ZSM-5 Coatings on β-SiC Monoliths: Possible New Structured Catalyst for the Methanol-to-Olefins Process

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Structured zeolite/silicon carbide composites were succesfully synthesized by ZSM-5 coatings deposited on macroscopic β-SiC foams with medium surface area. A homogeneous coverage of the support (30 wt % zeolite) by ZSM-5 crystals, having 1 μm average size, was reached after a double-coating procedure. The ZSM-5/β-SiC composite materials were characterized by BET, XRD, SEM, and H/D exchange methods. ^{27}Al MAS NMR analysis revealed that all aluminum was present in a tetrahedral coordination, thus sitting in the zeolite framework. The existence of a nanoscopic layer of silica and silicon oxycarbide on the surface of the support ensures the strong anchoring of the zeolite crystals on the β-SiC substrate. The lack of secondary chemical reaction between the synthesis solution and the support allows a precise control of the Si/Al ratio in the final zeolite. The use of ZSM-5 coated β-SiC foam packings in the methanol-to-olefins reaction presents substantial activity/selectivity improvements compared to conventional zeolite packings. Moreover, the structured composites exhibit a higher stability toward deactivation by coking, compared to the powdered form of the zeolite.
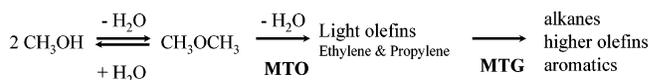
1. Introduction

In heterogeneous catalysis it is already recognized that a catalyst is not a new chemical compound, but a finely designed material. Chemical composition can efficiently work only in combination with well-organized micro- and macrostructure of the material. Moreover, the texture and mechanical properties of the catalyst strongly influence the appropriate choice of the chemical reactor and the technology employed,[1,2] and hence the investment cost.

Zeolites are known to possess a microporous structure with well-defined pore architecture and size. Moreover, the zeolites can be loaded via ion exchange by cations to suit the requirements of a specific chemical transformation. Therefore, a control of chemical composition and microstructure is ensured by zeolite synthesis. In contrast, the macrostructure of zeolite catalyst packings is still fairly undefined. Zeolites are used in catalytic fixed beds, randomly packed by powdered microgranules or extrudated pellets a few millimeters in size. The main drawbacks of fixed beds are (a) the high-pressure drop during the gas passage through the catalytic bed, (b) limited heat and mass transfers, (c) flow maldistribution leading to loss of selectivity, and (d) susceptibility to fouling by dust.

Furthermore, the use of inorganic binders for shaping the final zeolite material presents an important limitation, since these binders partly block access to the zeolite active centers, which diminish the zeolite efficiency in catalytic reactions.

During the past decade there has been a growing interest in catalytic reactor engineering based on structured catalytic beds.[3] Compared to traditional randomly dumped packed bed reactors, structured catalytic beds provide improved hydrodynamics. This leads for example to narrower residence time distribution,

SCHEME 1: Main Reaction Steps of the Methanol Conversion to Hydrocarbons

allowing control of consecutive reactions and resulting in increased product selectivity. Therefore, the development of novel materials suitable for the design of structured catalytic beds is warranted. This is a valuable alternative to conventional fixed beds and slurry catalytic reactors.[3] Despite the increasing interest in structured catalytic beds, only a few practical applications have been reported consisting of structured zeolitic packings.[4−6]

Structured zeolitic packings can be prepared via a binderless hydrothermal synthesis on metal grids[7−9] or ceramics.[10−19] Even well-covered, metallic substrates are known to catalyze many reactions, and thus contribute to deep oxidation pathways. Another drawback of metallic supports for zeolite deposition is connected to the big difference in the dilatation coefficients of metals compared to silicates, which may cause a zeolite attrition due to its detachment under temperature changes during reactor operation.[20] Moreover, prior to the synthesis, the chemical pretreatment of the metal support is crucial to increase the chemical affinity between the zeolite and its carrier,[21,22] thus complicating the preparation of the catalyst. Metal grid supports also exhibit high intrinsic weight, which is detrimental for the productivity per weight of the reactor unit.

