



Effect of acid treatment on ZSM-5 for methanol to olefins

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ZSM-5 has emerged as versatile catalyst for petrochemical industry due to its shape selectivity and strong acid strength. To produce olefins from methanol, optimized distribution of catalyst acid sites plays an important role. Acid treatment of ZSM-5 was performed for dealumination using four different acids, namely boric acid, nitric acid, phosphoric acid and tartaric acid at three different concentrations (0.1 M, 0.5 M and 1.0 M). All experiments were performed at a space velocity of 4 h^{-1} , 500°C and 1 atm pressure. Physical and chemical changes in catalyst were determined using XRD, BET, ICP-AES. It was observed that the ZSM-5 treated with 1 M boric acid emerged best amongst all in terms of olefins selectivity. Order of olefin selectivity with acid modified catalysts was observed as 1 M BZSM (83%) > 0.1 M TZSM (77%) > 1 M TZSM (75%) > 0.5 M NZSM (73%) > 0.1 M BZSM (69%) > ZSM (68%).

Keywords: Acid-treatment, ZSM-5, catalyst modification, methanol, olefins.

Introduction

Methanol conversion to hydrocarbons is emerging as alternative process for production of olefins, paraffins and aromatics¹. Among all heterogeneous catalysts, Zeolite Socony Mobil-5 (ZSM-5) is proven due to its high surface area, pore size and acidic sites for various reactions in petrochemical industry². It is well known that different mechanism of reactions applied for the production of chemicals where in an optimum combination of catalyst properties plays important role. These properties can be tuned to selectively optimize the yield of different hydrocarbons³. It is reported that both, acidity and structure of ZSM-5 can be modified by (i) different ratio of fillers and binders⁴, (ii) calcination⁵, (iii) steam treatment⁷, (iv) addition of transition or rare earth metals⁶, (v) protons substitution by Na^+ or other cations⁶, (vi) different silica-to-alumina ratio (SAR)⁷ and (vii) acid base treatment⁸.

Acid treated ZSM-5 performance have been reported in literature for different reactions. Both organic acids (oxalic acid and tartaric acid) and inorganic acids (boric acid, hydrochloric acid, nitric acid and phosphoric acid) have been used to modify the properties of catalysts. Literature reports that phosphoric acid removes framework Al(IV) and neutralizes

strong acid sites by P-OH groups. It is mentioned that propylene selectivity increases with the treatment of phosphoric acid⁹. The structure of zeolite is not affected by phosphoric acid treatment but the Si-OH-Al bonds are broken in thermal treatment. Further it is reported that the presence of phosphorus in zeolite structure improves hydrothermal stability which also helps in enhancement of olefins formation¹⁰. The acid treatment forms terminal Al-OH groups, decreasing strong acid sites with negligible extra-framework Al¹¹.

It is well acclaimed that the presence of Al in framework and extra-framework strongly influences the acidity of ZSM-5. Different methods has been explored for modifying internal as well as external acidic sites that helps in mitigating coke formation¹² and activity of the catalyst. Selective reduction of the external acid sites from framework has been reported which in turn inhibit the coke formation thereby improving both activity and selectivity¹³.

Use of HCl as ZSM-5 is reported which leads to production high silica ZSM-5 without any change in MFI¹⁴. Boron modified ZSM-5 has been reported showing great enhancement of propylene selectivity with almost 100% conversion¹⁵. Boron in the framework provides improved life-time and stability of the catalyst. Use of oxalic acid also showed an en-

hancement of the performance of the ZSM-5 catalyst by elimination of external acid sites on the surface¹⁶. A comparative study with tartaric and oxalic acid treated ZSM-5 showed less aromatics formation in presence of tartaric acid treated ZSM-5¹⁷.

Present study reports methanol conversion to olefins using four different acids, namely boric acid, nitric acid, phosphoric acid and tartaric acid. Detailed studies were carried out to study the effect of their concentration on olefins selectivity. While some work has been done on acid dealumination, as per our knowledge, such systematic studies have not been reported in literature.

Experimental

ZSM-5 was obtained from ACS materials. Other chemicals like methanol, boric acid (B), nitric acid (N), phosphoric acid (P) and tartaric acid (T) were of analytical grade and purchased from Fischer Scientific.

