

The methanol-to-olefins conversion over zeolite-coated ceramic foams

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Abstract

The use of ZSM-5-coated ceramic foam packing in the conversion of methanol to olefins showed substantial activity and selectivity improvements as compared with conventional extruded zeolite pellets. The formation of propylene was particularly favored over the coated foams. At 380 °C the amount of ethylene and propylene produced per unit volume of reactor packing was 2.5 times higher over the zeolite-coated foams than over pellets. However, at a lower temperature (320 °C) and higher space velocities the zeolite-coated foams were less active than the zeolite pellets. This behavior could be explained by the autocatalytic hydrocarbon pool mechanism. The species involved in the autocatalytic process, which are in equilibrium with the products, were decomposed and flushed off when the space velocity was high or the characteristic size of the catalyst bulk was too small. Thus the zeolite coat has to be optimized to ensure simultaneously a high effectiveness factor and sufficient buildup of catalytic species.

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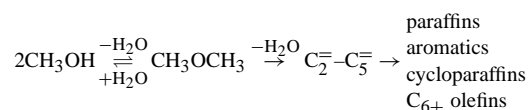
Keywords: MTO; Methanol conversion; Olefin; Hydrocarbon pool; Ceramic foam; ZSM-5; Zeolite washcoat; Structured packing; Propylene

1. Introduction

The conversion of methanol to hydrocarbons over zeolite catalysts is an alternative technology for the manufacture of petrochemicals and gasoline from feedstock other than oil, such as natural gas, coal, or biomass. A large research effort has been dedicated in the last decades to understanding the reaction mechanism, the kinetics, the influence of process parameters, the coking process, and the role of the zeolite catalyst [1–3].

The classical representation of the reaction path in the conversion of methanol to hydrocarbons comprises several consecutive reaction steps (Scheme 1), the first being the fast equilibration of methanol with its dehydration product, the dimethylether [1]. In the next step the equilibrium mixture of oxygenates is converted to light olefins. Most

researchers agree that this reaction proceeds mainly autocatalytically, after the C–C-coupling has produced some light olefins. The oxygenates are considered to be bound by the previously formed olefins [4] or by a so-called hydrocarbon pool consisting of polymethylated benzenes, residing in the micropores of the zeolite lattice [5]. The light olefins are subsequently formed by cracking. For the hydrocarbon pool mechanism very convincing evidence was accumulated in the literature [5–7]. The formation of paraffins, aromatics, and higher olefins proceeds through homologation and cyclization of the light olefins. The coke, which deactivates the catalyst, probably results from the polymerization of the aromatic species contained in the hydrocarbon pool inside the micropores [8]. The conversion of methanol to hydrocarbons (MTH) can be driven toward preferential olefin production (MTO) or gasoline production (MTG) by an appropriate



Scheme 1.

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choice of the catalyst/carrier system and operating conditions.

The present work is an investigation of the possibility of increasing the production of light olefins in the MTO operation mode by a convenient catalyst design. According to the reaction pathway in Scheme 1, the yield of the light olefins as intermediate products is controlled by the contact time of the reactants with the catalyst. In other words, the light olefins have to be quickly removed from the catalyst to prevent them from reacting further. As the catalytic reactor is a hierarchic system, the time needed by molecules to arrive or to leave the active centers consists of three components: (1) the time in the gas phase of the reactor (the space time); (2) the time spent in the catalyst bulk phase (grain diffusion); and (3) the time within the micropores in the zeolite crystal. Regarding the first time component, the yield of light olefins has indeed been shown to pass a maximum, whereas their selectivity continuously decreased with increasing reactor space time [9]. The third time component can be varied by means of the zeolite crystal size. Prinz and Riekert [10] have shown that the olefin selectivity increased with decreasing crystal size of the zeolite ZSM-5. Lowering the characteristic size of the catalyst bulk phase should also produce an increase in the selectivity of light olefins. However, a packing of small particles yields a high pressure drop. An alternative is to use the zeolite in the form of a coat supported on a low-pressure-drop carrier. Such an attempt was reported by Schulz et al. [11], who used fused silica spheres coated with a thin layer of HZSM-5 zeolite for the conversion of methanol to hydrocarbons.