Crystallization of zeolites on porous glass supports in alkaline media has already been reported.[16,23] The glass matrix is partially transformed into zeolitic material, and as a result a biphasic composite material with a bimodal pore system can be obtained. The synthesis procedure described takes place in basic media at high pH values.[10−13] The strong basicity of the zeolite growth medium renders less effective the use of silica or alumina

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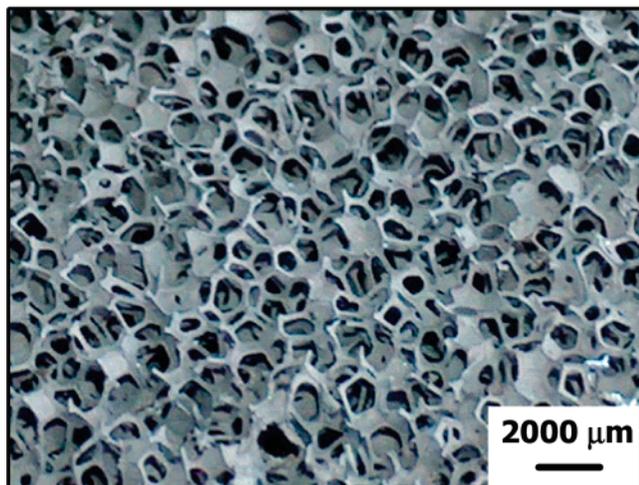
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Figure 1. Cellular structure of SiC foam monolith.

supports due to their partial dissolution, leading both to the deterioration of the support and a modification of the gel composition.[16]

Silicon carbide exhibits the necessary intrinsic properties required to become a valuable candidate as zeolite support: high thermal conductivity and mechanical strength, resistance to oxidation, chemical inertness, and ease of shaping.[24–26] All these advantages tend to indicate that SiC support can replace classical supports such as alumina, silica, and carbon, especially in highly endothermic and/or exothermic reactions.[27,28] Silicon carbide possesses a light weight which significantly reduces the fraction of useless weight of the support within the overall weight of the catalyst. Finally, β-SiC synthesized according to shape-memory synthesis (SMS)[26] also exhibits a medium surface area which renders it suitable for dispersing zeolite crystals on its surface.

The aim of this work was to prepare new structured and binderless ZSM-5 coatings via an in situ hydrothermal synthesis on SiC supports. Silicon carbide was also used in the present study as a foam monolith owing to its open structure which significantly reduces the pressure drop along the catalyst bed. The zeolite crystals were made to grow onto the structured supports kept in the synthesis mixture. Then, the zeolite/SiC composite was to be assessed for the catalytic conversion of methanol into olefins (MTO reaction; see Scheme 1). The conversion of raw methanol to hydrocarbons over MFI-based catalysts is an alternative technology for the manufacture of

petrochemicals and gasoline.[29–31] The MTO reaction was chosen for two reasons. First, light C_2–C_4 olefins are valuable intermediates in the chemical industry and their demand is still rising.[32] Second, the yield in C_2–C_4 olefins is controlled by the contact time of the reactants with the catalyst. Therefore, the light olefins have to be quickly removed from the catalyst surface to prevent them from reacting further.[33] On the basis on these considerations, as-prepared HZSM-5/SiC structured composite can be an effective MTO catalyst.

2. Experimental Section

2.1. β-SiC Characteristics. Silicon carbide was prepared by the gas–solid reaction between solid carbon and SiO vapors in the temperature range 1200–1400 °C according to the shape-memory synthesis developed by Ledoux et al.[24,34] The method allows the synthesis of silicon carbide with different sizes and shapes, depending on their subsequent uses, and having specific surface areas (SSAs) up to 150 m²/g. SiC was used in its β-crystalline structure since the SSA is higher than the one from α-SiC.[26] The support was used either in the form of extrudate pellets (2 × 6 mm in size) or as a foam (25 × 40 mm) having a pore openning of 2300 μm (Sicat Company, Otterswiller, France). Figure 1 shows the honeycomb structure of a SiC monolith. Prior to the synthesis, the support was calcined at 900 °C in air for 2 or 5 h in order to form a nanoscopic layer of SiO_2 on its surface. This layer ensures a strong interaction between the support and the gel during the zeolite synthesis through a superficial dissolution–precipitation sequence.

2.2. Preparation of the Zeolite Coatings. The open-cell SiC foams or extrudates (5 g) were placed in a Teflon-lined stainless steel autoclave (70 mL). Its volume was partially filled with the reaction mixture (50 mL). The solution was prepared by adding dropwise tetraethylorthosilicate (TEOS, 98%, Sigma-Aldrich) to an aqueous solution containing tetrapropylammonium hydroxide (TPAOH, 1 M, Sigma-Aldrich), sodium chloride, and sodium aluminate ($NaAlO_2$, 98%, Riedel-de Haën). The gel composition in molar ratios was as follows: TPAOH/ $TEOS/NaCl/NaAlO_2/H_2O$ 2.16:5.62:3.43:0.13:1000. The gel containing the support was aged for 4 h at room temperature. Then the autoclave was put in an oven and the temperature was raised within 1 h to 440 K; the synthesis took place during 48 h under autogenous pressure. After cooling, the ceramic– zeolite composite was filtered, washed several times with distilled water, and sonicated (45 kHz) for 15 min to remove residual gel or loosely attached crystals. Finally, the solid was dried at 373 K overnight.

