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Methanol conversion over acid solid catalysts

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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

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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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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].

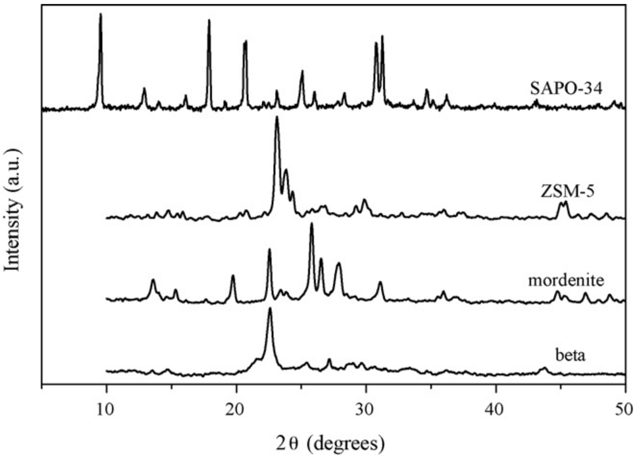

Fig. 1. XRD patterns of the catalysts.

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