On the basis of these considerations, a new type of MTO catalyst, consisting of a ceramic foam monolith coated with zeolite, was developed. The ceramic foams are open, tridimensionally reticulated structures build of ceramic struts that encompass polyhedral cells. The cells communicate through polygonal windows [12]. A picture of a ceramic foam carrier is shown in Fig. 1. The unconventional carrier was selected because of several considerable advantages: high porosity and permeability for gas flow, radial mixing, turbulent flow, and high geometric surface area. The mechanical strength of the ceramic foams is high enough to allow their use as catalyst carriers: their compressive strength usually amounts to 1–2 MPa (about 10–20 kg/cm²). The characteristic dimension of the catalyst bulk—the coat thickness—can be varied independently of the cell size of the foam. This makes it possible to decouple the hydrodynamics of the flow from the internal mass transfer characteristics of the catalyst. The foam packing can be operated at higher gas velocities required for low space-time without a considerable pressure drop. It was essential to choose a zeolite type that would ensure good stability against coking, as the fixed-bed operation requires. For this reason HZSM-5 was chosen as a catalyst. The zeolite crystals were uniform in size, which was about 500 nm. This size was chosen as a compromise between the need for a small



Fig. 1. Photograph of an open cell ceramic foam piece.

crystal size, as shown before, and the necessity to minimize reactions on the outer, nonselective crystal surface.

To assess the changes and improvements driven by the new catalyst form, the performances of the zeolite coated foam packing were compared with those of conventional extruded zeolite particles, which is one of the usual catalyst formulations for a packed bed.

2. Experimental

2.1. Preparation and characterization of the catalysts

The foam was specially designed for use as an inert catalyst carrier. It was manufactured by the polymer foam replication method without any ingredients that could interfere catalytically with the reaction studied [13]. It consisted of α -alumina bound with mullite and had a pore count of 45 PPI. The foam was pre-cut in cylindrical pieces 14 mm in diameter and 10 mm in length, to match the inner diameter of the reactor tube. The zeolite coat was applied to the foam carrier by the washcoating technique described in [14]. The coat thickness could be arbitrarily changed by the zeolite content of the coating slurry. The zeolite was ZSM-5, with a Si/Al ratio of 32 and a crystal size of 500 nm. After coating and calcination at 550 °C to remove the template, the zeolite changed to the H-form by an ion exchange with NH₄NO₃ (1.5 M, 3 h, 50 °C) followed by another calcination at 550 °C. The amount of zeolite loaded was determined by measuring the BET “surface area” (Micromeritics ASAP 2010, argon as a probe), by taking into account that the surface area of the carrier was negligible in comparison with that of the zeolite.

The cylindrical pellets (2-mm diameter, 7-mm length) were prepared from the same zeolite by extrusion with

boehmite (Sasol, Pural SB) as a binder. The calcined (550 °C) pellets contained 39 wt% zeolite; the balance was the binder in the form of γ -alumina. The extruded zeolite was subsequently submitted to the same ion-exchange procedure as the zeolite-coated foams. The pore size distributions of the pellets and coats were determined by mercury intrusion (Micromeritics, Autopore III).

2.2. Catalytic tests

The conversion of methanol to olefins was performed in a lab-scale unit equipped with a plug flow stainless-steel reactor with a 15-mm inner diameter and a 500-mm length. The reactor was heated electrically; the length of the isothermal zone (± 1 °C) was 200 mm. The catalyst was inserted into the middle of the isothermal zone. To preheat the reactant and regulate the gas flow, the reactor was filled upstream and downstream of the catalyst packing with inert α -alumina particles. In the case of the extruded zeolite pellets, they were diluted 1:10 (wt) with a silicon carbide split of 1 mm particle size, to ensure temperature uniformity and a packing length similar to that used in the case of the foam monoliths. The gap between the foam pieces and the reactor wall was sealed with quartz fabric. To ensure reaction conditions similar to those for the extrudates, and to minimize the overheating of the foam catalyst due to reaction, a layer of γ -alumina grains in the same weight ratio to the zeolite as in the extrudates was placed prior to the foam monoliths. The γ -alumina catalyzes the dehydration of methanol to dimethylether, which produces about a third of the heat release in the MTO reaction [9]. The reaction temperature was recorded with a thermocouple placed coaxially in the center of the reactor, with the tip in contact with the catalyst.