For the treatment of catalyst, 5 g ZSM-5 was mixed with 50 ml of 0.1 M, 0.5 M and 1.0 molar acid, each. This mixture was agitated for 2 h at 80°C. XZSM-5 (X = P, T, N and B) after treatment was washed with de-ionized water and dried at 110°C in hot air oven for 24 h. Dried catalysts were then calcined at 550°C for 5 h at ramp rate of 2°C per minute. All treated catalysts were designated as BZSM for boric acid, NZSM for nitric acid, PZSM for phosphoric acid and TZSM for tartaric acid.

Catalytic performance studies were performed as discussed. Methanol was fed at WHSV of 4 h⁻¹ and nitrogen was used as carrier and dilutant at 30 ml/h to the preheater at 200°C. Mixture of methanol vapor and nitrogen gas was passed through catalyst bed of acid treated catalyst (XZSM) maintained as 500°C in a fixed bed reactor. 1 g of calcined catalyst was used for each experimental run. Gases coming out from the fixed bed reactor were passed through condenser maintained at 4°C. The liquid product, if any, was collected at bottom. The gas coming from the top of separator was taken for sample analysis in Porapaq-Q column of GC FID. Gas standards of ethylene, propylene, butylene and pentene were used for calibration and applied for product analysis.

Characterization of as purchased and acid treated ZSM-5 was performed for understanding the changes in catalyst

crystal structure, topography, surface area, catalyst composition. X-Ray diffractions were obtained from PANalytical X'Pert Pro diffractometer using Cu K α rays in the range 5° to 70°. BET surface analyser Micromeritics ASAP 2010 was employed to obtain the catalyst surface area, pore diameter and the pore volume. Atomic Emission Spectroscopy (ICP-AES) was performed on ARCOS, Simultaneous ICP Spectrometer.

Results and discussion

X-Ray diffraction spectra were obtained for all four treated catalysts as well as untreated catalyst. The spectra (Fig. 1) shows minute changes in treated samples as compared to the original ZSM-5 (011), (200), (022), (002), (051) and (053)¹⁸. In all treated samples *hkl* values were changed for (200) and new peaks were obtained with (020). Only PZSM could retain (011). This indicates that there is a significant change in crystallinity and hence cage structure of catalyst. A reduction in intensity of the 2 θ peaks of treated samples was observed indicating change of the catalyst crystallinity.

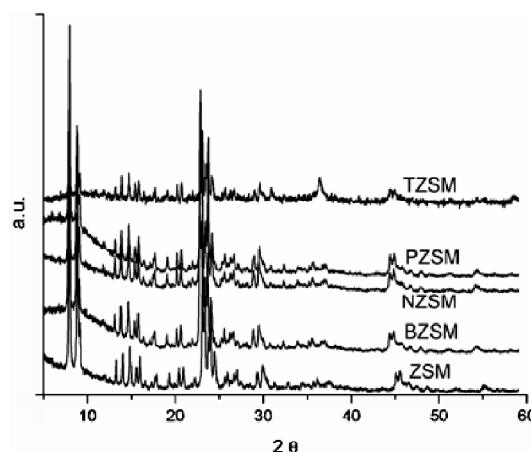


Fig. 1. XRD analysis of acid treated catalysts.

Table 1 shows the BET analysis of each catalyst treated with 1 M acid. A reduction in surface areas of all acid treated catalysts from 18 to 26% was observed. Maximum decrease in surface area was obtained in case of PZSM indicating maximum change of the porous catalyst by dealumination of alumina from frame work. Interestingly contradicting result were obtained in case of pore volume wherein no significant change was observed. A significant increase in pore size was observed in PZSM from 37.2 Å to 50.6 Å whereas pore size

Table 1. Textural properties of the acid treated catalyst

Catalyst	Unit	ZSM	BZSM	NZSM	PZSM	TZSM
BET surface area	m ² /g	312.47	254.46	240.45	229.10	250.25
Micropore area	m ² /g	177.08	158.74	170.71	162.58	178.83
External surface area	m ² /g	135.39	95.72	68.37	65.11	71.62
Total pore volume	cm ³ /g	0.29	0.24	0.21	0.29	0.28
BJH pore diameter	Å	37.27	37.43	34.78	50.61	44.27

in case of BZSM (~37.4 Å) was similar to untreated ZSM. This could be due to kinetic diameter size of phosphorous molecule which replace Al atoms¹⁹.