A second synthesis was performed by repeating the coating procedure, placing the ceramic–zeolite composite in a fresh solution having the same molar composition.

The organic template was removed by treating the material in air at 773 K for 5 h. The composite was then ion-exchanged with an aqueous 1 mol L^{-1} NH_4Cl solution (100 mL) for 16 h at 338 K, and subsequently calcined at 773 K for 5 h to produce the acidic H-form of the zeolite.

TABLE 1: Characteristics of ZSM-5/SiC Composites: Mass of Zeolite Coated, SSA Values, and Yield of the Synthesis for Both Types of Substrates, Extrudates and Foam

support/composite	mass of zeolite [g]	SSA value [m²/g]	yield [%]
SiC extrudates		5	
MFI/SiC extrudates after first coating	0.637	28	14.8
MFI/SiC extrudates after second coating	1.246	55	14.4
SiC foam		19	
MFI/SiC foam after second coating	1.656	120	19.2
MFI powder		445	

2.3. Characterizations. SSAs of the different materials (bulk or structured composites) were determined by N_2 adsorption–desorption measurements at 77 K employing the BET method (Micromeritics sorptometer Tri Star 3000). Prior to N_2 adsorption, the samples were outgassed at 573 K for 4 h in order to desorb water and moisture adsorbed on the surface and inside the porous network.

X-ray diffraction (XRD) patterns were recorded on a Brucker D8 Advanced diffractometer, with Ni detector side filtered Cu Kα radiation (1.5406 Å) over a 2θ range of 5°–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.

^{27}Al ($I = 5/2$) magic angle spinning nuclear magnetic resonance (MAS NMR) was carried out on a Brucker DSX 400 spectrometer operating at $B_0 = 9.4$ T (Larmor frequency $\nu_0 = 104.2$ MHz). A single pulse of 0.7 μs with a recycle delay of 300 ms was used for all experiments. The spinning frequency was 10 kHz. Measurements were carried out at room temperature with $[Al(H_2O)_6]^{3+}$ as external standard reference.

Pressure drop measurements were performed on a setup equipped with a Testo 435-1 gas velocity anemometer, with a hot wire probe (0–20 m s^{-1}) having a small diameter to limit the gas flow perturbation. The pressure drop was measured with a differential pressure sensor (Keller Druckmesstechnik PD-41, 0–200 mbar), and the gas used was air.

The amount of carbonaceous species deposited on the sample after the reaction was analyzed using temperature-programmed oxidation (TPO). The sample was packed in a vertical quartz reactor and flushed in flowing helium at room temperature for 30 min. The helium flow was replaced by a mixture of O_2 (20 vol %) diluted in helium with a total flow rate of 50 mL·min^{-1}, and the reactor temperature was increased from room temperature to 973 K with a heating rate of 5 °C min^{-1}. CO_2 was continuously monitored by a micro-TCD.

The Brønsted acidity of the materials was evaluated by using a H/D isotope-exchange technique reported elsewhere.[35] This technique also allows determination of the chemical composition of the as-synthesized composite material (Si/Al ratio, unit cell formula).

The coverage of the different packings was defined as the mass of zeolite coated, referred to the geometric surface area of the support (g/m^2). The ratio of the amount of silicon incorporated into the zeolite matrix to the initial amount of silicon in the gel was defined as the yield of the zeolite coating procedure.

