Influence of the zeolite synthesis route on its catalytic properties in the methanol to olefin reaction

Svetlana Ivanova *, Charline Lebrun, Estelle Vanhaecke, Cuong Pham-Huu, Benoit Louis *

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, UMR 7515 du CNRS, Université Louis Pasteur, 25 rue Becquerel, 67087 Strasbourg, France[1]
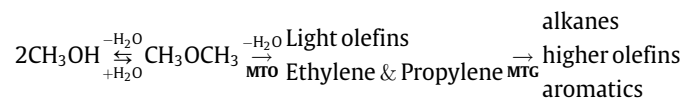
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ABSTRACT

The influence of the zeolite ZSM-5 synthesis procedure (hydroxide and fluoride route) on its catalytic performances in the methanol to olefin (MTO) reaction has been investigated. ZSM-5 crystals have been successfully coated on pre-shaped SiC foams structured catalysts, being prepared either by the classical alkaline or by the fluoride-mediated route. In addition, a new concept in the preparation of zeolite materials has been employed, so-called in situ zeolite synthesis. The silica superficial layer from the support itself was used as a silica source in this procedure. Moreover, the in situ route avoids addition of any external silicon source.

As-prepared structured catalysts have been tested in the conversion of methanol mainly into light olefins (MTO process). Depending on the preparation procedure, structured zeolite catalysts exhibited different performances in terms of activity and selectivity.

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1. Introduction

The synthesis of light olefins has attracted a huge attention during the last decades in order to fulfil the increasing worldwide demand toward ethylene and propylene [1]. Projected growth rates for the production of light olefins are expected to remain high in the years to come. The market demand toward propylene will rise faster than toward ethylene [1,2]. Hence, there is a need to develop catalysts that can increase the propylene to ethylene ratio [2]. The methanol to olefin technology (MTO) was developed as a two-step process, which first converts natural gas, via syngas, into methanol, followed by its transformation into light olefins. The conversion of methanol to olefins proceeds through the following path:

$$2CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \underset{MTO}{\overset{-H_2O}{\rightarrow}} \begin{array}{c} \text{Light olefins} \\ \text{Ethylene \& Propylene} \end{array} \underset{MTG}{\rightarrow} \begin{array}{c} \text{alkanes} \\ \text{higher olefins} \\ \text{aromatics} \end{array}$$

The initial step is the dehydration of methanol to dimethyl ether (DME), which then reacts further to produce ethylene and propylene. In the process, small amounts of butanes, higher olefins, alkanes, and aromatics are usually produced [3].

The MTO reaction has been studied over different types of acid catalysts, mainly zeolites and other molecular sieves, under different reaction conditions [4,5]. Silico-aluminophosphate SAPO-34 is recognized as a valuable catalyst for this reaction, thus generating a high selectivity to light olefins due to its moderate acid strength and small pore opening [6,7]. However, a high rate of deactivation is usually observed for this kind of material due to the rapid coke deposition [8–11], and its quite sophisticated preparation hinders its application. ZSM-5 zeolite-based catalysts are often used despite usually lower olefin yield and propylene selectivity [2]. Numerous studies targeted to achieve an increasing selectivity toward light olefins on these MFI-based catalysts; the different attempts can be classified into three groups:

(i) modification of the reaction conditions with respect to those of the MTO process, via either co-feeding water, changing the temperature, decreasing the pressure, or diluting the oxygenates with an inert gas;
(ii) modification of the zeolite with the aim to reduce the number and the strength of acid sites, or playing with steric constraints and increasing shape selectivity [12];
(iii) change in the reactor configuration [13].

In general, zeolites are prepared by hydrothermal crystallization from alkaline reaction mixtures, where OH⁻ anions act as a mineralizer [14]. A significant breakthrough in zeolite science occurred when hydroxyl anions were replaced by fluorides, rendering

* Corresponding authors. Present address: Instituto de Sciencia des Materiales, Avda Americo Vespucio 49, 41092 Sevilla, Spain (S. Ivanova).
E-mail addresses: svetlana@icmse.csic.es (S. Ivanova), blouis@chimie.u-strasbg.fr (B. Louis).

their synthesis possible in neutral and slightly acidic media [15]. Fluoride ions as mineralizing agent induce several advantages, namely: the formation of larger and defect-free crystals [16,17], ease of isomorphous substitution with elements sparingly soluble in basic media [18,19], and the direct formation of zeolite ammonium form, which avoids repeated ion-exchange steps. Recent studies have shown that even after calcination, fluorine can be present in the zeolite structure, modifying neighboring Si by its high electronegativity, and thus influencing the catalytic properties of the zeolite [20–23].

