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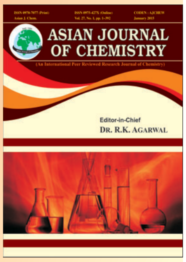

Synthesis of Template-Free ZSM-5 Catalysis for Cyclohexene Hydration

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Template-free ZSM-5 zeolites were synthesized in the tetraethyl orthosilicate, sodium metasilicate and silica sol systems, respectively. Moreover, detailed analysis on the two different synthesis routes with sodium metasilicate as silica source were carried out. Catalytic performance in the cyclohexene hydration reaction was also investigated. The crystallinity, particle size, surface area and acidity varied of products were characterized by X-ray powder diffraction, scanning electron microscope, nitrogen adsorption, Fourier transform infrared spectroscopy, temperature-programmed desorption of ammonia (NH_3-TRD) and thermogravimetric. Remarkable performance in the cyclohexene hydration reaction can be attained by using Na_2SiO_3 as silica source. It was shown that the improved Na_2SiO_3 synthesis route is the most suitable for synthesis of ZSM-5 catalysts.

Keywords: ZSM-5, Silica source, Synthesis route, Template-free, Cyclohexene.

INTRODUCTION

Cyclohexanol is an important intermediate for nylon production and is thus produced on the megaton scale worldwide per year[1]. There are three principal methods of preparation of cyclohexanol: phenol hydrogenation, cyclohexane oxidation and cyclohexene hydration. The cyclohexene hydration is the best method to overcome the disadvantages of the previous two, such as complex process, low conversion rate, poor selectivity and high energy consumption[2,3]. Catalysts play a vital role in the process of hydration reaction and many kinds of catalysts[4-7] have been studied to improve the cyclohexanol yield. ZSM-5 zeolites have been regarded as the most prominent one because of its unique characters such as uniform pores, large internal surface areas, high chemical stability and well-defined crystalline structure[8-10]. At present, the preparation methods of ZSM-5 zeolites are mainly hydrothermal synthesis[11,12], dry-gel conversion[13-15] and confined space synthesis[16,17]. Reding *et al.*[18] have evaluated different preparation methods of ZSM-5 zeolites and the hydrothermal crystallization was identified since it can be easily reproduced. With the easy control of interface reactions, less air pollution and low energy consumption, the hydrothermal synthesis is always the focus of research[9]. In the synthesis process of ZSM-5 zeolites, a variety of templates, such as tetrabutylphosphonium (TBP) cation, ethanol and ethylamine, have been used to improve the quality of products[20,21]. Although the template effect is excellent, it also causes many problems like poison-producing and high production cost. Now, many researches focus on ZSM-5 synthesis without templates to overcome the detrimental problem[22,23].

In addition to selecting the appropriate synthesis route to optimize the physico-chemical properties[24,25]. It has been found that zeolites formation are sensitive to the reactants, especially dependent on the silica source selected[26-28]. Kalipcilar and Culfaz[29] found the silica source employed can affect the purity, crystallization rate and particle size of template-free ZSM-5. Mohamed *et al.*[30] have reported the nature of silica source can not only affect the process of ZSM-5 crystallization but also lead to change in the properties of the final products. Therefore, to choose appropriate synthesis route and source of silica are essential to optimize the zeolite catalysts.

This paper describes the effects of different silica sources on the physicochemical properties of the template-free ZSM-5 zeolites. In addition, two different ZSM-5 zeolites synthesis routes and catalytic performance in the cyclohexene hydration reaction were also studied. The main objective of this work is to find a high-performance ZSM-5 zeolite which obtained by using the best suitable silicon source and improved synthesis method.

EXPERIMENTAL

Catalyst preparation: ZSM-5 zeolites were prepared using sodium hydroxide pellets (A.R) and aluminum sulfate

(G.R) as alkaline and aluminum source, respectively. Silica sources included tetraethyl orthosilicate (TEOS, 98 %), sodium metasilicate (Na_2SiO_3, SiO_2 = 19.3 wt. %, Na_2O:SiO_2 = 1.03:1), silica sol (SiO_2 = 26 wt. %, Tianjin Guangfu). The molar composition of the resulting synthesis mixtures were in the ratio $14Na_2O:100SiO_2:2Al_2O_3:2500H_2O$.

(I) Two different synthesis routes with Na_2SiO_3 as silica source. Traditional synthesis route (products are abbreviated as unheated-ZSM-5) was followed the prepared order: a certain amount of Na_2SiO_3 was dissolved in distilled water at room temperature and moved to a three-necked round bottom flask with stirrer as A solution. Sulfuric acid (98 %) was added to a aqueous solution of $Al_2(SO_4)_3$ as B solution. Hereafter A solution was stirred for 1 h, B solution was slowly added and the synthesis mixture kept on stirring for another 3-4 h.

