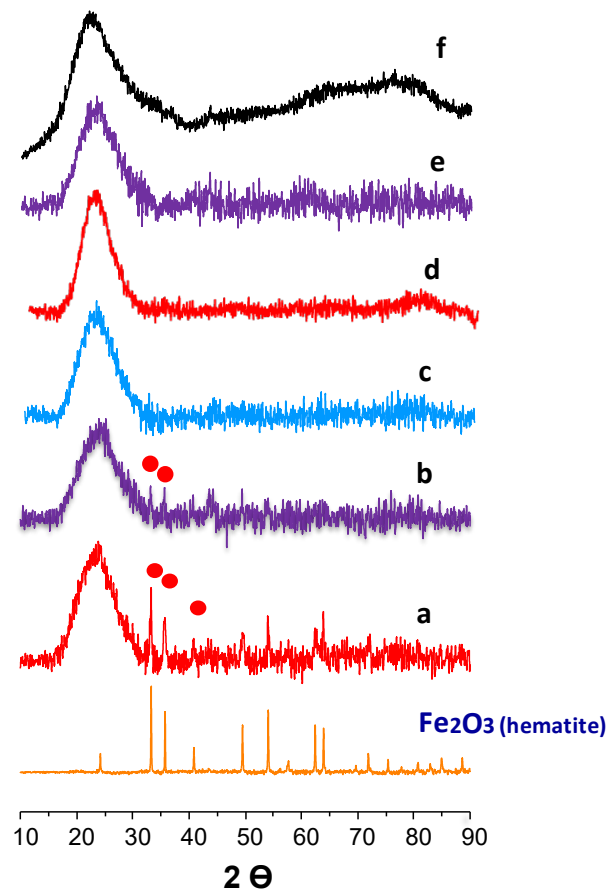


Fig. 1

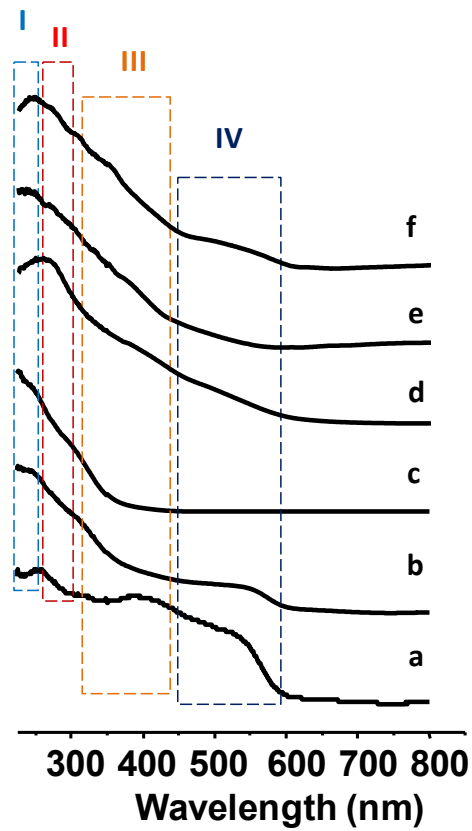


Fig. 2

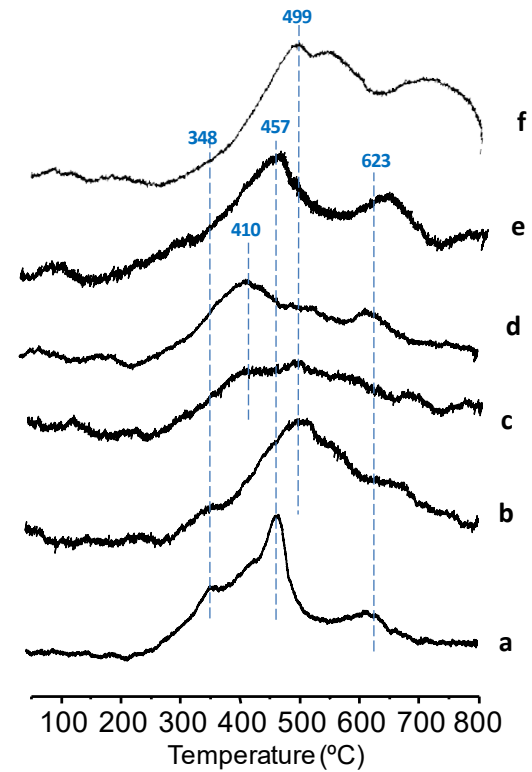


Fig. 3