The reaction mixture, consisting of 20 vol% methanol in nitrogen, was prepared in a saturator. The reaction pressure was kept constant at 1.65 bar, and the temperature was varied between 320 and 420 °C. After each run the catalysts were regenerated by burning the coke at 550 °C in a stream containing 5% oxygen in nitrogen. The carbon balance was monitored by means of an infrared gas analyzer placed after an afterburner that completely oxidized the combustible gas components. The reactant and product mixtures were analyzed by gas chromatography (HP 6890 with FID detection, Poraplot Q) after premixing with a constant neopentane flow for reference.

2.3. Reaction data analysis

On the basis of the chromatographic analysis, the dimensionless concentrations of the chemical species in the product stream, on a carbon basis, were calculated as

$$y_i = \frac{\dot{n}_i \varepsilon_i}{\dot{n}_{\text{MeOH},0} \varepsilon_{\text{MeOH}}}, \quad (1)$$

where the subscript 0 refers to the inlet flow. For the products, the dimensionless concentrations equal the reactor yields.

The conversion was related to both methanol and dimethylether, designated as “oxygenates,” as a lumped reactant species:

$$X_{\text{MeOH+DME}} = 1 - y_{\text{MeOH}} - y_{\text{DME}}. \quad (2)$$

The reactor selectivity for the product i was calculated as

$$S_i = \frac{y_i}{X_{\text{MeOH+DME}}}. \quad (3)$$

The space velocity was always related to the amount of zeolite loaded into the reactor:

$$\text{WHSV} = \frac{\dot{m}_{\text{MeOH},0}}{m_{\text{zeo}}}. \quad (4)$$

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows the characteristics of the catalysts used in this study. The zeolite-coated foams were prepared with two coat thicknesses, 5 and 18 μm . The measured mean pore diameter of 150 nm for the coats corresponds to the interstices between the 500-nm crystals. In the 2-mm-diameter extruded pellets the 500-nm zeolite crystals were embedded in the γ - Al_2O_3 binder matrix. The mercury intrusion measurements gave a mean pore diameter of 10 nm.

3.2. Activity and catalyst effectiveness

Fig. 2 shows the evolution of the oxygenate conversion with the space velocity for different temperatures. At 320 °C and low space velocity the coated foams perform better than the zeolite pellets, but with increasing space velocity the pellets are more active (Fig. 2a). At 380 °C and higher temperatures the coated foams are the most active in the entire space velocity range (Fig. 2b). The highest activity level is reached over the foam with the thicker zeolite coat. Measurements at 350 °C (not shown) displayed an intermediate behavior.

To account for this behavior, let us consider the kinetics of the methanol-to-olefin reaction in relation to diffusional transport limitations. As pellets have much narrower pores and a larger characteristic bulk size than the coats, one would expect higher catalyst effectiveness in the coat than in the

Table 1
Relevant features of differently shaped HZSM-5 catalysts: coats on 45-PPI alumina-mullite foams or alumina-bound extruded pellets

Catalyst	Zeolite content ^a (wt%)	Coat thickness, μm / pellet diameter, mm	Pore diameter (nm)
Zeolite coat/ ceramic foam	14.0 3.9	18 5	150
Zeolite pellets	39	2	10

^a Related to the total catalyst mass comprising carrier or binder.