Improved Na_2SiO_3 synthesis route (products are abbreviated as heated-ZSM-5): after A solution was prepared, an excess water was added to the three-necked round bottom flask again, the solution was heated to 90-100 °C until the excess water evaporated. When the temperature of A solution cooled down to 30-40 °C, the B solution was added to the three-necked round bottom flask, stirred for another 3-4 h to obtain a clear homogenous solution.

(II) Sol-ZSM-5 zeolites (silica sol as silica source) were prepared from a synthesis mixture by sodium hydroxide and aluminum sulfate in distilled water in a beaker. The contents of the beaker were carefully mixed and silica sol was slowly added to the above mixture under stirring. The final synthesis mixture was stirred at room temperature for several hours.

(III) TEOS-ZSM-5 zeolites (TEOS as silica source) were prepared as follows: $Al_2(SO_4)_3$ was added to 1 M NaOH solution and the mixture was stirred at room temperature to obtain a clear solution before adding TEOS. The final mixture was stirred at room temperature for 5 h to hydrolyze TEOS completely.

The above synthesis mixtures were left for 24 h at room temperature and then hydrothermal crystallization for 24 h in an autoclave at 170 °C. All solid products were filtered and washed with distilled water until the pH is dropped to 9 and the products were dried at 110 °C overnight. Ion exchange was conducted two times with 1 M NH_4NO_3 solution at 80 °C each for 3 h, followed by calcinations at 540 °C in air for 3 h to obtain H-ZSM-5[20]. The unlined autoclaves were cleaned with 10 % NaOH at 120 °C prior to each experiment to avoid adventitious seeding.

X-ray diffraction patterns were recorded with a Rigaku Miniflex system operating at 40 kV and 200 mA equipped with a nickel-filtered CuK_α radiation (λ = 1.54056 Å) and operating in a 2θ range of 7-9° (and 22-25°) at a scanning rate of 1°/step and 60 s/step. The morphology and crystalline size of the samples were examined under a scan electron microscope (SEM, S4800) by using samples coated with an Au film. Samples were magnified 5000 times. BET surface area and pore structure of the catalysts were measured using a Micromeritics Tristar 3000 analyzer by nitrogen adsorption at 77 K. Samples were previously outgassed to remove impurities at 250 °C in a helium stream during 1 h. Then a mixture of 30 % N_2/He was allowed to flow through the sample previously immersed in a liquid nitrogen bath at -196 °C.

FT-IR spectra in the vibrational range of 4000-450 cm^{-1} were recorded on a Vertex 70 infrared spectrometer with 16 cm^{-1} resolution. The wafers were prepared with a ratio of ZSM-5: KBr = 1: 200. The thermal analysis experiments were performed with a Shimadzu model TGA-50 with a working station (TA-50WSI) for collecting data in a nitrogen flow of 30 mL/min. The reactor temperature was increased to 800 °C at a ramping rate of 10 °C/min.

NH_3-TPD spectra were recorded on a 2910 Chemisorption Instrument (Micro-meritics). The catalyst (50 mg) was pretreated at 200 °C under Ar flow (30 mL/min) for 1 h and was then cooled down to 50 °C. NH_3 was then introduced into the flow system for 0.5 h. The TPD spectra were recorded at a ramp rate of 10 °C/min from 50 to 600 °C under He.

Catalyst testing: The catalytic performance of the catalysts was carried out in cyclohexene hydration reaction in a 500 mL autoclave reactor, high purity N_2 being used as a carrier gas. 130 mL of water and 30 g of the H-ZSM-5 zeolites were added in the autoclave, heated to 125 °C with the stirring speed of 1000 rpm. Then 100 mL of cyclohexene was added *via* feed tank. After reaction for 2 h, the temperature of products was cooled down to the room temperature by using ice bath[31]. The composition of products were analysed by using a gas chromatograph (GC Fuli 9790II, 50 m × 0.32 mm × 0.4 μm) equipped with an flame ionization detector (FID).

RESULTS AND DISCUSSION

X-ray diffraction: The phase of ZSM-5 was identified by typical peak positions reported[24]. The synthesized products exhibit high crystallinity and no impurities were detected (Fig. 1).