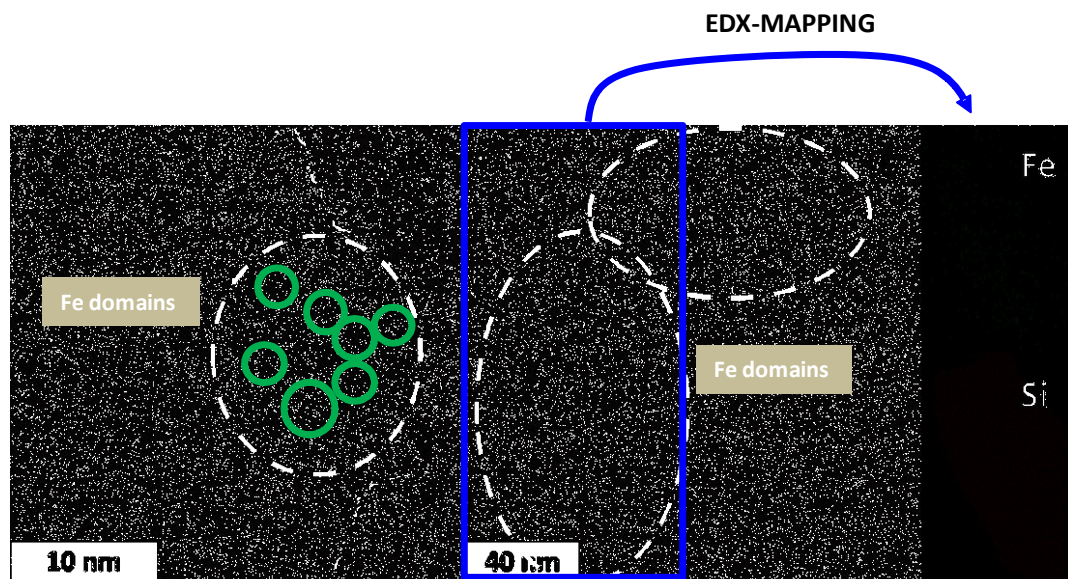


Fig. 4

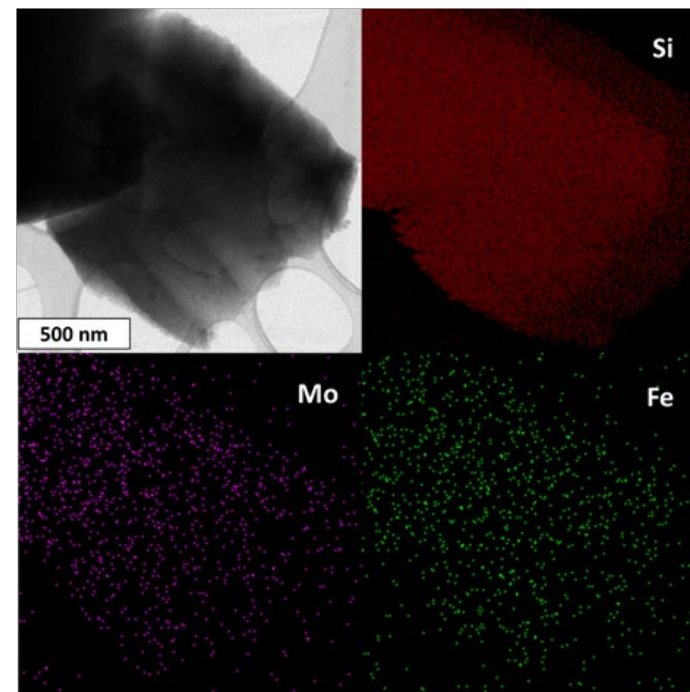


Fig. 5

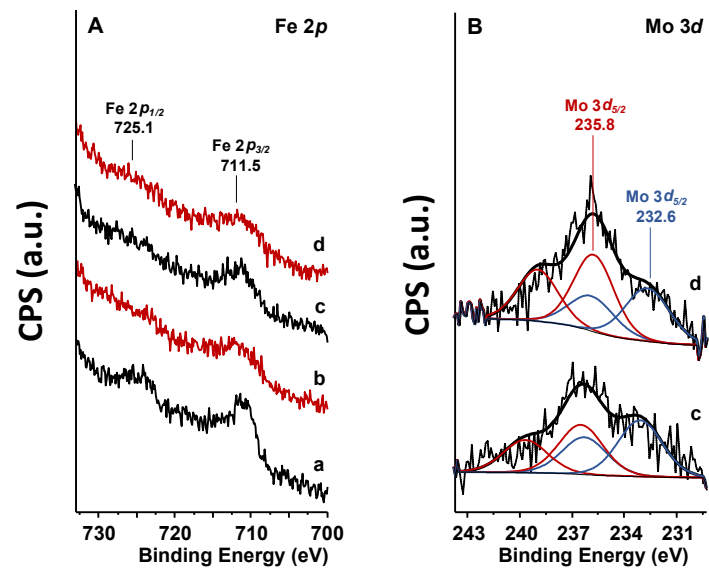


Fig. 6

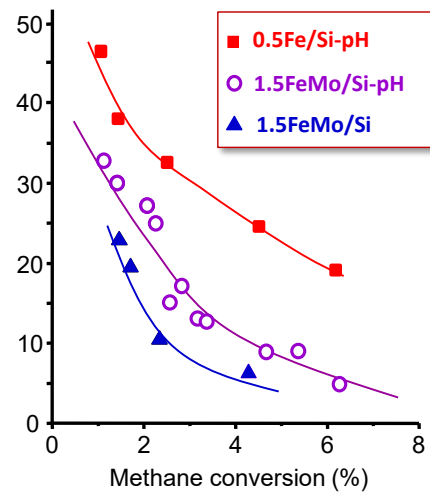