In heterogeneous gas-phase catalytic reactions, zeolites are traditionally used in fixed bed reactors packed as powdered microgranules or extrudated pellets. During the past two decades, there has been a growing interest in catalytic reactor engineering based on structured catalytic beds [24]. Indeed, the development of novel materials suitable for the design of structured catalytic beds was warranted. In spite of focused interest on the structured catalytic beds, only few practical applications have been reported consisting mainly of structured zeolitic packings [25–27]. Structured coatings of zeolite crystals were prepared via a binderless hydrothermal synthesis on metal grids [28–30] or on ceramics [31–41].

The aim of the present study is to prepare new structured ZSM-5 coatings via an in situ hydrothermal synthesis on β-SiC foam supports while using different mineralizing agents, F⁻ or ⁻OH anions. The silicon carbide was used in the present study as a foam monolith, which provides an improved hydrodynamics. Thanks to the open structure, the pressure drop throughout the catalyst bed is seriously reduced, even after coating with zeolite crystals [53]. The other approach to use the foam monolith consists in its direct use within the zeolite synthesis mixture, using the natural layer of silica present on the silicon carbide surface, and thus generating a self-assembly of zeolite crystals via silicon carbide substrate self-transformation [42]. Finally, all zeolite/SiC composites were to be assessed for the catalytic conversion of methanol into light olefins (MTO reaction).

2. Experimental section

2.1. Support

Silicon carbide was prepared by a gas-solid reaction between solid carbon and SiO vapors in the temperature range of 1200 to 1400 °C according to the so-called Shape Memory Synthesis [43,44]. The method permits the synthesis of silicon carbide in its β-SiC form with different sizes and shapes, depending on their subsequent uses, and having specific surface areas (SSA) up to 150 m²/g. The support was used in the form of a foam monolith (25 × 40 mm) having a pore opening of 2300 μm (SiCat company, Otterswiller, France). Prior to the synthesis, the support was calcined at different temperatures between 500 and 900 °C in air for 5 h in order to produce and estimate the content of a nanoscopic layer made of SiO_2 on the SiC support surface. Table 1 summarizes the results obtained for the different calcination temperatures. The quantity of SiO_2 was estimated by considering the mass increase of the material after the thermal treatment, which is being caused by the transformation of SiC into SiO_2. The formation of this layer is very important to insure a strong interaction between the support and the zeolite coating.

As expected with an increase in the treatment temperature, the quantity of amorphous silica layer raises; the temperature of 900 °C was, therefore, chosen for all pre-treatments, since it insures a high silicon source reservoir on the support surface which is necessary for the in situ zeolite preparation procedure.

2.2. Preparation of the zeolite coatings

The open-cell SiC foams (4 g) were placed in a Teflon-lined stainless steel autoclave (70 mL). The volume was partially filled with the reaction mixture (50 mL). The chemicals were used as received – tetraethylorthosilicate (TEOS, 98%, Sigma–Aldrich), tetrapropylammonium hydroxide (TPAOH, 1 M, Sigma–Aldrich), sodium chloride, sodium aluminate (NaAlO₂, 98%, Riedel-de Haën), tetrapropylammonium bromide (TPABr, 98% Sigma–Aldrich), and ammonium fluoride (NH₄F, Fluka). The different synthesis mixtures for preparing MFI zeolites are given in molar ratio and are fully described in Table 2. Two general procedures can be distinguished, the classical synthesis with the silicon source (TEOS) and the in situ anomalous procedure without any external silicon source addition. Only the silica layer created after the thermal treatment of silicon carbide was used in the later route. The reaction conditions for the different synthesis performed: temperature and duration are given in Table 2.

The gel containing the support was kept for 4 h at room temperature for all syntheses. Afterwards, the autoclave was put in the oven and the temperature was raised to 170 °C. The synthesis took place under autogeneous pressure. After cooling, the ceramic zeolite composite was filtered, washed several times with distilled water, and sonicated (45 kHz) for 30 min to remove weakly attached crystals. Finally, the solid was dried at 100 °C overnight. The organic template was removed by treating the material in air at 550 °C for 5 h. The composites synthesized in alkaline media (HC and HIS) were exchanged with an aqueous 1 mol L⁻¹ NH₄Cl solution (100 mL) for 16 h at 80 °C, and subsequently calcined at 550 °C for 5 h to produce the acidic H-form of the zeolite.

