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Methanol conversion over acid solid catalysts

Leonardo Travalloni [a], Alexandre C.L. Gomes [a], Alexandre B. Gaspar [b], Mônica A.P. da Silva [a,*]

[a] Escola de Química, UFRJ, Centro de Tecnologia, Bl. E, Ilha do Fundão, Rio de Janeiro, RJ 21949-900, Brazil
[b] Instituto Nacional de Tecnologia, Av. Venezuela, 82, Sl. 518 Centro, Rio de Janeiro, RJ 20084-310, Brazil

Abstract

A molecular sieve SAPO-34 with high density of strong acid sites was synthesized and its performance in methanol conversion was compared with the performances of ZSM-5, mordenite and beta commercial zeolites. Each catalyst was characterized by X-ray diffraction, X-ray fluorescence, textural analysis (BET method), and temperature programmed desorption of ammonia. The effects of temperature and time of reaction on methanol conversion were evaluated. Among the studied catalysts, SAPO-34 showed the highest initial selectivity to C_2 and C_3 compounds at 450 °C; however, it seems that the high density of strong acid sites of SAPO-34 resulted in an extremely fast deactivation of these sites, giving insignificant light olefins production after 1.5 h of reaction and turning the catalyst highly selective to dimethyl ether. Mordenite showed high selectivity towards C_2 and C_3 compounds at low temperatures, but underwent fast deactivation of its strong acid sites at high temperatures. ZSM-5 and beta zeolites were much more stable and also selective towards C_2 and C_3 compounds, proportionally to their densities of strong acid sites.

Keywords: Methanol to olefins; SAPO-34; Deactivation; Zeolites

1. Introduction

Recent discoveries of large reserves of natural gas have motivated the development of viable methods to convert this cheap energy source into higher value products. The technology of methanol production from natural gas is already mature and widely used. A great growth of the demand for ethene and, especially, propene is foreseen for the future. In this context, methanol conversion to light olefins, known as MTO conversion, has attracted attention as a potential indirect route for the production of ethene and propene from natural gas. The MTO process is, nowadays, in the way of being commercialized with an economic advantage in comparison with conventional processes of naphtha cracking and other technologies of use of natural gas. It is known that MTO conversion is catalyzed by acid solids. However, the selective production of ethene and propene is still a challenge for the catalysis researchers. Until the passed decade, most of literature discussed the use of ZSM-5 zeolite as MTO catalyst, verifying that aromatic hydrocarbons are obtained as by-products.

More recently, the use of microporous silicoaluminophosphate molecular sieves (SAPOs) has been studied, with especial attention on SAPO-34, which allows the production of hydrocarbons in a narrower band. Selectivities above 80% to C_2–C_4 olefins for complete methanol conversion have been obtained when catalysts based on SAPO-34 were employed, indicating the great potential of these catalysts for application in the industrial production of ethene and propene.

The aims of this work were to synthesize SAPO-34 molecular sieve according to one of the several methodologies available in literature and evaluate the performance of this catalyst and of the commercial zeolites ZSM-5 (Degussa-Hüls), mordenite-40, and beta-40 (Süd-Chemie) in methanol conversion driven to light olefins production.

2. Experimental

2.1. SAPO-34 synthesis

SAPO-34 was synthesized according to the procedure reported by Prakash and Unnikrishnan [1] and the calcination of

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* Corresponding author.
E-mail address: monica@eq.ufrj.br (M.A.P. da Silva).

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the solid was carried out by a procedure adapted from Gomes et al. [2].

2.2. Catalysts' characterization

X-ray diffraction (XRD) analyses were carried out in a Rigaku Miniflex diffractometer, using Cu Kα radiation (λ = 1.5417 Å) and operating at 30 kV and 15 mA. X-ray fluorescence (XRF) analyses were carried out in a Rigaku Rix 3100 spectrometer, equipped with a rhodium X-ray generator tube. Textural analyses were carried out according to the BET method in a Micromeritics ASAP 2000 equipment. Temperature programmed desorption of ammonia (TPD) analyses were carried out in a multipurpose unity coupled with a Balzers QUADSTAR 422 QMS 200 mass spectrometer. For the TPD analyses, NH_3 adsorption was carried out at 100 °C, by submitting the samples to a 4% NH_3/He mixture flow of 60 ml/min during 30 min; desorption was carried out by heating the samples from 100 to 550 °C at 10 °C/min, under He flow of 60 ml/min.

2.3. Catalytic tests

Methanol conversion was carried out under atmospheric pressure in a continuous reacting system composed by a Pyrex tubular reactor containing a fixed bed of approximately 0.1 g of catalyst. Methanol was fed to reactor from a saturator using N_2 as carrier gas. The saturator temperature was kept at 0 °C (methanol partial pressure of 0.04 atm) by a thermostatic bath and N_2 flow was kept at 30 ml/min (WHSV = 0.94 h^{-1}) by valves. Before each test, catalyst was dried *in situ* under N_2 flow of 30 ml/min, according to the following thermal program: heating from ambient temperature to 500 °C at 10 °C/min, keeping at 500 °C for 2 h and cooling to the temperature required to the beginning of the reaction.