2.4. Methanol-to-Olefins (MTO) Reaction. The setup used for the catalytic tests consists of a feed section, a quartz tubular reactor (800 mm length and 25 mm inner diameter), and an analytical part. Methanol was supplied by an HPLC pump at a 0.5 mL·min^{-1} flow rate, vaporized and fed in an Ar flow (60 mL·min^{-1}). The zeolite structured catalyst packing (4 g) was placed into a quartz plug-flow reactor. The reaction was carried out at 673 K and atmospheric pressure. The conversion of methanol was calculated from the difference between the reactor inlet and outlet concentrations. The selectivity toward hydrocarbons was defined as the molar ratio of the hydrocarbon produced versus the methanol converted. The activity of the zeolite/ceramic composite has been compared to that obtained on the unsupported zeolite powder.
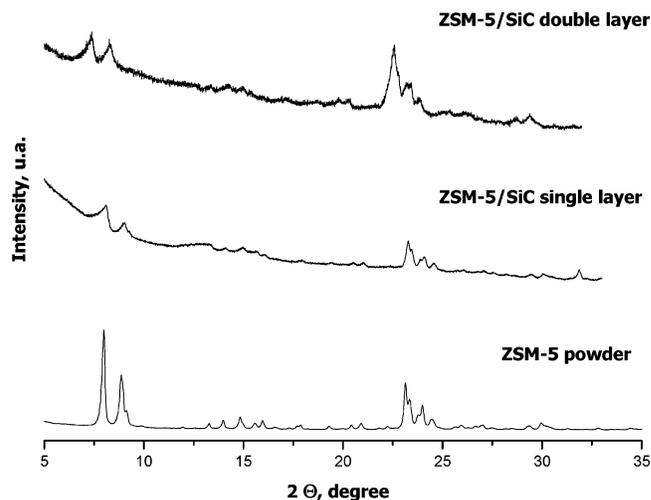

Figure 2. XRD patterns of ZSM-5 coatings: after one and two synthesis steps, compared to ZSM-5 in powdered form.

The analytical part was equipped by an on-line gas chromatograph Varian CP 3800 equipped with FID and a DB-1 column (length 30 m, internal diameter 0.53 mm). All hydrocarbons formed and unreacted methanol were analyzed, and the carbon mass balance has been verified to be higher than 93%.

3. ZSM-5/SiC Composite Characterization

Table 1 summarizes the values of the mass of zeolite deposited on the SiC substrates as a function of the number of synthesis step, SSA values, and the yield of zeolite coating (based on Si). The mass of zeolite coated on the SiC support (extrudates) appears to be the same after the first or the second synthesis step, and is about 0.6 g per synthesis step. The yield of the coating is close to 15%, which is higher than conventional values found in the literature.[12,21] Furthermore, after a two-step synthesis, extremely high coverages in terms of zeolite coated per geometric surface unit of silicon carbide were reached: 5.3 g of ZSM-5/m^2 of SiC (extrudates) and 8.2 g of ZSM-5/m^2 of SiC (foam). Kraushaar-Czarnetzki et al. have shown that a homogeneous coverage could be achieved over ceramic foams with the deposition of 3 g of MFI nanocrystals/m^2 of foam.[11] It appears therefore that the values obtained in the present work are high enough to ensure a homogeneous coverage of the support, along with the advantages of structured catalysts.[3]

The increase in the SSA values while starting from the naked β-SiC supports to the ZSM-5/β-SiC composites also confirms the presence of zeolite crystals on the support surface. Furthermore, microporosity appeared in the composite material (14% after two synthesis steps) while it is absent in the bare β-SiC substrate, thus confirming the formation of microporous zeolite material. For comparison, unsupported powdered ZSM-5 presents a 55% microporous volume for 445 m^2 g^{-1} specific surface area.

The quantity of zeolite supported has also been estimated by dissolution of the zeolite crystals in a hydrofluoric acid solution (40 wt %) and compared to the bare support. The amount of ZSM-5 has been calculated to be 12% after a single-coating procedure (extrudates). After a second coating, this value was further increased to 24% (extrudates) and reached 30% on the structured foam material.

The XRD patterns of zeolite/SiC foam (after a single-step and a two-step synthesis procedure) are presented in Figure 2. Both samples exhibit the MFI structure with major peaks located at ~7.9° and ~8.9° and the characteristic triplet at ~23.5°.[36,37]

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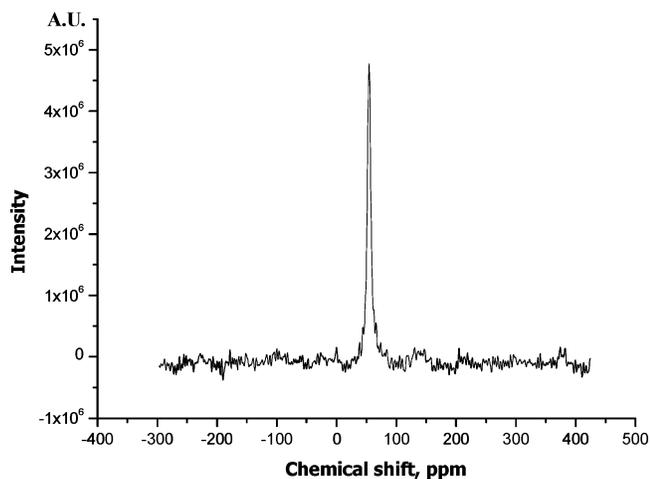*J. Phys. Chem. C, Vol. 111, No. 11, 2007* **4371**

Figure 3. ^{27}Al MAS NMR spectrum of ZSM-5/β-SiC composite (after a two-step procedure).