The zeolite synthesis in fluoride medium was performed for longer time since more time is needed for crystallization , due to the lower rate of nucleation and growth when compared to the alkaline synthesis [45].

Both synthesis routes (F⁻ and OH⁻ mediated) need a slightly different gel composition due the different mechanisms of dissolution of the SiO_2 surface layer. The dissolution process for the SiO_2 phase present on the external surface of bare SiC substrate via the alkaline route requires more OH⁻ anions as mineralizer than conventional synthesis. In contrast, the fluoride-mediated path presents a sufficient amount of F⁻ for allowing proper zeolite crystallization.

2.3. Characterizations

Specific surface areas (SSAs) of the different structured composites were determined by N₂ adsorption–desorption measurements at 77 K employing BET-method (Micromeritics sorptometer Tri Star 3000). Prior to nitrogen adsorption, the samples were outgassed at 300 °C for 4 h in order to remove the moisture adsorbed on the surface and inside the porous network.

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer, with a Ni detector side filtered Cu Kα radiation (1.5406 Å) over a 2θ range of 5° to 50° and a position sensitive detector using a step size of 0.02° and a step time of 2 s.

Scanning Electron Microscopy (SEM) micrographs were recorded on a JEOL FEG 6700F microscope working at 9 kV accelerating voltage. Before observation, the sample was covered by a carbon layer to decrease the charge effect during the analysis.

Table 1
Thermal treatment of the silicon carbide foam.

Temperature of thermal treatment (°C) 5 h duration	SiO_2 (mol.%)
500	2
750	4
900	22

Table 2
Gel composition and synthesis conditions.

Sample ZSM-5/SiC	Gel composition, molar ratios	Synthesis conditions, temperature and duration
Hydroxide classical (HC)	TPAOH:TEOS:NaCl:NaAlO$_2$:H$_2$O 2.16:5.62:3.43:0.13:1000	170 °C 48 h
Hydroxide in situ (HIS)	TPAOH:NaOH:NaAlO$_2$:H$_2$O 12:340:1:7919	170 °C 72 h
Fluoride (F)	TPABr:TEOS:NH$_4$F:NaAlO$_2$:H$_2$O 7:100:112:1:7990	170 °C 135 h
Fluoride in situ (FIS)	TPABr:NH$_4$F:NaAlO$_2$:H$_2$O 7:112:1:7990	170 °C 232 h

Table 3
Specific surface areas, zeolite coverage, and Brönsted acidity.

Sample	Specific surface area (m^2 g^{-1})	Yield (%)	Concentration of Brönsted acid sites (mmol g^{-1})	Si/Al ratio
SiC	10	–	0.11	0
Hydroxide classical (HC)	120	37	0.62	26
Hydroxide in situ (HIS)	70	21	0.41	40
Fluoride (F)	142	43	0.31	53
Fluoride in situ (FIS)	156	47	0.21	78

2.4. Catalytic tests

Methanol to olefins (MTOs) reaction has been carried out on an experimental set-up consisting in a feed section, a quartz tubular reactor (80 cm in length and 25 mm as inner diameter), and an analytical part. Methanol was supplied by a HPLC pump at a flow rate of 0.6 mL min^{-1}, vaporized, and fed in an Ar flow (60 mL min^{-1}). The zeolite- structured catalyst packing (4 g) was placed into a tubular quartz reactor. The reaction was carried out at 400 °C under atmospheric pressure. The temperature was measured by means of an internal thermocouple in the reactor which was situated in the middle of the sample. The analytical part was equipped with on-line gas chromatograph Varian CP 3800 with FID and DB-1 column (length 30 m, internal diameter 0.53 mm). All hydrocarbons formed and un-reacted alcohol were analyzed and carbon mass balance was verified to be higher than 93%.

The activity of the samples is expressed in terms of total methanol conversion, which is calculated from the difference of inlet and outlet concentration of methanol as well as in terms of specific activity, i.e. the transformation of methanol to the products of reaction without taking into account the formation of the intermediate product of the reaction, namely dimethyl ether. The calculation of selectivity has, therefore, been made as the mole ratio of each product on the amount of converted methanol to products other than DME.

3. Results and discussion

3.1. Surface properties of the zeolites

The specific surface area of the composites was determined by BET-method based on the nitrogen adsorption–desorption. Since the presence of microporous materials such as zeolites certainly increase the SSA values when compared to the bare substrate alone, it should give precious insights on the synthesis outcome and on the amount of zeolite coated. Table 3 presents SSA values of the composites obtained after the different procedures. It is noteworthy that the composites prepared in the fluoride media exhibit a higher SSA value than those obtained under basic conditions. The yield of zeolite coated on the foam support was calculated by taking into account the SSA of the powdered un-supported zeolite, i.e; 320 m^2 g^{-1}. From such an increase in SSA, it appears that the cov-erage by the zeolite is very high. Furthermore, microporosity was observed in the composite material while it is absent in the bare β-SiC substrate, thus confirming the formation of zeolite material on the substrate surface.