To study the effects of temperature on methanol conversion, the reaction was carried out, sequentially, at 250, 300, 350, 400, 450 and 500 °C. Samples of reactor effluent were taken after 45 min of reaction at each temperature and about 10 min after each sampling the reactor was heated to the next reaction temperature, in such a way that the interval between two consecutive samplings was approximately of 1 h. To investigate the effects of time on stream on methanol conversion, the reaction was carried out at 450 °C throughout 5.5 h. Samples of reactor effluent were taken after the first 30 min of reaction and, afterwards, in intervals of 1 h.

Reactor effluent was analyzed by on-line gas chromatography in a HP 6890 Plus chromatograph equipped with a flame ionization detector and a HP-PONA capillary column (50 m). Selectivities to interest products were expressed as mass percentages of each product among all detected reaction products.

3. Results and discussion

3.1. Catalysts characterization

Fig. 1 shows the X-ray patterns of the catalysts, where the characteristic peaks of each crystalline structure can be observed, indicating high crystallinity and purity [1,3].

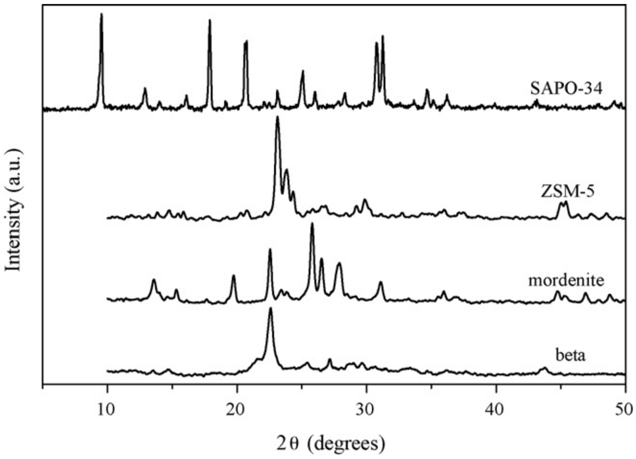

Fig. 1. XRD patterns of the catalysts.

Table 1 presents the catalysts' chemical compositions, provided by XRF. The oxide contents observed for the synthesized SAPO-34 are similar to the relative contents verified by Prakash and Unnikrishnan for the non-calcined solid [1]. The zeolites show high silica contents and, consequently, high SiO_2/Al_2O_3 molar ratios (SAR).

Table 2 shows the textural properties of catalysts. The specific area and micropore volume values observed for SAPO-34 are consistent with typical values observed in literatures [4–6], while the observed mesopore volume is significantly lower than the value reported by Aguayo et al. [6]. It can be observed that the structure of SAPO-34 is mainly microporous, because the mesopore area and volume are relatively small. Results obtained for ZSM-5 are very close to the values reported in literature, corroborating with the high crystallinity observed by XRD. The high values of specific area and micropore volume observed for mordenite suggest high crystallinity, which is confirmed by XRD results. The textural analysis of beta zeolite also confirms the crystallinity of this material [7]. Mordenite and beta zeolites show micropore volumes very similar and, as well as ZSM-5, are mainly microporous, because their mesopore volumes are small.

Figs. 2–5 show the NH_3 desorption profiles of SAPO-34, ZSM-5, mordenite, and beta zeolite, respectively. Each desorption profile was well fitted by three gaussian curves: the first at lower temperatures (218–252 °C), related to low acid strength sites; the second at intermediate temperatures (315–348 °C), related to moderate acid strength sites; the third at higher temperatures (457–536 °C), corresponding to stronger

Table 1
Chemical composition of the catalysts

Catalyst	SiO_2 (wt.%)	Al_2O_3 (wt.%)	P_2O_5 (wt.%)	SAR
SAPO-34	14.1	38.3	40.0	0.62
ZSM-5	93.2	6.7	–	23.6
Mordenite	95.1	4.8	–	33.7
Beta	94.5	5.3	–	30.3

