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PRODUCTION OF ANTIKNOCK ADDITIVE IN GASOLINE (METHYL tert-BUTYL ETHER, MTBE) USING ZEOLITE CATALYSTS

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Abstract

The etherification of a mixture of methanol and t-butanol (1:1 mol) on hydrogen-, fluorinated-, alumina–deficient and aluminum-exchanged forms of ZSM-5, mordenite and Y zeolites was carried out in a flow reactor operated at atmospheric pressure and temperature of 50-400 °C using a flow of nitrogen 20 cm^3 min^{-1}. The effect of methanol/t-butanol molar ratio of 0.5-3.0 and carrier gas flow rates of 10-60 cm^3 min^{-1} was studied. The activities of these zeolite catalysts for MTBE production were correlated with their acid sites strength distribution, using temperature-programmed desorption (TPD) of ammonia in a differential scanning calorimeter (DSC), as well as with the channels opening dimensions and Si/Al ratio of the zeolites. It is shown that the high acidity and bulk Si/Al ratio has a marked influence on the formation for MTBE. The hydrophobic/hydrophilic character of the catalysts was also discussed. The alumina-dificient and fluorination of a zeolite increases its framework Si/Al ratio, thus increases its hydrophobicity, whereas Al-exchange may decrease this ratio and increases its hydrophilicity.

Keywords: methyl tert-butyl ether, MTBE, etherification, ZSM-5, mordenite, Y zeolite, catalyst

Introduction

MTBE (methyl tert-butyl ether) is currently used as antiknock additive in gasoline. The octane rating is one of the most known measures of gasoline quality. In order to achieve an acceptable octane number, oxygenates like MTBE, ETBE (ethyl tert-butyl ether) or TAME (tert-amyl methyl ether) are added to gasoline to ensure clean combustion. In United States MTBE is by far the most important oxygenated gasoline additive to replace lead alkyl anti-knock agents. In addition to improving octane, MTBE also assists in promoting the combustion of gasoline and is reducing the emission of carbon monoxide and unburned hydrocarbon.

Relative to other oxygenates, MTBE, has many attractive properties including low heat of vaporization, low blending Ried Vapour Pressure, and insensitivity to water.[1-3] Conventionally, MTBE is synthesized industrially from methanol and isobutene over an strongly acidic ion-exchange resin catalysts,[4-7] mostly Amberlyst 15, which is actually a macroreticular cation-exchange resin. Although the commercial catalyst is very efficient, it suffers from several drawbacks including thermal and chemical instability. Although this reaction is highly selective,[8] yet the resin catalyst cannot tolerate temperatures above 100 °C. Moreover, the resin activity is seriously inhibited by small amounts of water.[9] Therefore, more stable catalysts are a matter of active research, where zeolites seem to be most promising.[10-13]

Results and Discussion

The most frequently used synthetic zeolite in the catalytic petroleum processing and petrochemical industry are Y-zeolite, mordenite and ZSM-5 zeolite. These zeolites are thermally stable and commercially produced at reasonable prices. In the present work, these zeolites in their H-, AD-, F- and Al-forms are prepared and examined as catalysts for the synthesis of MTBE. The alumina-dificient and fluorination of a zeolite increases its framework Si/Al ratio, thus increases its hydrophobicity,[14] whereas Al-exchange may decrease this ratio and increases its hydrophilicity. Lok et al.[15,16] have reported that fluorination causes dealumination and structural stabilization of the zeolite, and that the hydrophobicity of the catalysts increases. Scherzer[17] and Jacquinot et al.[18] have found that mild acid-leaching removes primarily non-framework Al, whereas advanced acid-dealumination removes Al from both non-framework and framework positions. The alumina-dificient and fluorinated zeolites under study can be assumed to possess less non-framework Al than the corresponding H-forms. On the other hand, Michiels and De-Herdt[19] in their patents compilation monograph indicated that provision of Al out of the crystal lattice of the zeolite is performed via exchange, impregnation or in matrixing compounds. Hence, the Al incorporated via exchange with aluminium chloride to produce the Al-HZSM-5, Al-HM and Al-HY zeolites under study, provides extra loading with non-framework Al that was found to amount to around 20% of the total Al content.