For comparison the XRD pattern of the bare zeolite formed at the bottom of the autoclave is also presented. The diffraction lines corresponding to the zeolite are relatively weak for the MFI/SiC composite after a single coating procedure, probably due to the low amount of deposited material. These diffraction lines significantly increased after a second synthesis step, indicating the presence of a higher amount of coated zeolite material.

^{27}Al MAS NMR was used to confirm aluminum incorporation in the zeolite/ceramic composite (Figure 3). A single and narrow

signal was observed at 52 ppm, which can unambiguously be attributed to tetrahedrally coordinated aluminum atoms in the zeolite framework.[38] The absence of the typical signal at 0 ppm indicates that no traces of extraframework aluminum species are present. In other words, all aluminum atoms were succesfully incorporated into the MFI framework, thus confirming the nature of the ZSM-5/SiC composite. The full width at half-maximum (FWHM) of the ^{27}Al peak was around 8.5 ppm. This value reflects an average crystal size of about 8 μm for the as-prepared zeolite according to the results reported by Jacobsen et al.[39]

The morphology of the support and the size of the zeolite crystals have been studied by SEM (Figure 4). The micrographs showed that the morphology of the starting carrier, either extrudate or foam, does not change after the synthesis (Figure 4A,C). At higher magnification a complete coverage of the support surface by prismatic MFI zeolite crystals can be observed (Figure 4B,D). The silicon carbide surface has been homogeneously covered by randomly oriented crystals, having 1 μm length for the samples supported on SiC foam. Slightly larger crystals were produced on SiC extrudates, about 3 μm in length.

The discrepancy in the crystal size values, observed by SEM and calculated by NMR, can be explained by the presence of a mixture of crystals (very large crystals), thus enhancing the FWHM.

H/D isotope exchange was performed to evaluate the acidity of the MFI/β-SiC composites according to the method developped by Louis et al.[35] The total number of Brønsted acid sites was measured for the powdered zeolite, and thus allowed us to
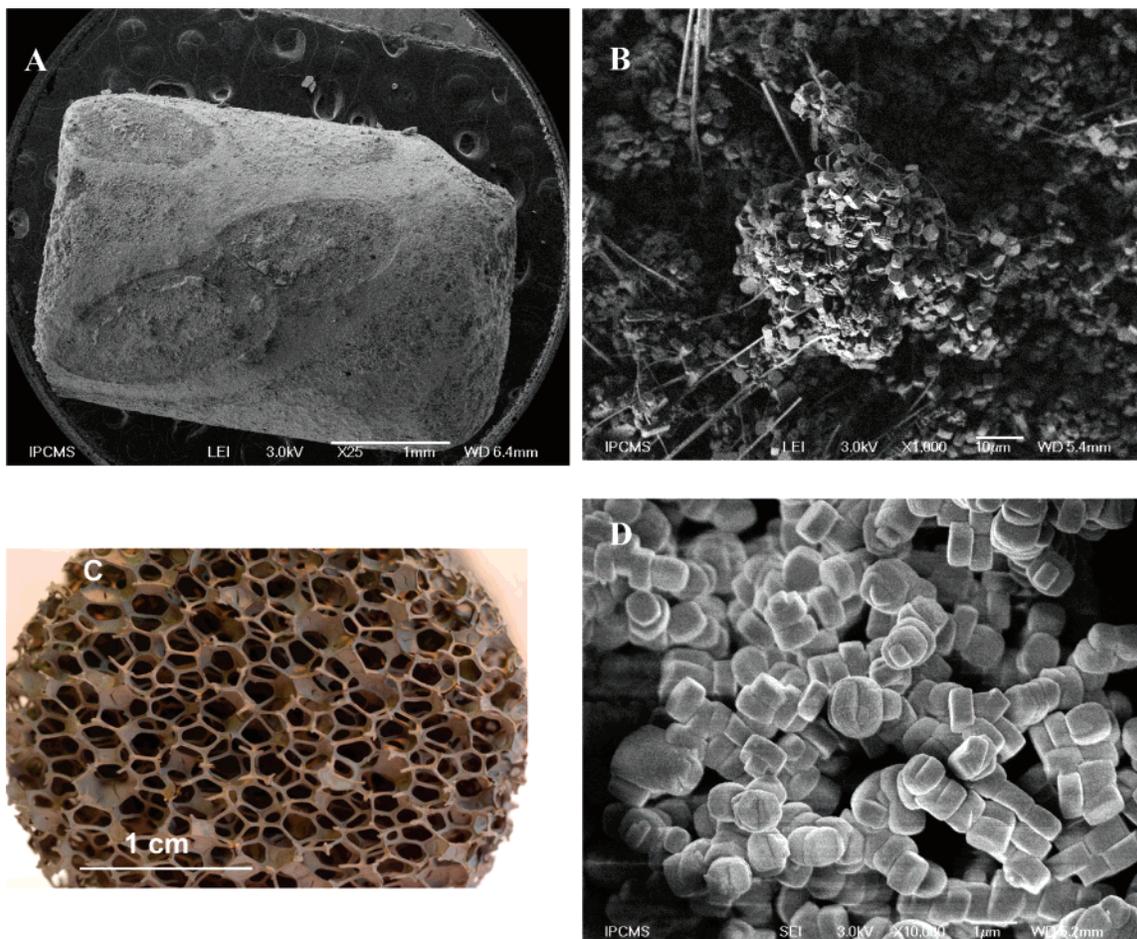