Table 2
Textural properties of the catalysts

Catalyst	Specific area (m^2/g)	Micropore area (m^2/g)	Micropore volume (cm^3/g)	Mesopore area (m^2/g)	Mesopore volume (cm^3/g)
SAPO-34	536	570	0.27	0.2	0.002
ZSM-5	345	348	0.16	30	0.02
Mordenite	569	527	0.25	50	0.10
Beta	530	494	0.23	56	0.07

acid sites. The temperature of the gaussian curve related to strong acid sites and, consequently, the acid strength of the catalysts reduced in the order: mordenite > beta zeolite > SAPO-34 > ZSM-5. For the zeolites, the acid strength reduction accompanied the SAR ratio reduction, which was already reported in literature [8]. Based on the area under each desorption profile, the total desorbed NH_3 amount by mass unity of each catalyst was calculated and the results are shown in Table 3. In view of the distinct specific areas of the catalysts, Table 3 also shows the total desorbed NH_3 amount by area unity of each catalyst, which is related to the acid site density in each catalyst. Among the zeolites, ZSM-5 showed the higher acid site density, which is related to its smaller SAR ratio [8]. However, although mordenite shows the highest SAR ratio among the zeolites, this catalyst showed a higher acid site density than beta zeolite. For SAPO-34, the observed acid site density is much higher than the values reported by several authors [4,6,9,10]. In all desorption profiles, valleys can be seen at temperatures around 340 °C. The area under each desorption profile for temperatures up to 340 °C was related to the weak

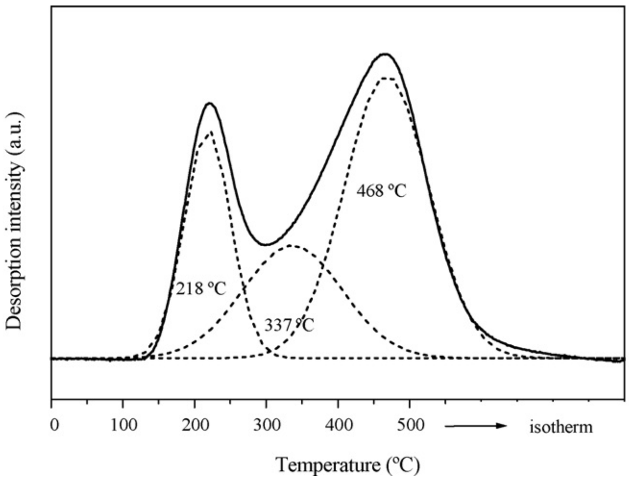

Fig. 2. NH_3 desorption profile of SAPO-34.

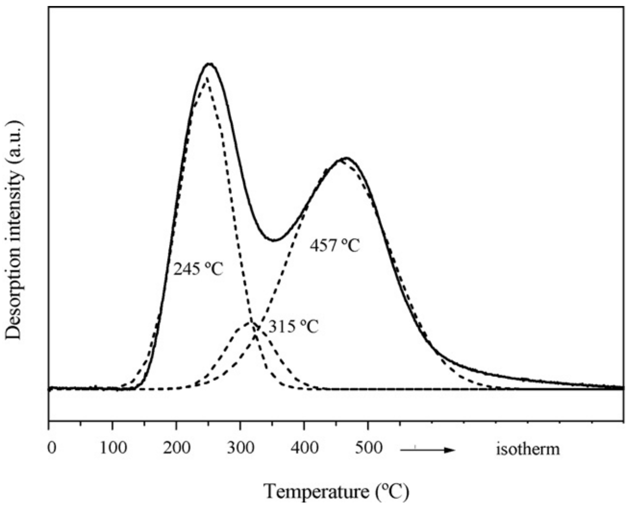

Fig. 3. NH_3 desorption profile of ZSM-5.

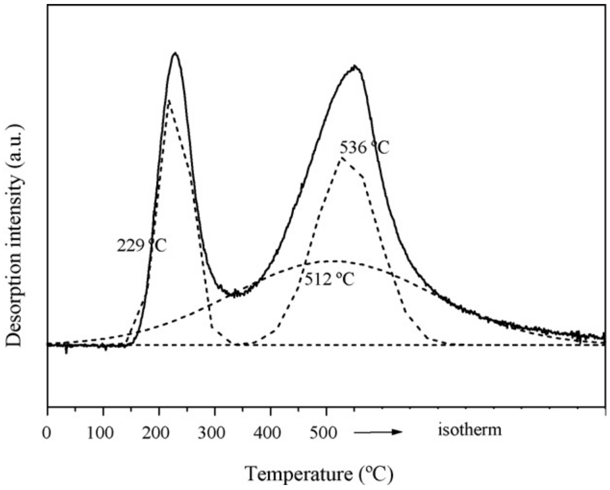

Fig. 4. NH_3 desorption profile of mordenite.