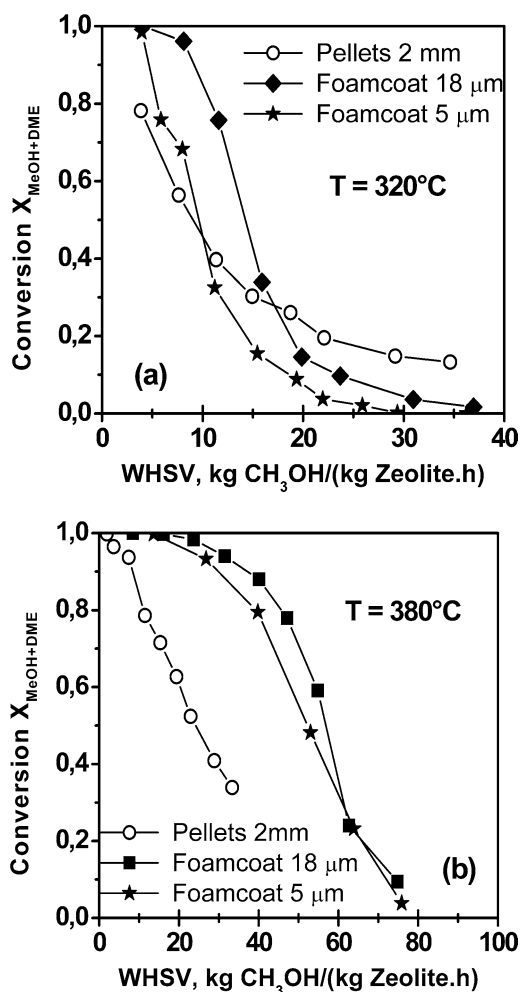


Fig. 2. Comparison of HZSM-5 extruded pellets (alumina bound) with coated foams of different coat thickness: the conversion of oxygenates over space velocity at 320 °C (a) and 380 °C (b).

bulky pellet, provided that the rate of the internal diffusion is comparable to or lower than the reaction rate. To evaluate the influence of the internal diffusion on the observed kinetics, the apparent rate constants for the conversion of oxygenates were calculated from the conversion-space velocity data. According to the literature, the conversion rate of oxygenates is first order with respect to the lumped oxygenate concentration [4,15,16]. Although the first-order kinetics might be to some extent an oversimplification, the resulting first-order rate constants are useful in a comparison of the catalysts' activities and evaluation of the extent of diffusional limitations. Therefore the first-order rate constants were calculated as

$$k_{\text{obs}} = \frac{1}{\tau_{\text{PFR}}} \ln \frac{1}{1 - X_{\text{MeOH+DME}}} \quad (5)$$

The contact time τ_{PFR} was calculated as the volume of zeolite contained in the packing divided by the volumetric flow rate at reactor conditions.

Subsequently, the Wagner–Weisz–Wheeler modulus and hence the extent of diffusional limitations were evaluated as

follows [17]:

$$M_{\text{W}} = L^2 \frac{k_{\text{obs}}}{D_{\text{e}}} \quad (6)$$

Values of M_{W} well above 1 mean that the reaction is strongly influenced by internal diffusion. If the value is well below 1 the internal diffusion does not influence the rate.

The characteristic size of the catalyst bulk L was taken as half the cylinder radius for extruded particles, and half the thickness of the zeolite coat, respectively [17].

The effective diffusion coefficient D_{e} was evaluated on the basis of the textural data (Table 1) as

$$D_{\text{e}} = \varepsilon \chi D_{\text{p}}, \quad (7)$$

with the pore diffusion coefficient [18,19]:

$$D_{\text{p}} = \left(\frac{1}{D_{\text{K}}} + \frac{1}{D_{\text{M}}} \right)^{-1}, \quad (8)$$

$$D_{\text{K}} = 48.5 d_{\text{p}} \sqrt{\frac{T}{M_i}}, \quad (9)$$

$$D_{\text{M}} = \frac{0.001858 T^{3/2} [(M_i + M_2)/M_i M_2]^{0.5}}{p \sigma_{i_2}^2 \Omega}. \quad (10)$$

Dimethylether was chosen as the probe component i for the molecular (D_{M}) and Knudsen (D_{K}) diffusion coefficients. The second component for the molecular diffusion was nitrogen. For the calculation of the Knudsen diffusion coefficient the mean pore diameter (Table 1) was employed. The tortuosity factor χ was taken as 0.3, as recommended by Baerns et al. [18]. The catalyst bulk porosities, as determined by mercury penetration, were $\varepsilon = 0.59$ (pellets) and $\varepsilon = 0.43$ (coats).

Selected values of the calculated kinetic variables are listed in Table 2. The analysis of the Wagner module shows that the pellets are in the pore resistance-controlled regime at all temperatures, whereas the zeolite coats are in the reaction-controlled regime within the entire temperature range. This means that at equal zeolite amounts in the reactor, the coated foams should yield higher conversions than the pellets, a fact that is indeed demonstrated at high temperatures in the whole space velocity range. But it is still unclear why at lower temperatures and high space velocities the conversion levels on foams fall below those on the pellets.