Using acidic ion-exchang resin catalysts, it is necessary to react methanol with iso-olefin because water impairs these resins.[9] However, zeolites are more tolerant to water, which is formed during reacting methanol with tert-butanol. Hence, we use tert-butanol instead of iso-butene by virtue of the easier handling of the alcohol. Reaction temperature, methanol/tert-butanol molar ratio and the carrier gas flow rate are the operating parameters of prime importance in flow reactions; hence, the activities of the catalysts under study are investigated using these parameters.

1. Acid Sites Strength Distribution

The TPD profiles for HZSM-5, HM and H-Y zeolites are given in Figure 1. Each profile consists of two endothermic peaks; a low temperature peak (LT) representing desorption of ammonia from the weak acid sites and a high temperature peak (HT) representing desorption of ammonia from the strong acid sites. The latter endothermic DSC effect is of relevance to the catalyst etherifiction reaction under study, therefore, only values for this effect are given in Table 1. The HT- ammonia desorption enthalpy is proportional to the number of strong acid sites in a zeolite, and the HT-peak temperatures may compare the strength of these strong acid sites. Also, TPD curves that are similar to those shown in Figure 1 were obtained for AD-, F- and Al-zeolite forms and their HT endothermic peak data are given in Table 1.

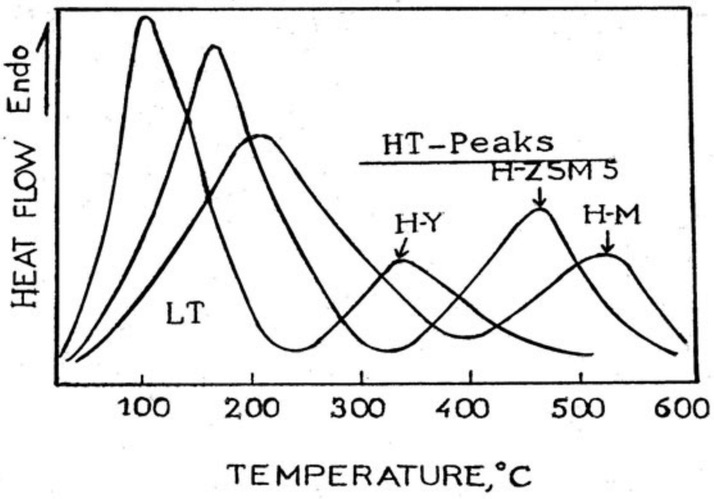

Figure 1. TPD of ammonia from the H- forms of ZSM-5, M and Y zeolites.

Table 1. HT- Ammonia desorption enthalpy and HT- peak temperature for the zeolite catalysts.

Catalysts	ΔH, Jg^{-1}	HT-Peak temperature, ºC
HZSM-5	123.2	457
HM	98.3	530
HY	88.5	335
F-HZSM-5	100.5	470
F-HM	75.3	550
F-HY	67.7	342
AD-HZSM-5	105.1	464
AD-HM	85.2	542
AD-HY	72.1	338
Al-HZSM-5	145.1	412
Al-HM	110.5	478
Al-HY	104.1	303

2. Effect of Reaction Temperature Using Zeolite Catalysts

2.1. Using H- Zeolites as Catalysts

The conversion of tert-butanol to MTBE as a function of reaction temperature up to 400 °C over HZSM-5, HM and HY has been investigated as shown in Figure 2a. It is observed that the conversion increases with reaction temperature and reaching a maximum at 150 °C depending on the type of zeolite catalyst, beyond which the activity decreases. At lower temperatures, i.e., 50-150 °C, where MTBE formation is thermodynamically favored at 150 °C, the maximum activities of HZSM-5, HM and HY are 53.0%, 46.0%, and 29.0%, respectively.