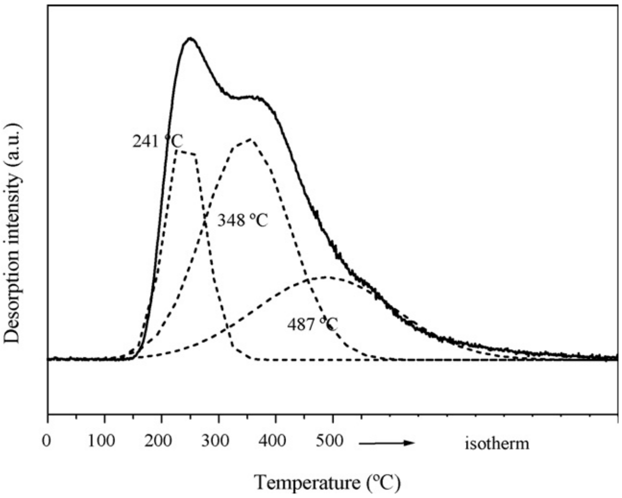

Fig. 5. NH_3 desorption profile of beta zeolite.

Table 3
Acid properties of the catalysts

Catalyst	Weak acid site density (mmol/g)	Strong acid site density (mmol/g)	Global acid site density (mmol/g)	Global acid site density (μmol/m^2)
SAPO-34	1.65	2.90	4.55	8.48
ZSM-5	1.62	1.90	3.52	10.20
Mordenite	0.62	1.49	2.11	3.70
Beta	0.72	0.80	1.52	2.87

acid site density of each catalyst; the remaining area was related to the strong acid site density of each catalyst. The strong acid site density by mass unity of catalyst reduced in the order: SAPO-34 > ZSM-5 > mordenite > beta zeolite.

3.2. Catalytic tests

Fig. 6 shows the effect of temperature on methanol conversion over each catalyst. For the adopted reaction conditions, conversion over ZSM-5 and mordenite was of the order of 90% at the lower evaluated temperature (250 °C), reaching 100% at 300 °C. For mordenite, however, conversion was reduced at 400 °C and kept slightly lower than 90% up to 500 °C. This indicates that mordenite underwent deactivation at high temperatures, which can be related to the high acid strength of that catalyst, because coke formation over catalyst surface is proportional both to the acid strength of its active sites [6,8] and to temperature. For beta zeolite, conversion was 94% at 250 °C, reaching 100% at 350 °C. For SAPO-34, conversion at 250 °C was also of the order of 90%; however, at 300 °C conversion was only 27%. This suddenly reduction of conversion can be due to an intense deactivation of the stronger acid catalyst sites, which are more active, while the weaker acid sites kept active because the increase in temperature from 300 to 400 °C resulted in a large increase in conversion (from 27 to 75%). At temperatures higher than 400 °C, conversion over SAPO-34 kept slightly lower than 80%. The fast deactivation of the stronger acid sites of SAPO-34 can be related to the high density of these sites, which seem to be associated with hydrocarbon formation from methanol [11,12]. At temperatures as low as 300 °C, coke formation is slow, but ethene and propene (that are often indicated as the first hydrocarbons to be formed) can suffer oligomerization [13]. The oligomers, produced in large amount, would not suffer cracking (due to low temperature) and would not diffuse through the narrow pores of SAPO-34 (due to the large dimensions of those molecules), blocking the inner active catalyst sites [14].

The chromatographic column used in this work did not provide the separation of ethane/ethene and of propane/propene. However, several authors, studying the MTO conversion over catalysts of the same types studied in this work, reported that the produced amounts of ethane and propane were significantly lower than the amounts of the correspondent olefins [4,15–17]. In this way, the selectivity to C_2 and C_3 compounds is a good indicative of the selectivity to ethene and propene. Fig. 7 shows the effects of temperature on selectivity to C_2 and C_3 compounds for the catalysts employed in this work. For ZSM-5, that selectivity increased with temperature, reaching 52% at 500 °C. This behavior is also verified for mordenite up to 350 °C, temperature at which 48% of C_2 and C_3 compounds were obtained. However, at higher temperatures, the selectivity of mordenite to C_2 and C_3 compounds reduced rapidly, following the reduction of conversion observed in Fig. 6. This confirms that the active

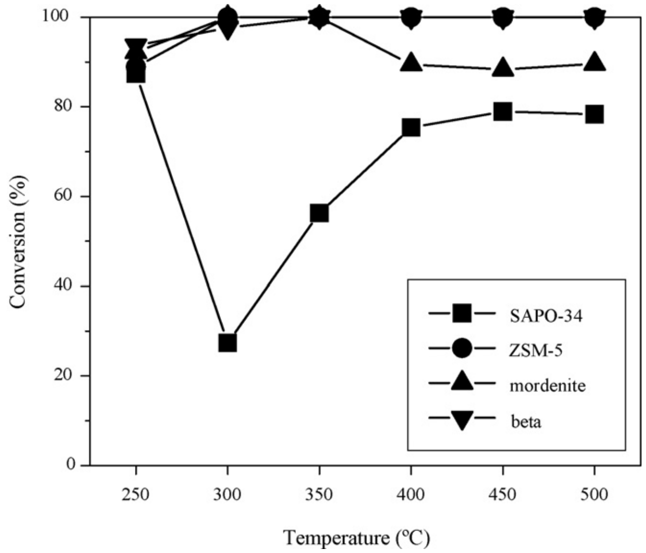

Fig. 6. Effects of temperature on methanol conversion.