Analysis of the kinetic data from Table 2 also shows that the apparent first-order rate constants decrease strongly with increasing space velocity on the coated foams. For the pellets, the first-order rate constants remain almost unchanged. A possible explanation for this unusual behavior can be given on the basis of the autocatalytic hydrocarbon pool mechanism. This states that the bounding of oxygenates, as a first step in their conversion to olefins, is performed by polymethylbenzene molecules residing in the zeolite microchannels. It follows that the conversion rate of the oxygenates should be proportional to the internal

Table 2

Observed 1st order rate constants and estimated Wagner moduli for the HZSM-5 catalysed MTO conversion over extruded pellets and coated foams

Temperature (°C)	WHSV (kg/(kg h))	Pellets		Foamcoat 18 μm		Foamcoat 5 μm	
		k_{obs} (s^{-1})	M_{W}	k_{obs} (s^{-1})	M_{W}	k_{obs} (s^{-1})	M_{W}
320 °C	4	7.5	30.8	59.5	4.6×10^{-2}	21.2	1.3×10^{-3}
	15	6.9	28.2	4.0	6.5×10^{-3}	3.3	2.1×10^{-4}
	30	6.0	24.5	1.5	1.5×10^{-3}	0.1	4.7×10^{-6}
380 °C	8	28.9	112.9	136.5	9.9×10^{-2}	–	–
	15	27.0	105.7	136.8	9.9×10^{-2}	114.1	6.8×10^{-3}
	30	21.4	83.5	124.7	9.1×10^{-2}	101.8	6.1×10^{-3}
	50	–	–	68.9	5.0×10^{-2}	49.0	2.9×10^{-3}

stationary concentration of the polymethylbenzenes. The reaction products, the olefins, are produced by cracking of the alkylated polymethylbenzenes. This was demonstrated experimentally by the group of Kolboe et al. [5,8]. They have shown that upon flushing with inert gas the polymethylbenzenes deposited in the zeolite were quickly decomposed to light olefins and methylbenzenes with fewer (2, 3, or 4) methyl groups that escaped from the zeolite. By continuously feeding methanol to the zeolite, they could keep the aromatic deposit stable. This suggests that during the MTO reaction the concentration of the polyalkylated benzenes acting as catalysts is stabilized at a level such that the rate of homologation through methanol or dimethylether equals the rate of olefin splitting.

These considerations account for the activity pattern of the coated foams and the extruded pellets. At higher space velocities and the small characteristic dimension of the catalyst bulk, as in the zeolite coats, the leak rate of olefins and lower methylated benzenes from the zeolite increases. The probability of readsorption in the zeolite and reaction of this species with the oxygenates to form the polyalkylated aromatics decreases. As a consequence, the stationary concentration of the aromatic catalyst in the zeolite becomes lower. In contrast, in the extruded pellets the decomposition and flushing of the catalytic species are hindered by the larger bulk volume and smaller pores. Consequently, the catalyst concentration in the zeolite micropores would be higher and less influenced by the increased gas velocity at the exterior of the pellets.

With increasing temperature the reaction of the oxygenates with the aromatic catalyst is likely to be faster. The alkene splitting from the catalyst will also be faster, but the diffusion of the olefins and lower methylated benzenes from the catalyst bulk into the gas phase will be negligibly influenced by the temperature increase. Hence the decomposition products can readsorb into the zeolite and undergo further reactions with oxygenates to build aromatic rings. As a consequence, higher stationary concentrations of polymethylbenzenes can be achieved at higher temperatures. The space velocity needed to leak the decomposition products into the gas phase becomes herewith larger at higher temperatures.

From the complex behavior displayed by the coated foams, it follows that the characteristic dimension of the catalyst bulk, as well as its textural properties, has a great influence on the activity in the conversion of methanol. The decrease in the bulk size and increase in the mean pore diameter improve the efficiency, but at the same time they deteriorate the storage of catalytic species within the zeolite micropores. Therefore, to provide a more active catalyst, a compromise has to be found between these opposite tendencies, meaning that an optimal coat thickness has to be found for a given coat texture. Larger zeolite crystals are likely to be less sensitive to the decomposition and wash-up of the catalytic species, but they will also deactivate faster and probably show lower intrinsic olefin selectivity.