Data in Table 1 and Figure 1 show that the number of strong acid sites (HT- peak) in the H-forms of the zeolites under study can be arranged in the order:
HZSM-5 > HM > HY, whereas the strength of these acid sites may be arranged in the order: HM > HZSM-5 > HY. Nevertheless, the order of the activities of these catalysts for MTBE production can be arranged in the order:
HZSM-5 > HM > HY, which is compatible with the order of the number of strong acid sites, but not with the order of their strengths. However, the effective pore opening of these zeolites, which is considered the relevant parameter for diffusion of the reactant molecules along the zeolitic channels, are 5.6, 6.7 and 7.8 Å, for the HZSM-5, HM and HY zeolites, respectively. It may thus be evident that the order of diffusion restriction along the catalytic pores is in accordance with the order of activities of the catalysts for MTBE formation.

Wei[20] introduced a mathematical model showing that more significantly limited diffusion along the zeolitic channels gives greater opportunity to reactant molecules contact with a larger number of active catalytic sites, and hence, a higher catalytic activity is observed. Moreover, Chu and Kuhl[21] assumed that the restricted diffusion encountered for the bulky t-butanol molecules in the channels of H-ZSM-5 zeolite provides a better opportunity to come in contact with a large number of adsorbed methanol molecules (nucleophil) which are much less bulky than t-butanol molecules and can diffuse more easily.

2.2. Using AD - Zeolites as Catalysts

The results obtained for the formation of MTBE using AD-zeolite catalysts at different reaction temperatures (50-400 °C) are represented in Figure 2b. It is found that aluminum-deficiency of the three zeolites under study has significantly enhanced their activities for the etherification reaction between methanol and tert-butanol, producing MTBE. The selectivity for MTBE is > 90% at all temperatures. The most significant enhancement of catalytic activity is observed via dealumination of the Y-zeolite. Although AD-HY is less active than AD-HZSM-5 and AD-HM, the MTBE production on AD-HY exceeds 70.0%, whereas on HY it is 29.0% at 150 °C. This enhancement of activity can be attributed to the increase of hydrophobic character[2,14] and Si/Al ratio of the zeolites[22,23] and, hence, its affinity to adsorb the reactants increases,[8] whereas its affinity to adsorb water decreases.[24] Since the etherification reaction is equilibrium-limited and water is continuously removed from the catalyst surface due to its hydrophobic nature, the catalytic activity of the AD-zeolites is greatly enhanced.

2.3. Using F- Zeolites as Catalysts

From recent studies carried out by author[25,26,27] on fluorinated catalysts, it has been found that a fluorine content of 3.0 wt% gives optimum hydroconversion activities; hence, this fluorine content is used in preparing the fluorinated zeolite catalysts under study. Figure 3a shows the curves of variation of the MTBE yield versus reaction temperature using the F- zeolite catalysts, F-HZSM-5, F-HM and F-HY. The conversion of tert-butanol to MTBE is almost complete with 99.9% selectivity than on the mother H- zeolite catalysts (Figure 2a), i.e, 95.6-99.5%, 90.0-94.2% and 86.7-91.5% on the former catalysts F-HZSM-5, F-HM and F-HY, respectively, as compared to 49.3-51.9%, 38.9-44.4% and 22.2-26.7% on the latter catalysts at temperatures of 50-200 °C, respectively. This significant enhancement of activity is attributed to a significant increase of the strength of Brönsted acid sites in the fluorinated zeolite catalyst due to the replacement of some surface-OH groups by F, whereby proton dilution is achieved on the zeolite surface, thus, decreasing the interaction of neighboring protons, and hence the remaining protons will be more strongly acidic.[28]

Van Mao et al.[29] also studied that the enhanced acidic properties of ZSM-5 zeolite, when doped with fluorine species in relatively low concentration and subsequently activated stepwise at high temperature, shows an enhanced surface acidity because of: (i) the formation of new Brönsted acid sites; and (ii) the strengthening of some acid sites of the parent zeolite. This is ascribed to the proton attack of the zeolite surface by the chemisorbed H^+ F^- ion pair. Therefore, the enhanced acid properties of zeolite catalysts under study are traduced by significant increase in the yield of MTBE. This is evident in Figure 1 and Table 1, where the curves obtained for NH_3 – TPD show lower ammonia desorption enthalpy (smaller number of acid sites) but a higher peak temperature in case of the F- zeolite catalysts than in case of the H- zeolite catalysts.