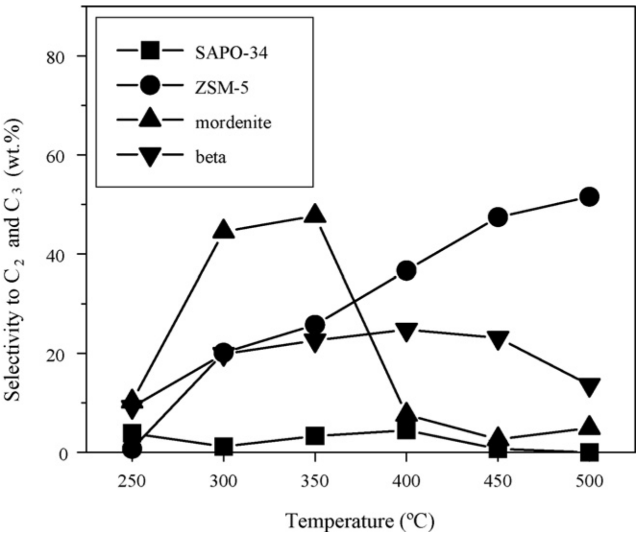

Fig. 7. Effects of temperature on selectivity to C_2 and C_3 compounds.

sites involved with ethene and propene formations are the stronger acid sites, which undergo faster deactivation. The excellent performance of mordenite at low temperatures (before an extensive deactivation) must be related to its high acid strength. Nevertheless, this characteristic also resulted in a higher coke formation. For beta zeolite, selectivity to C_2 and C_3 compounds increased up to 400 °C and reduced at higher temperatures, reaching a maximum of 25%. This value is much lower than the values reached by other zeolites, probably due to the low strong acid site density of beta zeolite. This characteristic results in a slow cracking of the heavier hydrocarbons formed from methanol, reducing the conversion of those compounds to light olefins [6]. In fact, beta zeolite was the catalyst that provided the higher formation of compounds with more than 4 carbon atoms per molecule at almost all evaluated temperatures (except at 300 °C, temperature at which the higher heavy compounds formation was provided by ZSM-5). For SAPO-34, selectivity to C_2 and C_3 compounds kept at values much lower than the values provided by zeolites, with a maximum of only 4% at 400 °C. This behavior was observed even at 250 °C, temperature at which the high conversion shown by SAPO-34 suggest that its stronger acid sites were yet active (accessible). The small light olefin production at 250 °C over SAPO-34, as well as over the other catalysts, can be due to a favoring of the simple methanol dehydration to dimethyl ether (DME) instead of the hydrocarbons formation, which is favored at higher temperatures [4,14].

The effects of temperature on the ratio between the selectivity to C_2 compounds and the selectivity to C_3 compounds (C_2/C_3 ratio) for each catalyst are shown in Fig. 8. For ZSM-5, the C_2/C_3 ratio was 1.2 at 250 °C and reduced to 0.4 at 350 °C, which can be associated with a modification of the active sites of the catalyst due to the deposition of coke precursors. At higher temperatures, the C_2/C_3 ratio of ZSM-5 increased slightly, returning to a value near unity at 500 °C. For beta zeolite, the C_2/C_3 ratio increased in an almost linear behavior between 250 and 450 °C (beginning from 0.4 and reaching 1.4) and increased more rapidly over 450 °C (reaching 3.4 at 500 °C). For mordenite, the C_2/C_3 ratio increased intensely since the lower evaluated temperature, beginning from 0.2 at 250 °C and reaching 5.1 at 450 °C. Increases of the C_2/C_3 ratio with temperature, as well as with time on stream, can be attributed to the increase in the coke amount in catalysts pores, imposing an increasing number of barriers to the diffusion of the reaction products. In this way, ethene would be easily desorpted from the catalyst than propene, due to the smaller dimensions of that molecule, resulting in the increase of the C_2/C_3 ratio [4,14]. For the zeolites, the increase in the C_2/C_3 ratio was proportional to the acid strength, because a higher acid strength results in a higher coke formation. For SAPO-34, however, the C_2/C_3 ratio reduced abrupt between 250 and 300 °C, at the same time of the supposed obstruction of its stronger acid sites. Nevertheless, the C_2/C_3 ratio provided by SAPO-34 increased from 0.6 at 300 °C to 7.3 at 450 °C, indicating the formation of new diffusion barriers, probably associated with the higher coke formation with increasing temperature.