3.3. Olefin selectivity and yield

Fig. 3a shows the evolution of the cumulative ethylene and propylene selectivity with the oxygenates' conversion. The data were collected from several runs at 320 °C, in which the space velocity was varied upward or downward. After each run the catalysts were regenerated by burning the coke. According to the data, the olefin selectivity increased decisively when switching from pellets to coated foams; the highest selectivities were found over the thinnest zeolite coat. This is actually the anticipated result for the light olefins as intermediates of a reaction sequence. The same selectivity ranking also occurs at higher temperatures.

The ratio between the propylene and ethylene selectivities as a function of the oxygenate conversion is shown in Fig. 3b. From the falling tendency of the propylene selectivity with increasing conversion (that is, at higher space time) it seems that propylene is less stable than ethylene toward further transformations. This explains why the ratio of propylene to ethylene increases when switching from pellets through the thicker coat to the thinner coat: the smaller the characteristic size of the catalyst bulk, the higher are the chances for propylene to escape further conversion. Consequently, the increase in olefin selectivity with the switch from pellets to the thinnest zeolite coat is likely to occur merely because of increasing propylene.

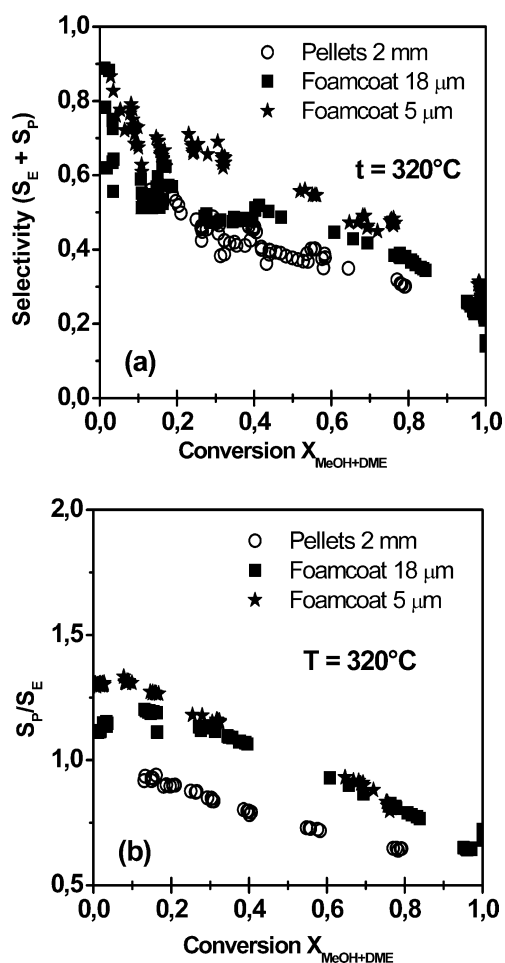


Fig. 3. Cumulative (ethylene + propylene) selectivity (a) and the propylene/ethylene ratio (b) at 320°C over HZSM-5 in form of alumina-bound extruded pellets or coated ceramic foams.

The cumulative yields of ethylene and propylene as a function of the space velocity at 320°C and 380°C are presented in Fig. 4a and 4b. The maximum in olefin yield occurs at a conversion level of about 80% at 320°C and 90% at 380°C, regardless of the catalyst form. The higher activity of the coated foam packing as compared with the pellets causes a shift of the maximum toward higher space velocity. At the same time, the increased olefin selectivity over the zeolite-coated foams results in larger values of the maximum yield.

The space-time yield of the olefins is proportional to both the space velocity and the olefin yield. As a result the zeolite-coated foams can give higher olefin productivity per unit volume of catalyst packing. For instance, at 380°C over a particle packing, a maximum olefin yield of about 22% can be achieved with a feed of $1.7 \times 10^3 \text{ kg}_{\text{methanol}}/(\text{m}^3_{\text{packing}} \text{ h})$, while over the foam with an 18- μm coat the maximum yield is ca. 32% at $3.1 \times 10^3 \text{ kg}_{\text{methanol}}/(\text{m}^3_{\text{packing}} \text{ h})$. This shows that the use of the zeolite-coated foam allows increased olefin production per unit volume of reactor by a factor of ca. 2.5.