2.4. Using Al-exchanged Zeolites as Catalysts

The activities and selectivities of the Al-zeolites under study for the MTBE production are significantly lower than those obtained using all types of H-, AD- and F-zeolites (Figure 3b). Using the Al-ZSM-5, Al-M and Al-Y zeolites, the selectivities for MTBE amount to 42.0–72.5%, 37.0–68.0% and 30.0–67.0%, respectively. The major by-product formed is iso-butene which is produced via the dehydration of tert-butanol over acid sites of the zeolite catalysts. In general, the activities of these catalysts (Figure 4) can be arranged in the order: Al-ZSM-5 > Al-M > Al-Y. Using these zeolite catalysts, it is observed that the activities increase with increasing reaction temperature until is reached the maximum value of 37.9% at 250 °C for Al-ZSM-5 and 30.0, 24.4% at 350 °C for Al-M and Al-Y, respectively, beyond which the effect of exothermicity becomes significant whereby MTBE formation decreases.

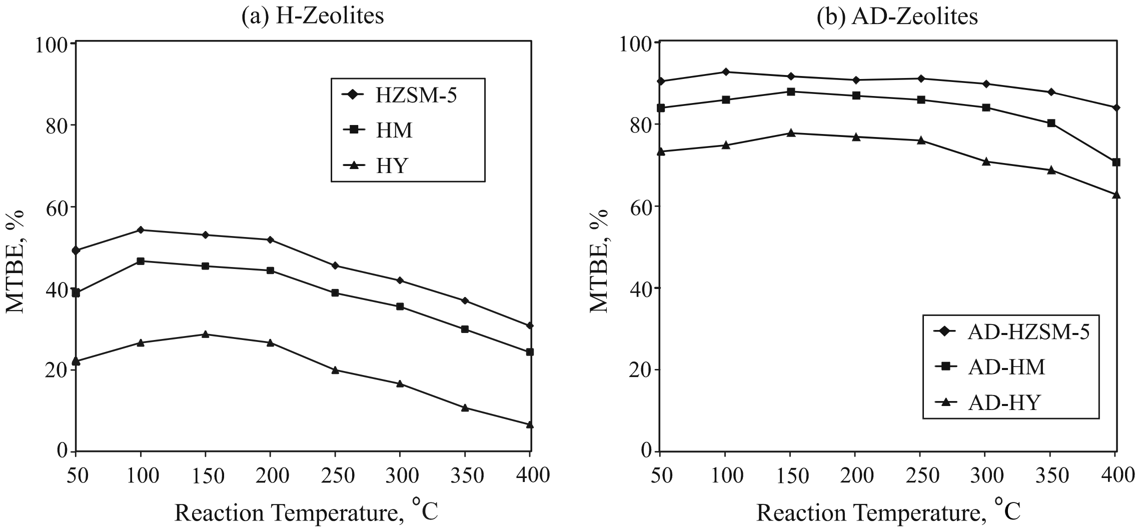

Figure 2. Effect of reaction temperature on the production of MTBE using (a) H-zeolites and (b) AD-zeolites.