Fig. 9 shows the effects of temperature on selectivity to DME for each catalyst. For SAPO-34, DME was the main product of methanol conversion at all the evaluated temperatures, with selectivities always above 92%, reaching 99% at 500 °C. The high DME production over SAPO-34 is probably due to a favoring of the methanol dehydration at the lower temperatures and an obstruction of the catalyst strong acid sites at the higher temperatures. For ZSM-5, DME production was observed only at 250 °C (with selectivity of 95%) and, at higher temperatures, a reaction product free of oxygenate compounds was obtained, because complete conversion was also verified for that zeolite at temperatures higher than 250 °C. For mordenite, selectivity to DME was 47% at 250 °C and the increase of temperature to 300 °C also resulted in the disappearance of that product and in complete methanol conversion. However, DME concentration in the reaction product of mordenite increased since 400 °C (reaching 62% at

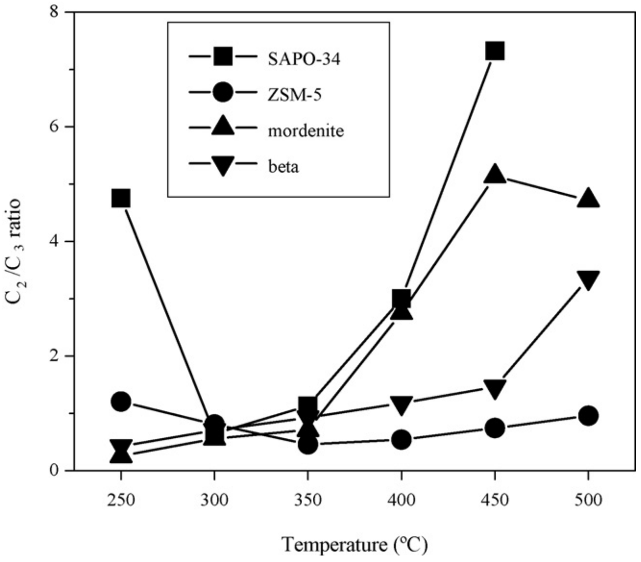

Fig. 8. Effects of temperature on C_2/C_3 ratio.

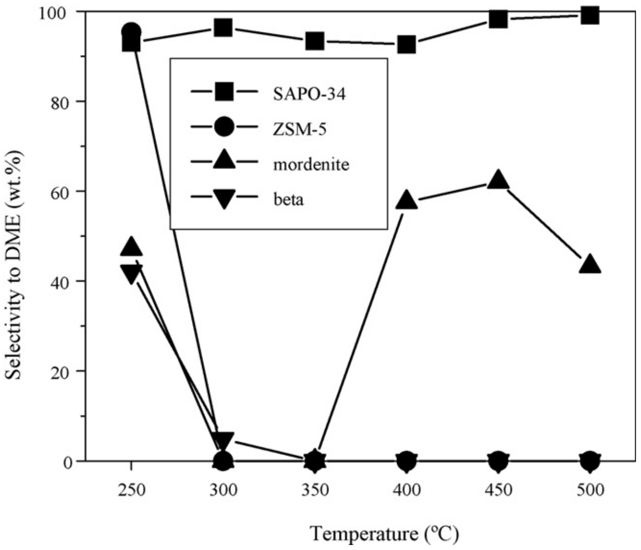

Fig. 9. Effects of temperature on selectivity to DME.

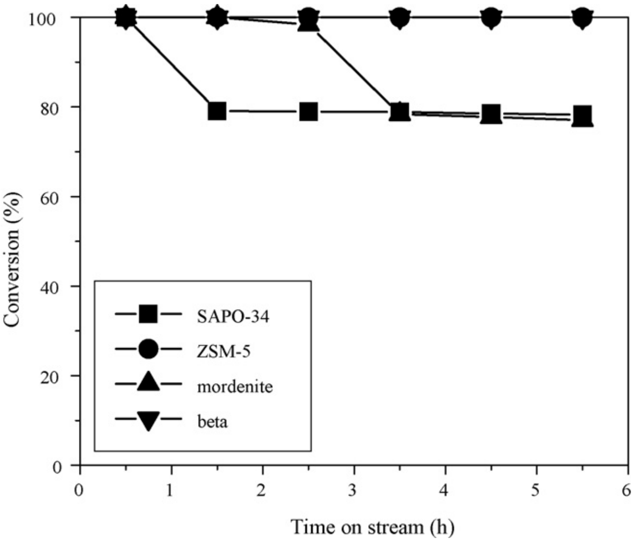

Fig. 10. Effects of time on stream on methanol conversion.

450 °C), following the reduction in light olefin production and the reduction of conversion, previously verified. This result exposes the higher resistance to deactivation of the weaker acid sites (which are capable only to dehydrate methanol) in comparison with the stronger sites. However, at 500 °C it was also observed a reduction of the DME production over mordenite. For beta zeolite, selectivity to DME was 42% at 250 °C, but reduced with the increase of temperature, becoming null from 350 °C, at the same time that methanol conversion became complete. It can be seen that, for the studied zeolites, the conditions that allow complete methanol conversion result in a product free of DME.