H/D isotope exchange was performed to evaluate the Brönsted acidity of the MFI/β-SiC composites according to the method developed by Louis et al. [55,56]. The total concentration of Brønsted acid sites was measured for the HC zeolite (0.62 mmol/g$_{zeolite}$), and thus allowed us to determine a Si/Al ratio of 26. The quantification of the concentration of OH groups was performed via subtracting the value of 0.11 mmol of OH/g of SiC. Table 3 shows the values for the different zeolite/SiC composites, and led us to deduce Si/Al ratio according to H/D isotope exchange that was developed earlier [55,57].

The fluoride route led to zeolites with lower Brönsted acidity in the final composite, and thus to higher Si/Al ratio.

3.2. Crystallinity and morphology of the zeolite composites

The XRD patterns of all synthesized composites are presented in Fig. 1. The major peaks were located at 2Θ 7.9° and 2Θ 8.9°, together with the characteristic triplet at 2Θ 23.5°, which further confirm the formation of the MFI structure [46,47]. However, after the in situ procedure, the reflexions were less intense, thus indicating the presence of less crystals (compared to HC and F procedures) on the support surface. A broadening in the reflexions for the two zeolites obtained via FIS and HIS routes confirms a lower crystallinity, probably due to a longer time needed to re-crystallize the silica upper-layer from SiC substrate [42]. Nevertheless, the zeolite prepared via caustic in situ procedure exhibits a strong reflexion at 18.5° indicating the presence of another zeolite structure (Fig. 1d). As the supersaturation of crystallizing species is higher in basic media, the number of metastable phases is increased, thus the crystallization becomes less regular: presence of competing phases, presence of defects [48,54]. Fig. 1d shows a characteristic pattern of the so-called X-ray amorphous zeolites [42]. The presence of a secondary semi-crystalline phase indicates compositional and chemical similarities to the parent MFI zeolite, but is lacking in long-range order. Such amorphization process can be due to partial dissolution of formed zeolite under hydrothermal conditions. The acidity of the material synthesized for 72 h (Table 1) when compared to conventional zeolite synthesis was decreased; this
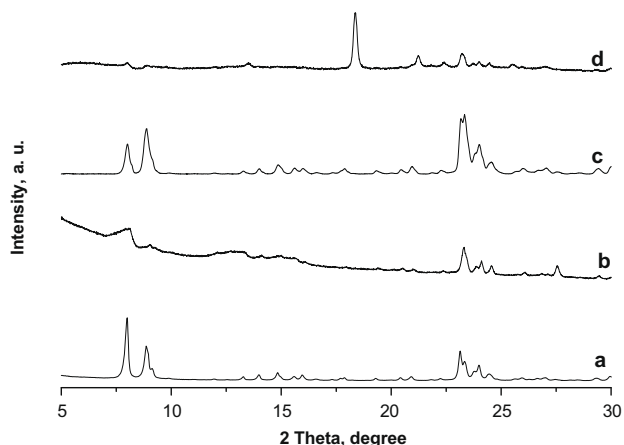
Fig. 1. XRD patterns of zeolite supported on SiC composites: (a) fluoride (F), (b) fluoride in situ (FIS), (c) hydroxide classical (HC) and (d) hydroxide in situ (HIS).

is further in agreement with a crystallization–dissolution process as suspected from XRD measurements.

The morphology and size of the zeolite crystals have been studied by SEM (Fig. 2). The morphology of the bare SiC support has already been reported elsewhere [42,53]. In line with XRD results, the syntheses where an extra-addition of silica source was performed led to a complete coverage of the support surface by prismatic MFI-type crystals (Fig. 2a and c) whatever the mineralizing agent used. However, a drastic difference was observed in the size of the crystals. The silicon carbide surface has been homogeneously

covered by randomly oriented crystals, having 1 μm in length for the samples produced in alkaline media (Fig. 2c), whereas larger intergrown and aggregated crystals were obtained via the classical fluoride synthesis (Fig. 2a). When the in situ synthesis was carried out in alkaline media a mixture of nanofibers and small crystals was observed, thus confirming the presence of two different structures (Fig. 2d).