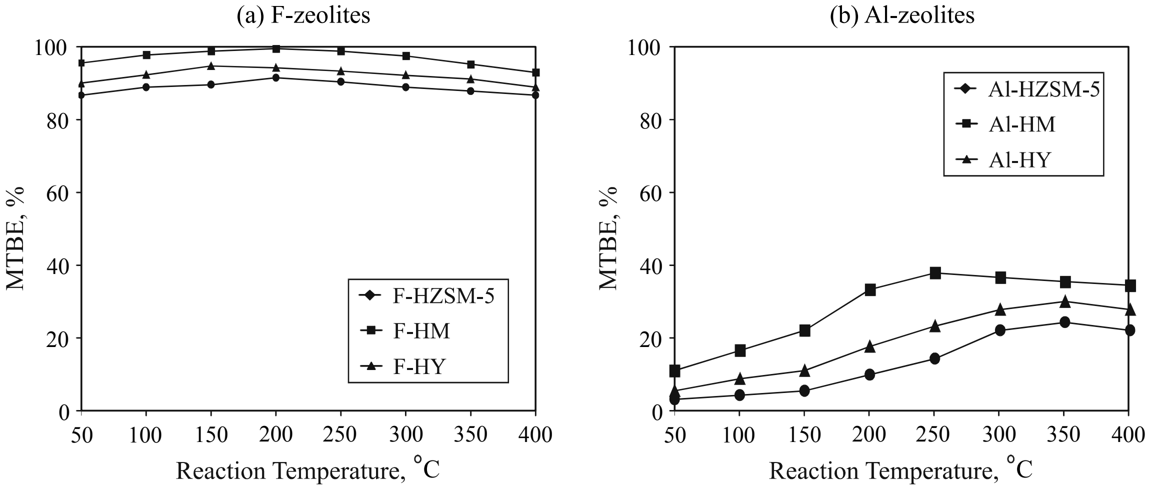

Figure 3. Effect of reaction temperature on the production of MTBE using (a) F-zeolites and (b) Al-zeolites.

3. Effect of Methanol/tert-Butanol Molar Ratio Using HZSM-5 Catalysts

Figure 4a shows that at a molar ratio of methanol/tert-butanol of 0.5, the conversion of tert-butanol to MTBE is lower than at ratio of 1.0 using all forms of HZSM-5 catalysts. At the latter ratio, MTBE formation amounts to 95.3, 90.0, 48.3 and 38.9% using the F-HZSM-5, AD-HZSM-5, HZSM-5 and Al-HZSM-5 catalysts, respectively. Using all forms of HZSM-5 catalysts, shows an increase of the methanol/tert-butanol ratio beyond 1.0 does not give significant variation of MTBE formation up to a ratio of 3.0, which is compatible with Wei's model.[20] Chu and Kuhl[21] studied MTBE production at ratios of the reactants between 0.9 and 1.15 using a HZSM-5 catalyst, whereas Pien and Hatcher[30] studied this reaction at a wider range of the reactants ratio (1.5-4.6) at different temperatures. Both teams of workers observed no change of MTBE formation with the variation of the reactants ratio. At all molar ratios, F-HZSM-5 is the most active catalyst, probably due to its relatively high acid sites number (Figure 1 and Table 1). Using Al-HZSM-5 catalyst, increasing the molar ratio of the reactants from 0.5 to 1.5 gives jump in MTBE production from 26.7 to 41.7%, respectively, which may be attributed to permitting a larger number of the reactive nucleophil molecules (methanol) to enter the Al- loaded channels (diffusion-restricted).

4. Effect of The Contact Time (Carrier Flow Rate) Using HZSM-5 Catalysts

Using the HZSM-5 catalyst, the increase of carrier flow rate from 10 to 20 cm^3min^{-1} increases the MTBE formation from 44.4 to 48.8% (Figure 4b). This can be attributed to accelerating the slow desorption of the bulky product (MTBE) molecules as well as water molecules which are formed during the etherification of the two alcohols from the catalytic sites. Increasing the flow rate beyond 20 cm^3min^{-1}, MTBE formation decreases linearly until a flow rate of 60 cm^3min^{-1} is reached. This activity decrease can be attributed to a corresponding decrease of the contact time. On the other hand, using the Al-HZSM-5 catalyst the increase of flow rate of the carrier from 20 to 60 cm^3min^{-1} gives a continuous decrease of MTBE production from 38.9 to 16.7%.