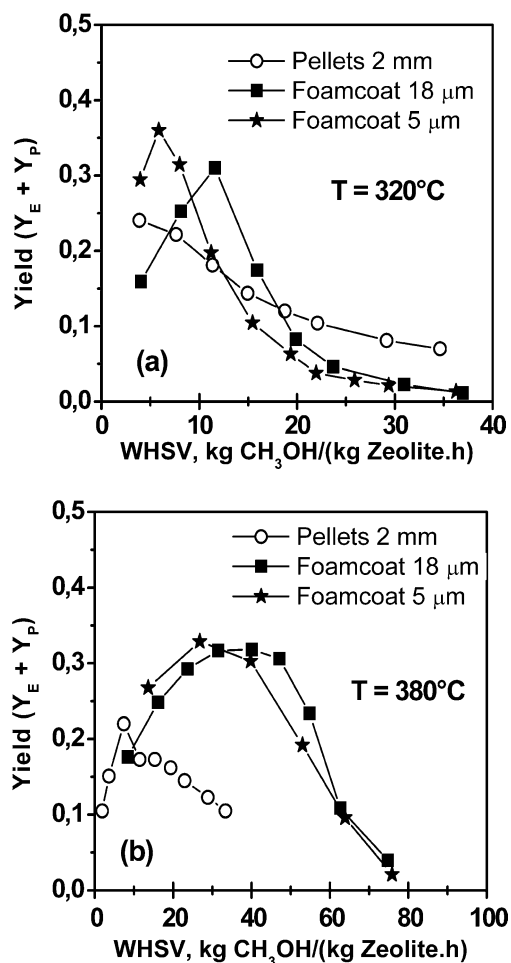


Fig. 4. The cumulative (ethylene + propylene) yield over HZSM-5 catalysts: the effect of catalyst shaping, reaction temperature and space velocity.

4. Conclusions

The present work shows that although the conversion of methanol to olefins has been studied for a long time, there are still generous resources that can be used to increase the reactor performances in this well-known process. The methanol-to-hydrocarbon conversion has some particular characteristics that make the improvement of the catalyst less straightforward than for a common reaction sequence. A notable feature is the involvement of an autocatalytic reaction mechanism that seems to require a certain bulkiness of the catalytic active phase to ensure enough catalytic species to maintain the methanol conversion. A catalyst with a small-size bulk phase and large pores has difficulty keeping the catalytic species confined in the micropores, allowing the decomposition products to be quickly flushed into the gas stream. On the other hand, a too bulky catalyst with small pores has low effectiveness and selectivity for light olefins. As a result of this complex problem, the search for a better catalyst at a certain reaction temperature is an optimization problem dealing with the characteristic size of the catalyst in relation to the pore size. The use of ceramic foams as car-

riers allows the variation of the catalyst bulk thickness with almost no influence on the hydrodynamics, providing at the same time a high turbulence and radial mixing inside the packing.

Acknowledgment

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Appendix A. Nomenclature

D_e	effective diffusion coefficient of the catalyst bulk (m^2/s)
D_p	pore diffusion coefficient of the catalyst (m^2/s)
D_M	molecular diffusion coefficient (m^2/s)
D_K	Knudsen diffusion coefficient (m^2/s)
d_p	pore radius (m)
k_{obs}	the apparent first-order rate constant (s^{-1})
L	characteristic size of the catalyst bulk (m)
M_W	the Wagner–Weisz–Wheeler modulus
M_i	molar mass (kg)
$\dot{m}_{\text{MeOH},0}$	mass flow of methanol at reactor inlet (kg/h)
m_{zeo}	the weight of zeolite in the reactor (kg)
\dot{n}_i	molar flow of species i (kmol/h)
p	pressure (Pa)
PPI	pores per linear inch: the pore count expressed in inch^{-1}
S_i	reactor selectivity for product i
T	temperature (K)
$X_{\text{MeOH}+\text{DME}}$	conversion of lumped oxygenates
y_i	dimensionless concentration of species i on carbon basis

WHSV	weight hourly space velocity (kg/(kg h))
ε	catalyst bulk porosity (–)
ε_i	the number of carbon atoms in the molecule of species i
Ω	diffusion collision integral (–)
σ_{i2}	binary pair characteristic length (\AA)
τ_{PFR}	contact time (s)
χ	tortuosity factor (–)

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