Fig. 7

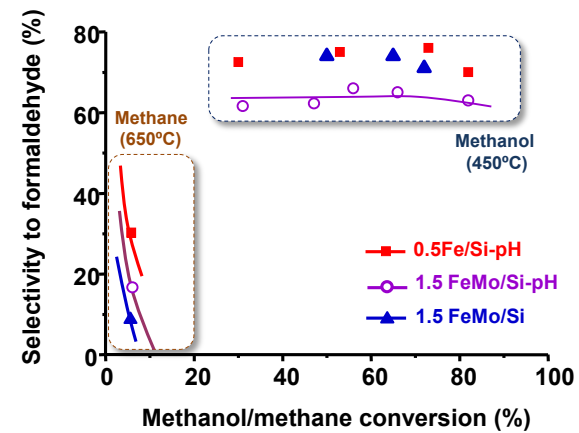


Fig. 8

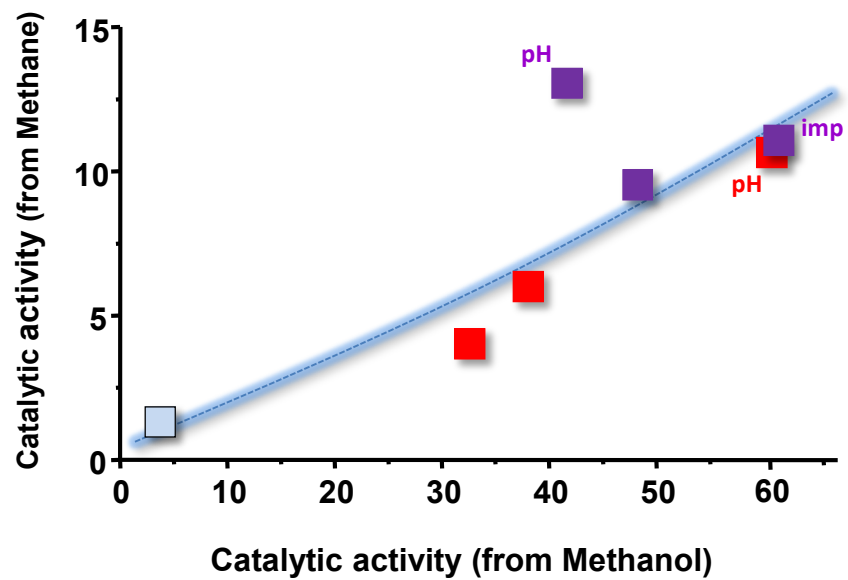


Fig. 9

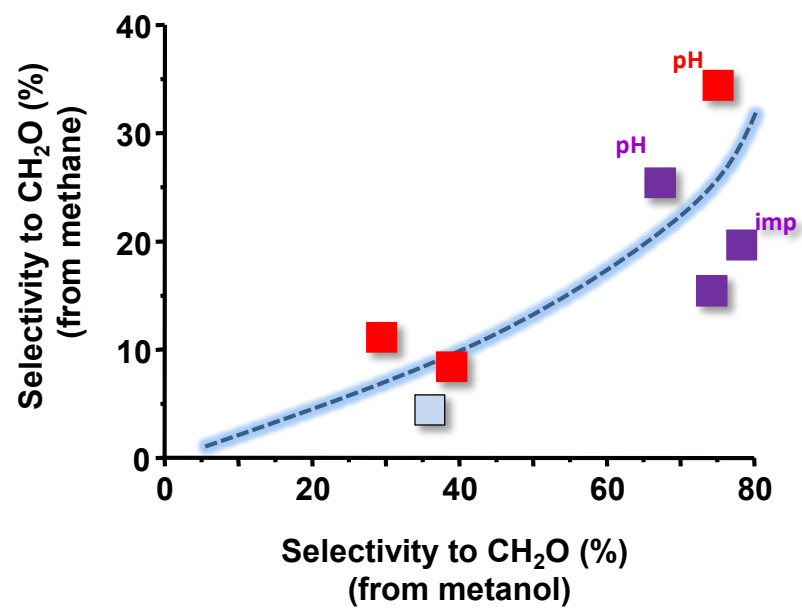


Fig. 10