MTBE formation is relatively impeded on the Al-HZSM-5 due to the stronger adsorption of water formed in the channels of these more hydrophilic zeolites. The larger number of charge-compensating exchanged Al^{3+} ions produces higher electrostatic fields and field gradients in the channels and cavities,[31] whereby these zeolite become more strongly hydrophilic. Therefore, a low flow rate of 10 cm^3min^{-1} is insufficient to desorb the formed water compared to the reaction at 20 cm^3min^{-1}. Beyond the latter rate, MTBE production decreases as a function of decreasing the contact time. Nevertheless, using the AD-HZSM-5 and F-HZSM-5 catalysts, the conversion of tert-butanol to MTBE is almost complete with 100% selectivity all over the carrier flow rate range investigated (10-60 cm^3min^{-1}).

However, using the AD-HZSM-5, the carrier flow rate seems to work as a contact time parameter. Moreover, using F-HZSM-5 as a catalyst, a somewhat higher activity is observed than that using AD-HZSM-5, probably due to the greater effect of traces of extra-framework Al remaining in the zeolite channels during the dealumination process.[22,30]

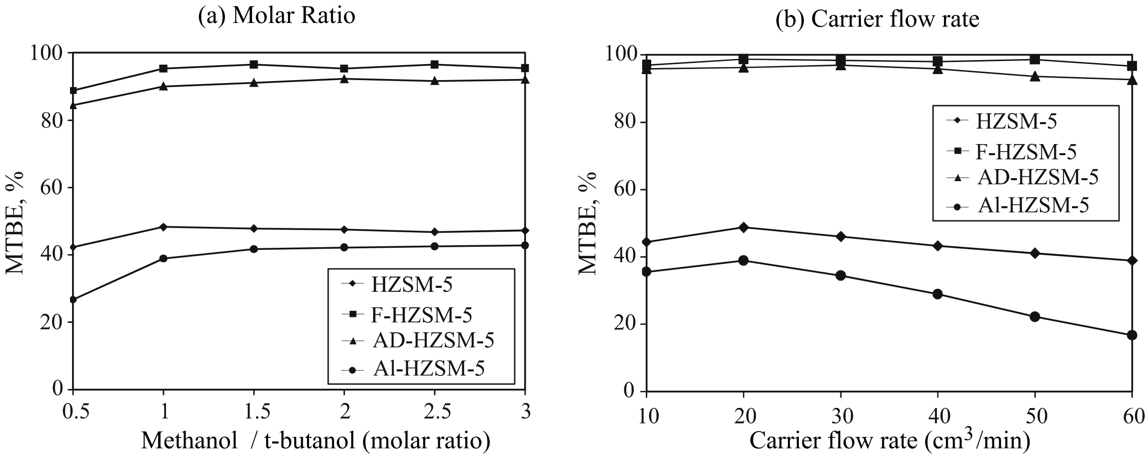

Figure 4. Production of MTBE using the H-, F-, AD- and Al-ZSM-5 catalysts; (a) effect of methanol/ tert-butanol molar ratio; (b) effect of carrier gas flow rate.

Conclusions

It was shown that the activities of different forms of the three zeolites under study for MTBE production can be arranged according to their types in the order: ZSM-5 > mordenite > Y-zeolite. Moreover, the activities of the zeolite forms according to their Si/Al ratio can be arranged in the order: F-zeolites > AD-zeolites > H- zeolites > Al-zeolites. The lower the Si/Al ratio, whether Al is incorporated in the framework or is extra-framework, the lower the activity for MTBE formation. Using the H-, AD- and F-forms of all types of zeolites, MTBE is produced at 90-100% selectivity; however, using the Al-forms, this selectivity is lower, which can be attributed to the individual action of non-framework Al. The number of acid sites may be more effective for MTBE formation than the acid site strenghth. Nevertheless, the fluorinated zeolite catalysts are the most effective for MTBE formation since the incorporation of F^- enhances the surface acidity, consequently increased MTBE yields were obtained. Moreover, the smaller the channel opening, the higher is the catalytic activity. Al-exchange of a zeolite, gives rise to a shift of the reaction equilibrium to higher temperatures, whereas fluorination and alumina-deficiency shifts the reaction to lower temperatures.