Figure 4. SEM micrographs of the composites: (A) extrudates; (B) double coating of ZSM-5 on SiC extrudates; (C) SiC foam; (D) double coating of zeolite/SiC foam.
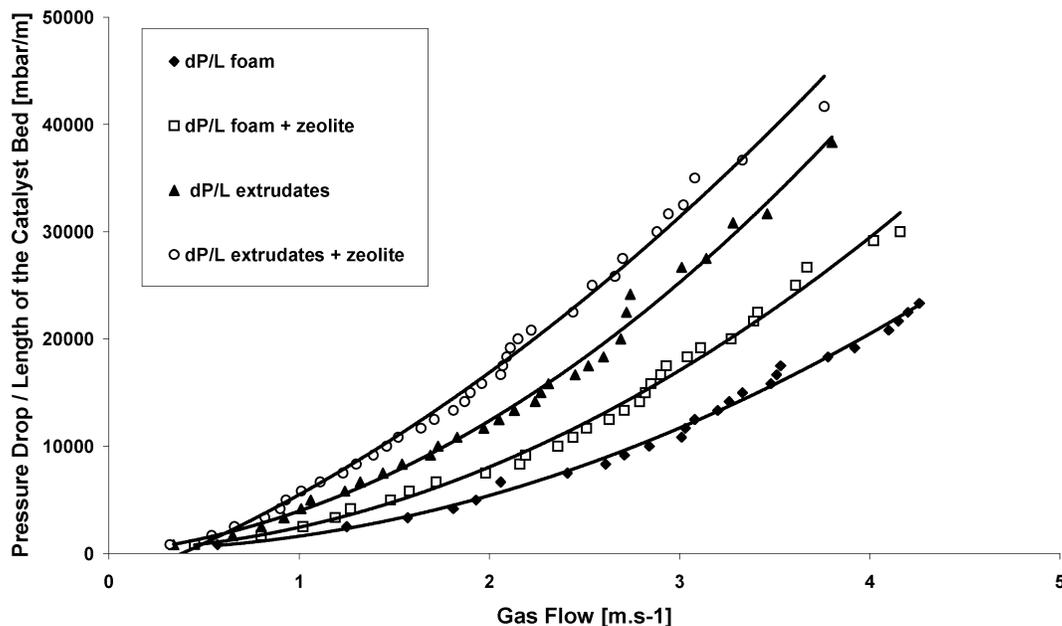
Figure 5. Pressure drop measurements for different SiC shapes before and after zeolite deposition.

determine a Si/Al ratio of 50. Hence, via measuring the number of OH groups of the MFI/β-SiC composite, while subtracting the value of 0.15 mmol of OH/g corresponding to the raw β-SiC material, an amount of 0.11 mmol of OH/g was measured for the H−ZSM-5 contribution. An estimation of the zeolite layer of 22 wt % for the double coating (extrudates) could therefore be made, which is in line with the 24 wt % value obtained after dissolution in hydrofluoric acid solution.