Table 2 shows ICP-AES analysis of acid treated catalysts. High dealumination in the TZSM was obtained whereas NZSM alumina content was almost similar to original ZSM-5. Approximately a decrease of around 22% is observed in alumina content in NZSM while 88% reduction was noticed in BZSM and PZSM.

Table 2. ICP-AES analysis of acid treated catalysts

Catalyst	Al%	Si%	Si/Al
ZSM	18.95	35.54	1.88
BZSM	2.27	33.65	14.82
NZSM	14.58	36.05	2.47
PZSM	2.96	32.20	10.88
TZSM	0.84	37.24	44.33

Catalyst performance:

Methanol to olefin conversion was performed in a fixed bed reactor. 100% Conversion was obtained only in presence of 1 M BZSM which was better than conversion obtained in presence of untreated ZSM-5 (~92%). NZSM was also able to give ~96% conversion. Significantly lower conversion (~68%) is obtained in case of PZSM. Lowest conversion in case of PZSM is due to drastic deformation of the catalyst pore size and cage structure was observed. Largest pores were obtained in PZSM indicating that the deactivation and pore blocking was fast as compared to other catalysts. In the crystallinity of the usually during methanol thermocatalytic reactions different type of hydrocarbons are obtained which includes paraffinic, olefinic and aromatics. However, in this work no aromatics were obtained. It is reported that aromatics mainly produce from secondary reactions. Secondary reactions of aromatization and simultaneous hydro-

gen transfer reactions are promoted by strong acid sites. In acid treated catalysts high dealumination is reported which suppressed the secondary reactions.

Effect of acid concentration on overall olefin production:

Fig. 2(a-d) shows individual ethylene, propylene and butylene and overall olefins selectivity obtained in presence of 0.1 M, 0.5 M and 1 M acid treated catalysts.

Maximum ethylene selectivity (~33%) was obtained in presence of 0.1 M NZSM whereas the minimum ethylene selectivity (13.7%) was also obtained in presence of 1 M NZSM. Almost insignificant difference in the ethylene selectivity was obtained at all concentrations of PZSM indicating structure collapse of the catalysts in all cases with similar type of pore openings. TZSM has shown high rate of deactivation and high ethylene formation in case of 0.5 M weight analysis confirmed lowest coking over 1 M NZSM leading to minimum ethylene formation.

Propylene selectivity obtained in presence of different acid treated catalysts shows that the maximum propylene (32.1%) is obtained in presence of 1 M PZSM while 1 M BZSM shows slightly lower (31.8%). Lowest propylene formation is obtained in case of 0.5 M TZSM which is due to large pore opening which helps in formation of larger olefins.

As discussed above, an optimum pore opening yield to formation of higher olefins hence good butylene selectivity (41.3%) was obtained with 1 M TZSM. Interestingly lower butylene formation was obtained with 0.5 M TZSM which may be due to the formation of higher hydrocarbons e.g. C₅ etc. Strong acidity favours the formation of bigger molecules and also results in faster coking. High kinetic diameter of tartaric acid prevents framework Al leaching of ZSM hence, the bronsted acidity is very high for TZSM-5²⁰. A variation in the different olefins in presence of different catalysts indicates that individual acid treatment can provide a different