Experimental

1. Catalyst Preparation

The acid form of the zeolites, HZSM-5, HM and HY, were prepared by repeated ion exchange of the commercially available Na- forms (1/16", 1.59 mm, extrudates, kindly provided by Süd Chemie, A.G, München, Germany) with 1M NH_4NO_3 followed by drying at 110 °C overnight then calcination at 500 °C for 4h in air.

Dealumination was then carried out through leaching with 2N HCl (10 mL HCl for each gram zeolite) at 150 °C under reflux for 4h. The alumina-dificient (AD) zeolite catalysts are washed till free of Cl^-, dried at 110 °C overnight and calcined at 500 °C for 3h in air.

Fluorinated zeolite catalysts, F-HZSM-5, F-HM and F-HY, were prepared by impregnation of H-zeolite forms with the quantity of HF solution required for preparing a catalyst containing 3.0 wt% F. The zeolite in the HF- containing solution was left at room temperature overnight then evaporated till dry on a hot plate with continuous stirring. The catalysts were then dried in a muffle at 350 °C for 2h. The Si/Al ratios obtained for the zeolites under study are given in Table 2.

Table 2. Si/Al ratio for the zeolites.

Zeolite Catalysts	Si /Al
HZSM-5	21.8
HM	06.1
HY	02.5
F-HZSM-5	42.9
F-HM	10.8
F-HY	07.2
AD- HZSM-5	39.3
AD-HM	08.6
AD-Y	05.8
Al-HZSM-5	17.0
Al-HM	04.6
Al-HY	02.0

2. Temperature-Programmed Ammonia Desorption (TPD)

The procedure adopted by the author[10] using differential scanning calorimeter (DSC) for detecting the desorption of ammonia from the catalysts via the programmed temperature increase by the system was used. Ammonia was primarily adsorbed on the catalyst acid sites after previous heating in air flow at 500 °C for 3h in a silica tube furnace. After cooling to 50 °C, a flow of NH_3 of 50 cm^3 min^{-1} was applied for 1h. The DSC measurements were then carried out using a DSC-30 unit (TA-3000 Mettler system) in a flow of pure nitrogen as a purge gas. The heating rate was 5 $Kmin^{-1}$ and the full scale range was 30 mW. The desorption enthalpy corresponded to the number of acid sites, whereas the DSC peak temperature corresponded to the strength of the acid sites.

3. Etherification Procedure and Analysis

The etherification reaction was carried out at reaction temperatures between 50 and 400 °C using 0.5 g catalyst placed in a fixed-bed flow reactor working atmospherically. A mixture of methanol and tert-butanol (molar ratio 1:1) was fed into the reactor via a linear dosing pump. The space velocity of 1g feed g^{-1} catalyst h^{-1} (WHSV) using a nitrogen flow of 20 cm^3min^{-1}. The reaction products was analyzed by a gas-chromatograph (Perkin Elmer Auto System) with FID using 4m column packed with 10% squalane on chromosorb.

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Povzetek

Na protoniranih, fluoriranih, dealuminiranih in z aluminijevimi ioni izmenjanih oblikah zeolitov tipa ZSM-5, mordenit in Y (sintetični faujasit) je bila v pretočnem reaktorju obratujočem pri normalnem tlaku v temperaturnem območju med 50 in 400 °C in v pretoku nosilnega plina dušika 20 cm^3 min^{-1} izvedena eterifikacija ekvimolarne mešanice metanola in t-butanola. Preučevan je bil vpliv molarnega razmerja v območju med 0,5 in 0,3 ter vpliv pretoka nosilnega plina v območju med 10 in 60 $cm^3 min^{-1}$. Določena je bila korelacija aktivnosti teh zeolitnih katalizatorjev pri tvorbi metil-tert-butil etra (MTBE) s porazdelitvijo kislinske jakosti aktivnih mest, pridobljene s pomočjo temperaturno programirane desorpcije (TPD) amonijaka in DSC, po eni plati ter s premerom odprtin kanalov v zeolitnih strukturah po drugi plati. Preučevan je bil tudi vpliv hidrofobnosti notranje površine zeolitnih katalizatorjev na potek reakcije.