3.3. Catalytic performance

The catalyst (MFI zeolite coated on SiC foams) system belongs to the concept of structured reactor, consisting in a macroscopic support coated with a nanoscopic active phase. Indeed, the time needed for molecules to reach and to leave active centers should be considerably reduced within the thin catalyst layer present on the macroscopic foam monolith [24,25,41]. On the basis of these considerations, one could expect a different activity and selectivity controlled by the different zeolite crystal sizes and morphologies for all the synthesized samples.

The activity of the samples will be expressed in terms of total methanol conversion, which is calculated from the difference of inlet and outlet concentration of methanol as well as in terms of specific activity, i.e. the transformation of methanol to the products of reaction without taking into account the formation of intermediate product dimethyl ether.

The activities of the four samples expressed in terms of total methanol conversion are presented in Fig. 3.

It is noteworthy that the activity in methanol transformation does not depend on the use of mineralizing agent, for the samples obtained by classical synthesis (HC and F) with an addition of a sil-
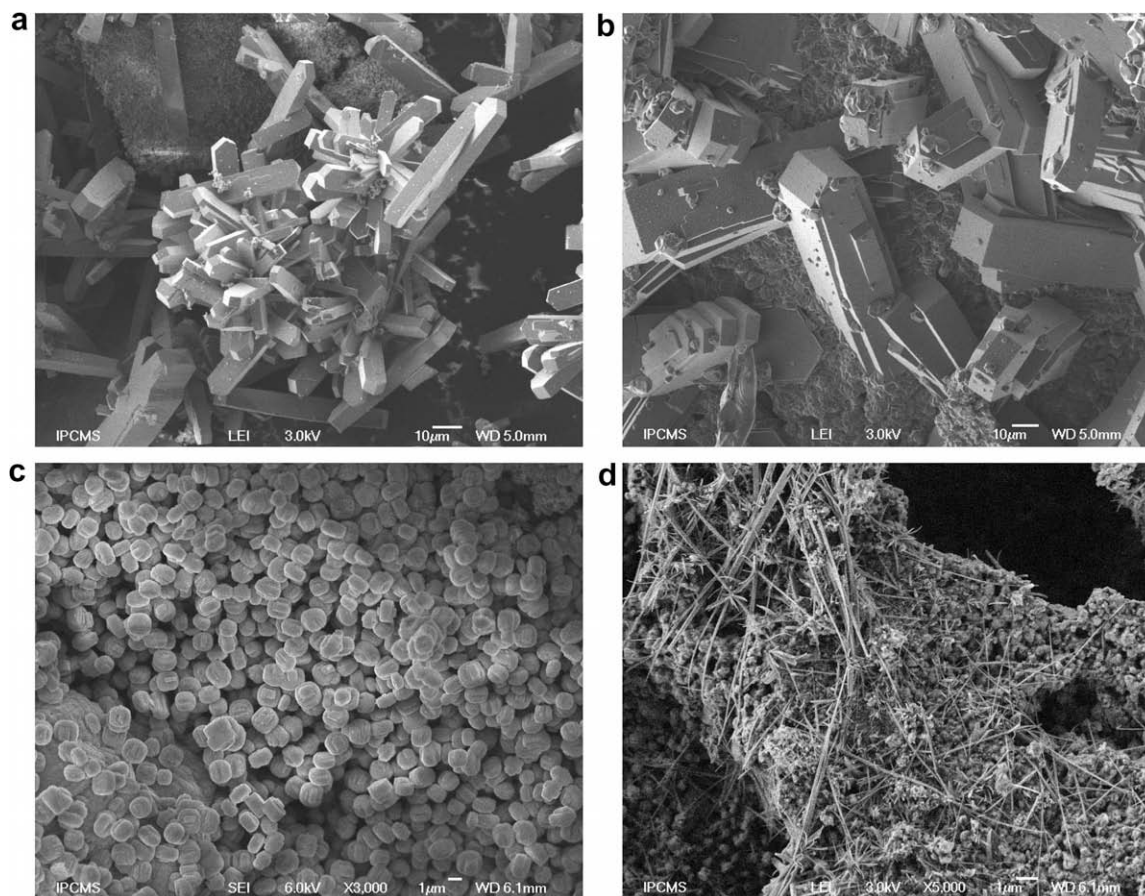