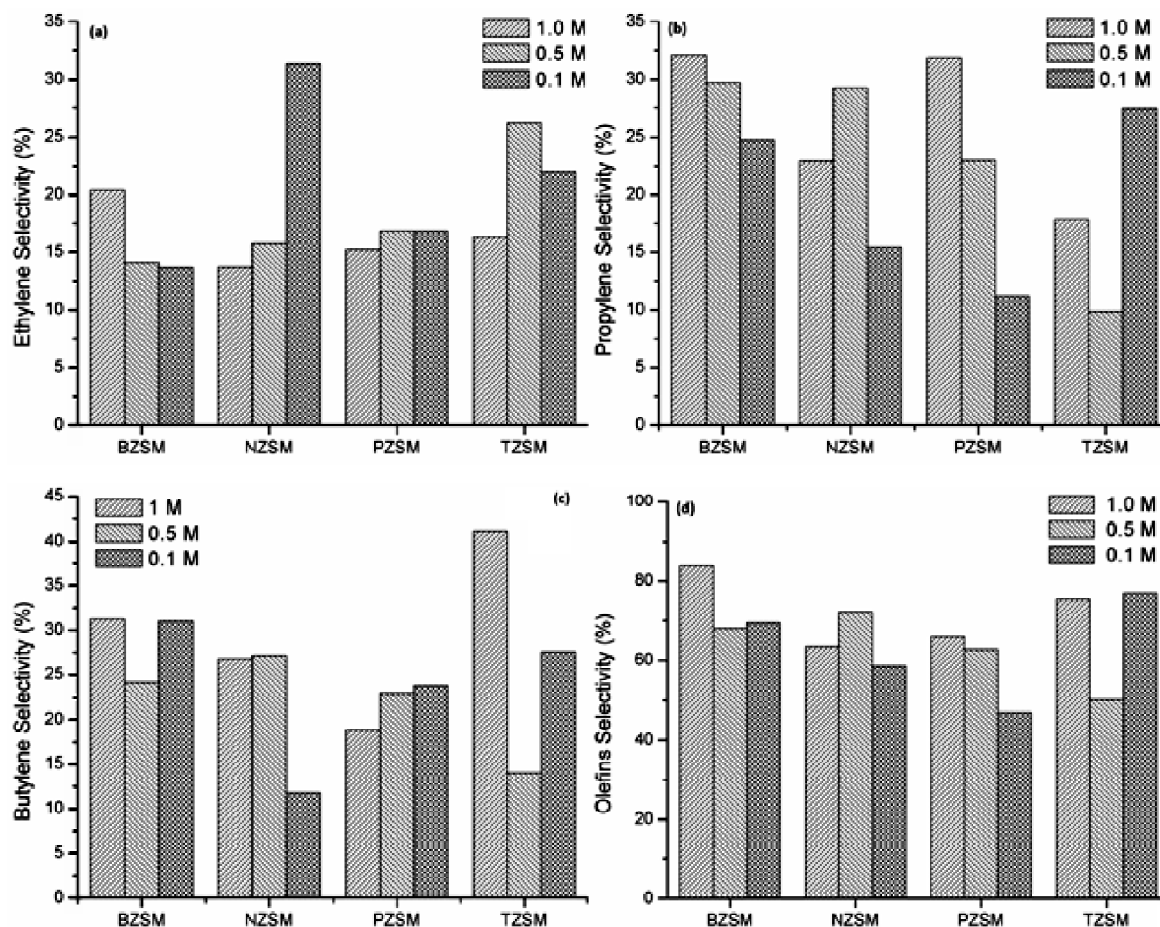


Fig. 2. Effect of acid concentration treatment of ZSM-5 for (a) ethylene, (b) propylene, (c) butylene and (d) total olefin.

combination of acid sites as well as crystalline structure which changes the amount of different olefins.

Total olefins selectivity bar chart shows that 1 M BZSM yields to maximum olefin content with approximately 81.3% $C_{2=}$, $C_{3=}$ and $C_{4=}$ olefins. Due to distorted catalyst properties, lowest olefins were obtained with 0.1 M PZSM. TZSM is a close competitor with BZSM however due to high dealumination it has fast deactivation rate. High yield, better catalyst stability and consistent performance make BZSM the best catalyst for conversion of methanol to olefins.

The effect of different acids on time on stream (TOS) analysis of olefins:

Fig. 3 shows ethylene, propylene and butylene and overall olefins selectivity of 1 M acid treated ZSM respectively. After 8 h operation, ethylene selectivity slowly increases for

BZSM and NZSM. This trend indicates that deactivation is not dominant in these catalysts even after 8 h run. PZSM shows a slight decrease whereas drastic reduction after the initial increase was observed with TZSM indicating higher deactivation of the catalyst or blockig of the pores due to carbon formation.

BZSM shows the highest ethylene at all times except for TZSM where, in initial hours, large ethylene was formed. For all the catalysts except for NZSM, propylene selectivity decreased after 5 h run. In spite of this trend in NZSM, BZSM continuously provides much better selectivity for propylene combined with 100% methanol conversion. Butylene selectivity was observed to decrease considerably with time for BZSM. However, for other catalysts, selectivity shows a decent increase. This may be due to smaller pore size of BZSM as compared to others. Small pore size prefers the forma-