Figure 5 shows the dependence between the pressure drop/ catalyst bed length ratio and the gas velocity for the composites after two coating procedures, and compared to the bare support. The pressure drop was increased with an increase in the gas velocity. However, the pressure drop is higher through the catalyst bed made of extrudates than for a SiC foam. Or, in other words, the pressure drop reached was equal when the gas velocity was 1 1/2 times higher through the foam structured bed. The coating of zeolite crystals on both macroscopic forms of the support led to an additional increase in pressure drop. As a comparison, the powdered zeolite presents a 10 times higher pressure drop under the same conditions (bed length, gas velocity) as the composites, while zeolite extruded pellets should exhibit an intermediary behavior. It can therefore be concluded that the composite ZSM-5/SiC foam exhibits an improved hydrodynamics, in terms of pressure drop and mass transfer, for its use in gas-phase reactions.

4. Activity and Selectivity in the MTO Process

Light olefins are, together with BTX (benzene, toluene, and xylenes), the most important petrochemical building blocks.[32] Nowadays, the methanol-to-olefins (MTO) reaction is considered to be a valuable option for the valorization of stranded gas reserves, and therefore several studies devoted either to the reaction mechanism or to the technology are reported in the literature.[40−45]

Figure 6 presents the methanol conversion as a function of time on stream for the different MFI catalysts. The initial conversion of the double-coated MFI/SiC composite approached 90% and is higher when compared to the single-coated (76%) or the powdered zeolite catalyst (70%). However, the single-coated structured catalyst stabilized its methanol conversion versus time on stream; hence only limited deactivation was
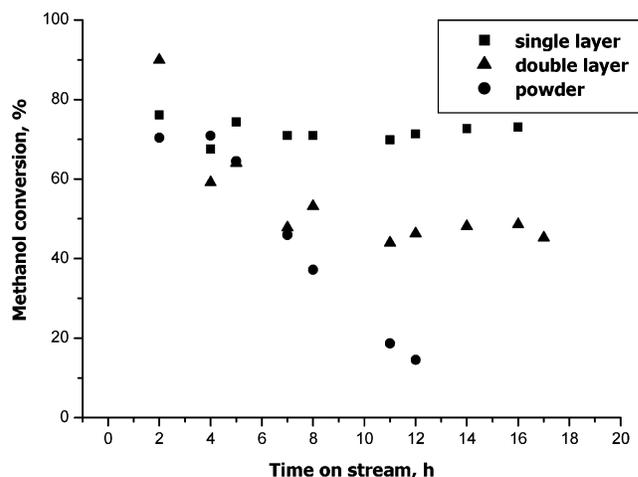

Figure 6. Methanol conversion as a function of time on stream for the different H−ZSM-5 catalysts: powdered and coatings on β-SiC extrudates.

observed during 8 h on stream. The methanol conversion decreased during the first 6 h for the double-coated material to about 45%. Then the catalyst was working at its steady state and almost no activity loss during at least 12 h was observed.

Recently a controversial "carbon pool mechanism" has been proposed to explain the distribution of the different hydrocarbons.[40] Once the C−C bond formation has started, an induction period for olefin formation is observed, where oligomerization−cyclization reactions are taking place. The coking rate is many times higher during this period, thus leading to the fouling of the catalyst surface. However, the methanol conversion is monotonically decreased over the powdered H−ZSM-5 zeolite at a rate of 10% (absolute) per hour. The amount of carbonaceous species deposited on the powdered catalyst (after the same time on stream) was 15% higher than on the zeolite coatings. It is worth noting that, on the bulk zeolite, the dense packing combined with a large crystal size could also favor the retention of the intermediate products, coke precursors, which in turn accelerate the rate of coking.