The effects of time on stream on the methanol conversion for each catalyst are shown in Fig. 10. For ZSM-5 and beta zeolites, conversion reached 100% during 5.5 h of reaction. For mordenite, conversion was almost complete until 2.5 h and, only 1 h after that, reduced to 78%, keeping relatively stable until 5.5 h. This abrupt conversion reduction must be related with the deactivation of mordenite's stronger acid sites, as discussed previously. SAPO-34 showed a similar behavior to the one of mordenite, but only at 0.5 h it was observed complete methanol conversion and, afterwards, conversion reduced to the same level to which the conversion shown by mordenite reduced. At 450 °C, the cracking of oligomers is more intense than it is at 250 °C, but, on the other hand, coke formation is faster, in such a way that, in this catalytic test, deactivation of the stronger acid sites of SAPO-34 must be essentially related to coke deposition over the catalyst surface, as well as in the case of mordenite. It can be seen that the stronger acid sites deactivation, SAPO-34 is extremely fast, even when compared with mordenite, in spite of the lower acid strength of SAPO-34. Once again, the high strong acid site density of SAPO-34 seems to have hindered the lifetime of these sites. After the deactivation of the stronger acid sites, SAPO-34 and mordenite showed similar activities.

The effects of time on stream on selectivity to C_2 and C_3 compounds for each catalyst are shown in Fig. 11. For ZSM-5 and beta zeolites, that selectivity reduced slowly with time (in 5 h, from 49 to 44% for ZSM-5 and from 30 to 27% for beta zeolite). For mordenite, the initial selectivity to C_2 and C_3 compounds was 56%, but reduced intensely in the first 3.5 h of reaction (and continued to reduce after that time), due to deactivation of the stronger acid sites of that catalyst. During 5.5 h, mordenite's selectivity to C_2 and C_3 compounds turned lower than 1%. For SAPO-34, a significant C_2 and C_3 compounds production was observed only at 0.5 h, but with the remarkable selectivity of 85%.

Fig. 12 shows the effect of time on stream on C_2/C_3 ratio for each catalyst. For ZSM-5, the C_2/C_3 ratio kept almost constant at 0.7 up to 5.5 h. For beta zeolite, the C_2/C_3 ratio increased continuously with time, beginning from 0.8 at 0.5 h and reaching 1.3 at 5.5 h. For mordenite, the C_2/C_3 ratio kept at 0.2–0.3 until 2.5 h and so increased intensely, reaching 1.5 at 5.5 h. Once again, the increase of C_2/C_3 ratio was proportional to the acid strength of the zeolites. For SAPO-34, the simultaneous formation of C_2 and C_3 compounds was observed only until

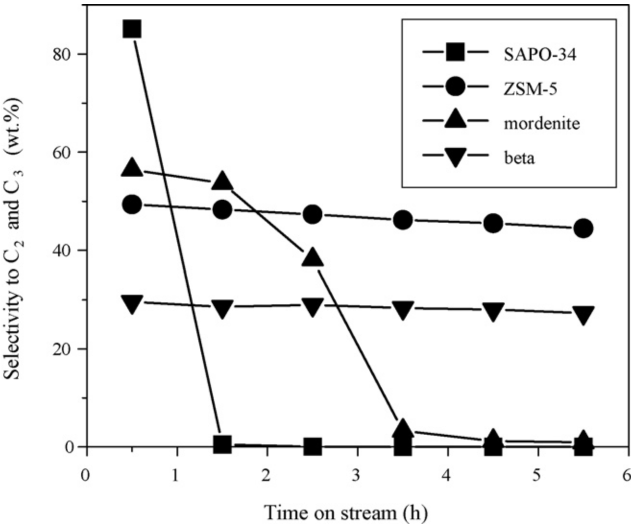

Fig. 11. Effects of time on stream on selectivity to C_2 and C_3 compounds.

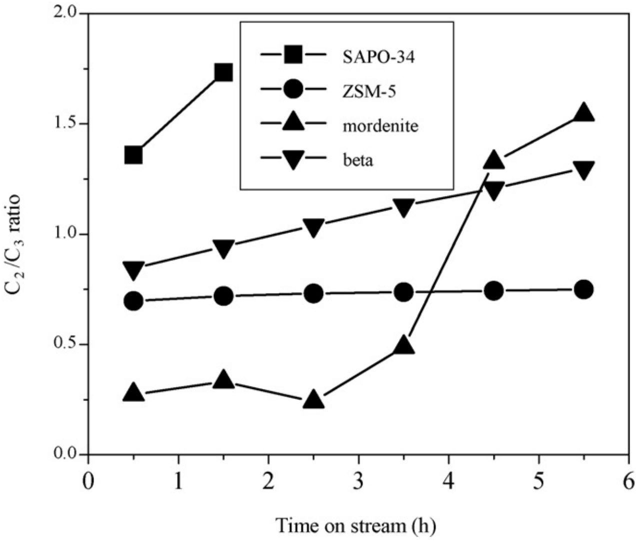

Fig. 12. Effects of time on stream on C_2/C_3 ratio.