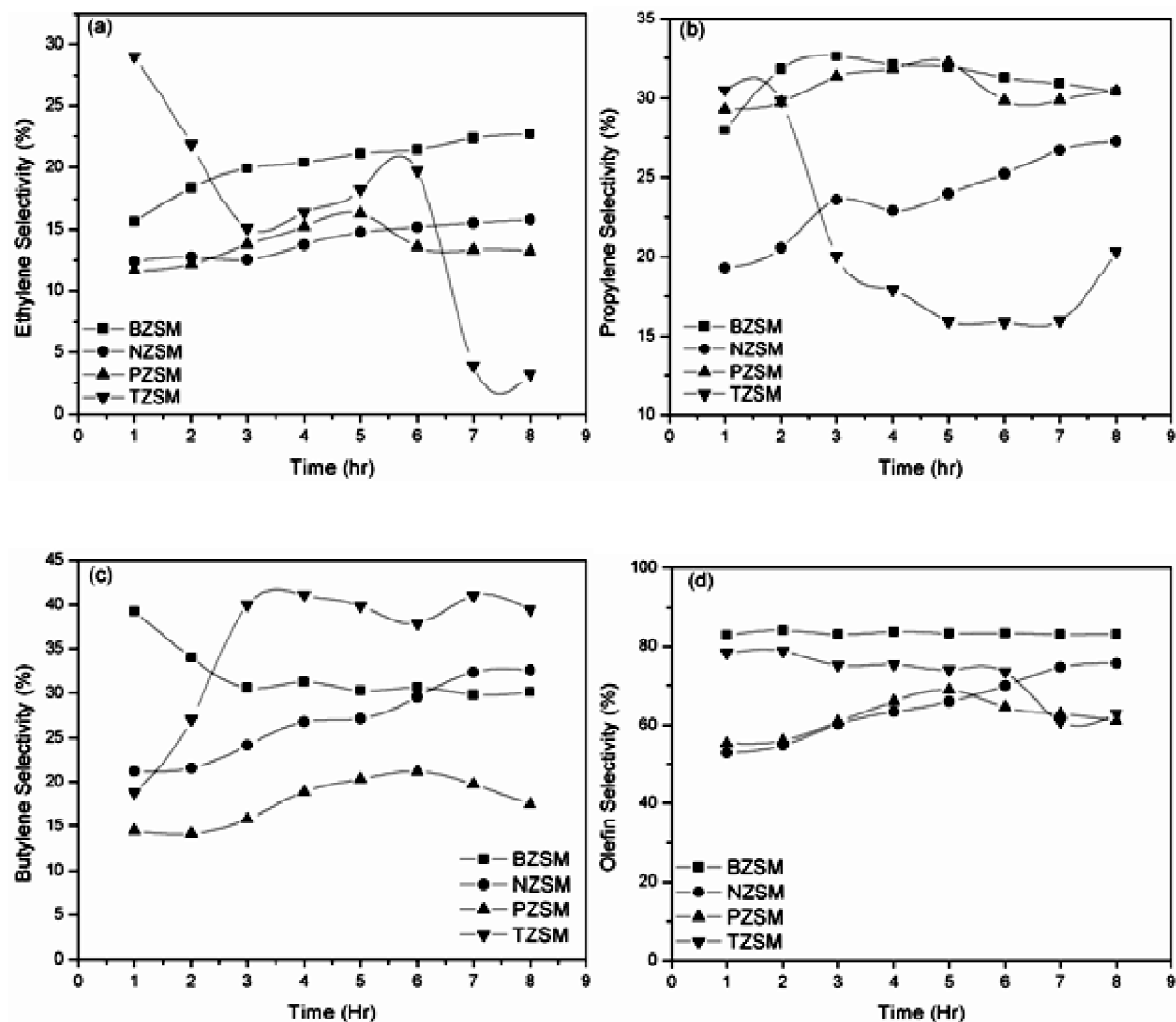


Fig. 3. Time on stream analysis of selectivity of (a) ethylene, (b) propylene, (c) butylene and (d) total olefin in presence of 1 M acid treated catalyst.

tion of smaller molecules and hence selectivity of butylene was slightly lower in BZSM. TZSM shows maximum increase. This indicates that the pore size is more suitable for the formation of higher hydrocarbons but can cause rapid deactivation also as explained earlier.

Conclusions

Overall olefins selectivity of BZSM is best amongst all (>80%) and nearly constant. This makes 1 M BZSM the best catalyst for olefins production. NZSM is a close competitor but does not provide the consistency like BZSM. Other catalysts show lower selectivity and declining olefins trend with time. As a result, TZSM can be considered only for buty-

lenes while PZSM may be used for propylene formation. Overall, the catalyst treated with boric acid was found to be the best suitable one for the production of olefins.

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