Therefore, on the bulk zeolite, no steady-state operating conditions could be observed, whereas on structured MFI/SiC
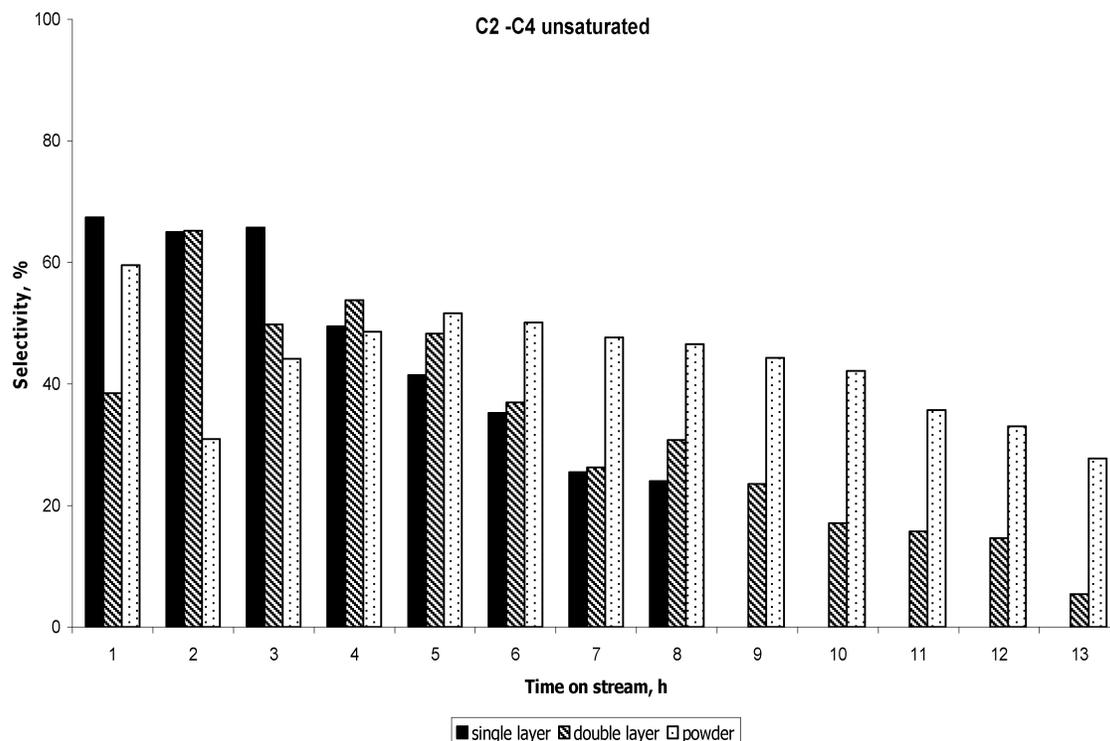
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Figure 7. Selectivity toward C_2–C_4 olefins for the different catalysts.

composite the stability toward deactivation was improved and a steady-state behavior was obtained after a few hours on stream. A possible explanation could be the characteristics of the silicon carbide material which provides a high thermal conductivity and should therefore allow rapid heat evacuation and mass transfer. The dispersion of the thin zeolite layer also favors the access of the reactants and the diffusion of the products outside the pores, thus playing an important role in the stabilization of the catalytic activity. The smaller size of the supported zeolite crystals could also contribute to a reduced coke formation inside the zeolite porosity.

Figure 7 presents the selectivity toward light olefins (C_2–C_4) as a function of time on stream. The single-coated MFI catalyst was the more stable catalyst, and hence also exhibits an extremely high selectivity (65%) toward light olefins during the first 3 h on stream. However, the selectivity to ethylene, propylene, and butenes respectively decreased to 42% after 5 h, to 25% after 8 h, and to no light olefins observed after 8 h on stream. Since methanol conversion was stabilized to 75%, the catalyst still continued to work, but producing exclusively C_1–C_4 linear paraffins obtained via hydride tranfer to the adsorbed carbenium ions.[40] It appears therefore that the single-coated material works as an MTO catalyst during the first hours on stream and then changes its behavior to produce light alkanes. This illustrates once again a different behavior of structured catalytic beds made of zeolites when compared to fixed beds.[46–49] The double-coated MFI/β-SiC composite presents an intermediary behavior between the unsupported material and the single-coated one, thus indicating that the zeolite layer of the coating should be as thin as possible to avoid the loss of the hydrodynamic advantages gained from the preparation of structured catalytic coatings. Despite a high activity loss, the powdered ZSM-5 sample kept its selectivity toward light olefins quite constant, during 10 h, close to 55%.

While tailoring the quantity of zeolite coated on the β-SiC surface (repeated synthesis or not), one can build structured zeolite packings having appropriate macroscopic shapes which

are more resistant to coking. Hence, it should be possible to modify the selectivity in different products for many chemical reactions.

5. Conclusion

ZSM-5 zeolite crystals were homogeneously deposited on the surface of preshaped silicon carbide supports (extrudate or foam). The zeolite was strongly anchored on the β-SiC surface (no zeolite attrition in the reactor) due to the presence of a thin silicon oxycarbide and silica layer, thus solving the problems encountered with silica or alumina supports.

Furthermore, these ZSM-5/β-SiC structured composites were successfully tested in the conversion of methanol into light olefins and gasoline. Depending on the thickness of the zeolite layer, one can change the selectivity toward the desired products, together with an enhancement of the catalyst stability. Both structured zeolite packings exhibit higher activity and selectivity (at least during the first hours on stream) than the powdered zeolite produced under the same synthesis conditions.

The essence of this work will be the design of novel structured packings made of zeolites, via combining a microscopic design (appropriate crystal size) together with a macroshaping which fits the required purpose.

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