Fig. 2. SEM Images of zeolite supported on SiC substrates: (a) classical fluoride (F), (b) fluoride in situ (FIS), (c) classical hydroxide (HC) and (d) hydroxide in situ (HIS).
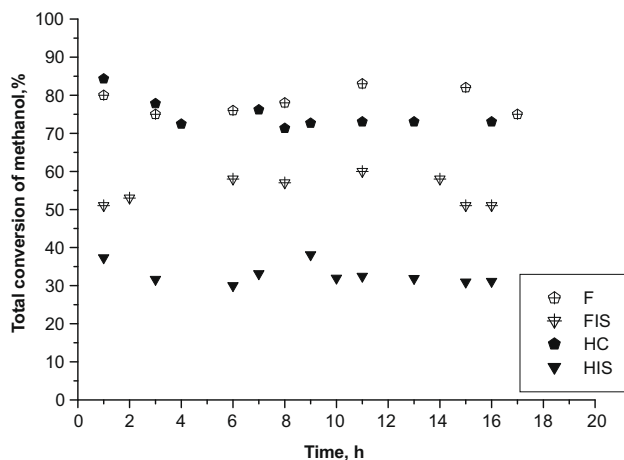
Fig. 3. Total methanol conversion of the ZSM-5/SiC composites as a function of time on stream.

icon source. Both zeolites exhibit the same methanol conversion, which is stable during several hours on stream at 75%.

While the activity of *in situ*-synthesized sample in fluoride media (FIS) remains fair at 55%, the activity of the materials prepared via the HIS route was drastically reduced to 30%. However, the total conversion remains stable for 15 h on stream. Such difference in the catalyst activities can be attributed to the difference in the preparation, which induce a different number of acid sites as well as a difference in the Brönsted acid sites strength [16,37].

When the specific methanol conversion to desired products was calculated (Fig. 4), it appears that the activity of as-prepared zeolite composites, via the classical paths, continuously decreased with time on stream for the samples. Whatever the mineralizing agent (F and HC samples) used, the production of light olefins diminished in favor of DME. In contrast, the material prepared via in situ route in the presence of F⁻ anions (FIS) exhibited a lower initial activity, but follows the same trend of catalyst deactivation. The sample prepared via in situ alkaline media (HIS) did not present a good specific catalytic activity toward light olefin production, thus remaining the worst catalyst. The relatively large crystal size, ranging from 1 to 50 μm, induces a longer diffusion path for the reactants/products within the crystal, and hence favor the deactivation of the zeolite [53,54]. The lower catalytic performance of HIS material further confirms a lower crystallinity and probably the presence of two competing phases [42].
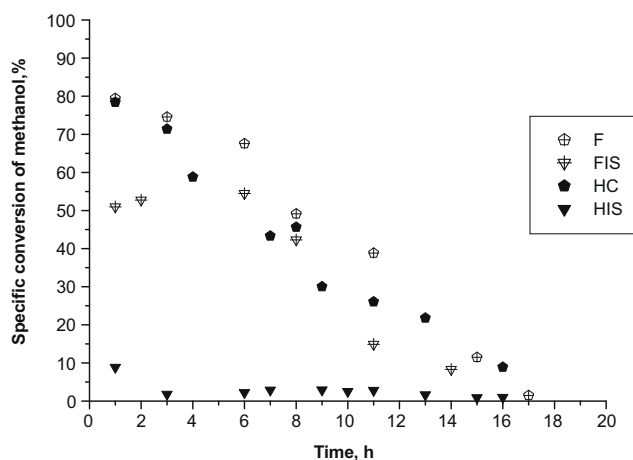

Fig. 4. Specific methanol conversion of the composites as a function of time on stream.

Figs. 5–8 present a comparison of the different zeolites in terms of selectivity to products being formed: ethylene, propylene, and others (higher olefins, alkanes and aromatics) are expressed.

HZSM-5 zeolite synthesized in the alkaline media produces ethylene and propylene in an equimolar ratio in the early stages of the reaction, in agreement with commercial catalysts [41,49].

After 10 h on stream, the production of light olefins decreased in favor of higher olefins formation. However, the propylene/ethylene ratio remains stable around unity. Such change in the catalyst behavior could be connected to the deactivation of the acid sites via coke formation, limiting the transformation of starting methanol to DME [5,51,52]. However, the TPO experiments performed after the catalytic test for all the samples did not show any significant difference. In the case of HC material there is a twice higher formation of coke but still not sufficient for blocking of complete acid sites (3.48×10^{-3} g$_C$/g$^*_{cat}$h$_{reaction}$ instead of around 1.8×10^{-3} g$_C$/g$^*_{cat}$h$_{reaction}$ for all other samples). Nevertheless, a complete poisoning of the acid sites is not a necessary condition to exclude that coke formation is a major source of deactivation.