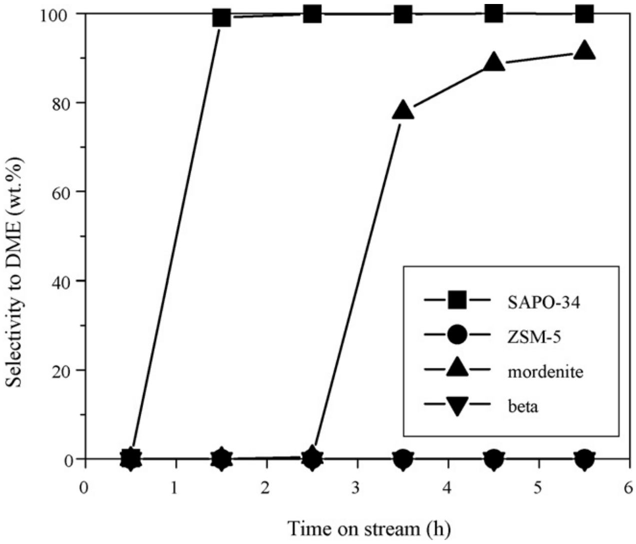

Fig. 13. Effects of time on stream on selectivity to DME.

1.5 h of reaction; in this short interval, the C_2/C_3 ratio increased from 1.4 to 1.7.

The effects of time on stream on selectivity to DME for each catalyst are shown in Fig. 13. The reaction product of ZSM-5 and beta zeolites was free of DME until 5.5 h, which was observed always that methanol was completely converted over the zeolites. For mordenite, selectivity to DME was null until 2.5 h and, afterwards, increased intensely, at the same time that C_2 and C_3 production turned irrelevant. At 5.5 h, the selectivity of mordenite to DME reached 91%, confirming that the weaker acid sites, involved only in methanol dehydration, are more resistant to deactivation than the stronger sites, responsible for olefin formation. For SAPO-34, the stronger sites are deactivated even more rapidly, in such a way that this initial selectivity of the catalyst to DME is almost null, but reach 100% in only 1.5 h of reaction.

4. Conclusions

A SAPO-34 molecular sieve with high density of strong acid sites was synthesized. Although those sites are essential to hydrocarbons formation from methanol, their high density in the synthesized SAPO-34 seems to have turned them very susceptible to deactivation, either at low temperatures (due to an obstruction by oligomers) and at high temperatures (due to coke formation). That behavior has hindered an expressive production of light olefins over SAPO-34. Consequently, the main product of methanol conversion over SAPO-34 at the evaluated temperatures was DME, because the catalyst's weaker sites are able to promote the methanol dehydration and are much more resistant to deactivation. However, among the studied catalysts, SAPO-34 provided the higher initial selectivity to C_2 and C_3 compounds at 450 °C, indicating a great potential for ethene and propene production if this catalyst's regeneration is carried out in parallel with the reaction. ZSM-5, mordenite and beta zeolites showed high activities, providing complete methanol conversion without production of DME at temperatures higher than 300 °C. However, mordenite also underwent fast deactivation of its stronger acid sites at high temperatures, probably due to that high acid strength of the catalyst, which results in a fast coke formation. This resulted in an intense reduction of light olefins production, turning mordenite selective to DME. The highest selectivities to C_2 and C_3 compounds were provided by ZSM-5 at high temperatures and by mordenite at lower temperatures, before an extensive deactivation of its strong acid sites. Beta zeolite showed lower selectivities to C_2 and C_3 compounds for the majority of the evaluated temperatures when compared to other zeolites, which should be related to the low strong acid site density of that catalyst. However, C_2 and C_3 compounds production over beta zeolite kept relatively stable during the first hours of reaction at 450 °C (which was also observed for ZSM-5), while the production of those compounds over mordenite reduced rapidly. It can be concluded that, to promote a significant and stable light olefins production, both the acid site density catalyst and its strength must be moderate. For mordenite and beta zeolites, the C_2/C_3 ratio increased both with temperature and with time on stream, and the increase was proportional to the acid strength catalyst, due to the higher coke formation. The C_2/C_3 ratio provided by ZSM-5 kept stable during the first hours of reaction at 450 °C, indicating that coke formation over this catalyst is relatively slow.

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