A plausible reason to explain such unexpected behavior, when compared to the outstanding contributions from Bjørgen et al. [58], can be due to a reduced heat release by the SiC foam monolith at lower conversion (due to deactivation of the zeolite). Indeed, a lower temperature in the reactor could change the selectivity toward the different products, and thus favor DME production.

Fig. 6 presents the results for HZSM-5 prepared in fluoride media (F). The selectivity toward aromatics and higher olefins is more pronounced and is about 50% during the first 10 h on stream. The formation of consecutive products seems to be connected to a
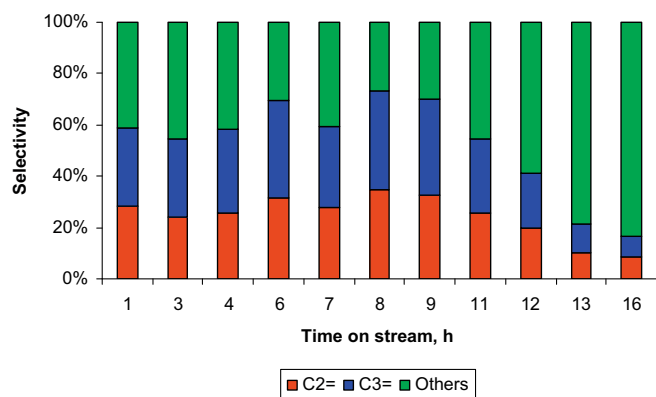

Fig. 5. Selectivity toward ethylene, propylene and others hydrocarbons for HZSM-5 zeolite synthesized in basic media (HC).
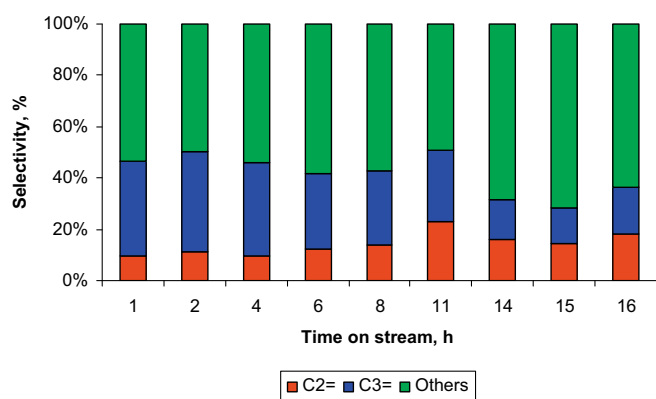

Fig. 6. Selectivity toward the different products obtained over HZSM5 synthesized in fluoride media (F).
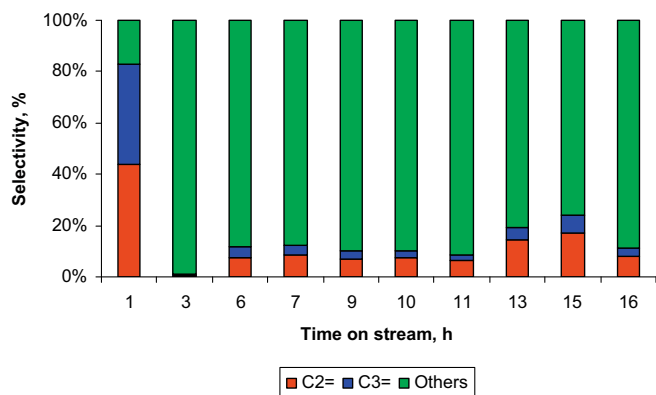
Fig. 7. Product distribution observed with respect to time over *in situ*-synthesized sample in alkaline media (HIS).
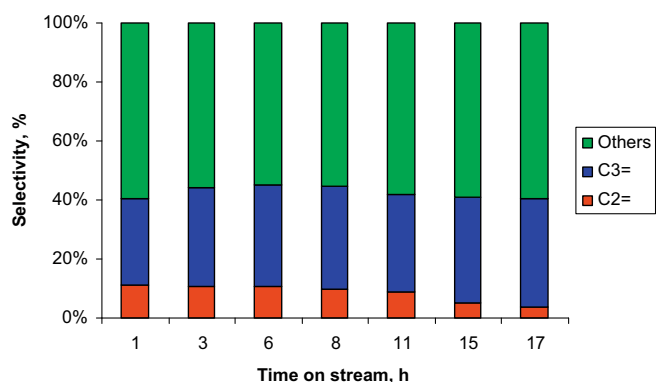

Fig. 8. Distribution of the products obtained over *in situ*-prepared MFI zeolite in fluoride media (FIS).

rapid deactivation occurring on these large prismatic crystals, where the diffusion length is seriously raised. Surprisingly, high propylene to ethylene ratio of 3 can be observed during the first 10 h of reaction. Unfortunately, this valuable propylene formation was decreased to a ratio of propylene to ethylene close to unity after 11 h on stream.

As the main difference observed among the two zeolites remains their crystal size, one can suppose a hindered diffusion of the products in the zeolite prepared in fluoride media. Hence, the formation of longer chain olefins and carbonaceous residues can progressively plug the zeolite channels and thus, initiate extensive deactivation by changing the propylene to ethylene ratio.

During an *in situ* synthesis of zeolites, the crystallization time is enhanced which can lead to an increase in the Al content at the external surface of the crystallites as claimed by Inui et al. [50]. In addition, no external silica source was used for the preparation, which further increases the possibility of excess of Al species at the zeolite external surface. Fig. 7 shows the distribution of the products obtained over HIS as-prepared composite. The selectivity is comparable to that of the other composites only in the first hour of reaction. In fact, both propylene and ethylene, in an equimolar ratio, were only detected during the first two hours of the reaction. After 5 h of reaction the formation of light olefins remains low. Hence the selectivity to ethylene, with an ethylene to propylene ratio close to 3 was observed; this is exactly the reverse behavior to the fluoride prepared composite. Higher formation of other products was observed for this sample with the prevailing presence of C_9 and C_{10} hydrocarbons. The lowest quantity of Brönsted acid sites present in this material can explain the low activity (30% of total methanol converted and 8% of specific conversion) together

with a poor selectivity toward light olefins. The presence of enriched Al species on the outer surface of the zeolite might introduce the necessary acidity for the methanol dehydration.

The MFI zeolite synthesized without any extra-addition of Si-source in fluoride media (FIS) exhibits the same selectivity (Fig. 8), than the MFI produced via the classical fluoride-mediated route (Fig. 6). The propylene to ethylene ratio is close to 3 with the same products distribution. Both aromatics and high olefins fractions are the major products during the whole course of the reaction.

Based on the XRD and H/D exchange data, it seems that HIS material is rather a mixture of two competing zeolite phases. These two metastable phases are probably not fully crystalline and rather "amorphous zeolite" as defined by Cundy and Cox [48]. This can explain both the low activity and also an unusual selectivity toward the reaction products (Fig. 7).

The physico-chemical characterizations of this MFI zeolite, as well as its catalytic behavior, do not allow us to differentiate the classical and the *in situ* synthesis in fluoride media. Indeed, a longer time of nucleation and crystallization successfully extract the silicon in the desired quantity, forming by this a new route for structure catalytic bed preparation using the support not only as a physical carrier but as a chemically integrated material.

It is noteworthy that as-synthesized zeolite/SiC composites obtained via fluoride route usually produced materials with higher crystallinity, together with reduced Brönsted acid site density [54,59]. Table 3 shows the total number of Brönsted acid sites for the different zeolites, and thus confirms these previous studies. While comparing, the MTO efficiency of these zeolites, it appears that both a reduced acid site density and a higher crystallinity led to higher performance for light olefins production. These assumptions are further supported by a reduced activity of HIS zeolite when compared to the higher performance of HC zeolite that exhibits a higher crystallinity.

Concerning the hydroxide-mediated route, the reasons for such a change in the selectivity in the course of the reaction have not been fully understood yet. However, it is possible to anticipate the changes in the zeolite channel architecture and accessibility by modifying the size of the crystal and the degree of crystallization. The local differences in Al content and, therefore, the change in the material acidity have to be further investigated.

4. Conclusions

This work reports the influence of $^-$OH and F^- mineralizing agents on the catalytic performance in Methanol to Olefins (MTOs) reaction. Whatever the procedure for the zeolite synthesis, it appeared that the MFI-type zeolite remains always strongly bonded and homogeneously coated on the silicon carbide surface.

An innovative zeolite preparation route has been developed without addition of external silicon source. This in situ procedure allows the design of structured catalysts while using the support not only as a physical carrier but also as a chemically integrated material.

Interestingly, all as-synthesized zeolite composites differ from both their crystal size, the degree of crystallization, and the morphology, allowing a different activity and selectivity in the transformation of methanol into valuable light olefins. High propylene to ethylene ratio up to 3 has been observed, thus providing an interesting basis for future studies and potential industrial interest.

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