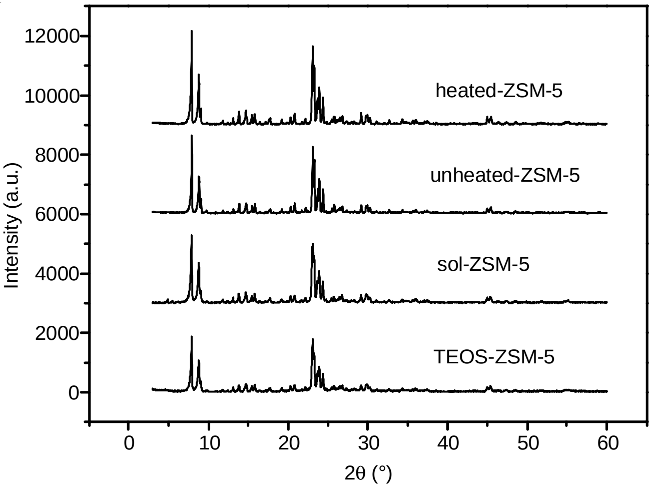

Fig. 1. Effect of silica sources and synthesis routes on the crystallinity of ZSM-5 zeolites

Table-1 shows that the products from Na_2SiO_3 synthesis mixtures (heated-ZSM-5 and unheated-ZSM-5) have higher relative crystallinity than that from other synthesis mixtures. It is found that the relative crystallinity of unheated-ZSM-5 decreases from 100 to 84.06 % compared with heated-ZSM-5, which indicates the effect of synthesis route on the crystallinity of ZSM-5 zeolites. In addition, when sodium metasilicate as silica source, Na^+ cations play a structural directing role enable the starting amorphous precursors integrate to become regular

TABLE-1
EFFECT OF SYNTHESIS CONDITIONS ON PROPERTIES OF ZSM-5 ZEOLITES

Sample	Relative crystallinity (%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Particle size (μm)	NH_3 adsorbed (mmol/g)		
					W[a]	S[b]	W + S[c]
Unheated-ZSM-5	84.06	232	0.185	4	0.481	0.529	1.01
Heated-ZSM-5	100.00	370	0.245	2	0.741	1.02	1.76
Sol-ZSM-5	66.91	381	0.251	2	0.756	0.826	1.58
TEOS-ZSM-5	37.14	313	0.202	3	0.630[d]	0.233	0.863

[a]Weak acid content; [b]Strong acid content; [c]Total acid content; [d]Total amount of acid corresponding to the first and middle peak

structure to generate sufficient crystal nucleus[32], meanwhile, the existence of vast sodium sulfate can also accelerate the crystal growth on the surface of the established crystal nucleus[10]. Additionally, the improved Na_2SiO_3 synthesis route (heated-ZSM-5) which was added by excess water and heated to 90-100 °C can afford a precursor mixture with lower viscosity and more homogeneous compared with traditional synthesis route. The process added by excess water is more important, which maybe in favor of generating more crystal nucleus. In this case, the sufficient crystal nucleus could direct the synthesis gel toward a desired crystal with high relative crystallinity[32].

However, the relative crystallinity of TEOS-ZSM-5 is only 37.14 % which is much lower than that of heated-ZSM-5. It is probable that although the vast ethanol plays a weak directing function in the synthesis process of ZSM-5[20], it can reduce the crystal growth rate simultaneously[33]. Beyond that, the hydrothermal crystallization is generally carried out over 48 h. However, we conducted hydrothermal crystallization for 24 h, which was not sufficient to crystal growth of ZSM-5 and leading to a low crystallinity. Therefore, the incomplete hydrolysis of TEOS can also put off the nucleation and crystallization process. As far as the sol-ZSM-5 is concerned, the relative crystallinity of 66.91 % is higher than TEOS-ZSM-5 but lower than unheated-ZSM-5. In the silica sol synthesis mixture, the precursor mixture is more homogeneous than Na_2SiO_3 synthesis system[30]. However, in the absence of the acceleration of Na_2SiO_4, the crystal growth rate may be slower than the latter which leads to a medium relative crystallinity among the as-synthesized ZSM-5 zeolites[24].

Scanning electron microscopy and surface area: For further verification of the possible influence of synthesis conditions, SEM is used to observe the morphologies of various samples. Fig. 2a shows that the crystals of unheated-ZSM-5 are having cuboid morphology with the crystal diameters about 4 μm or more. As seen from Fig. 2b, the heated-ZSM-5 with crystal diameters about 2 μm have the MFI-typical hexagonal morphology, meanwhile, the distribution of particle size is narrower compared with unheated-ZSM-5. This is attributed to that after a known aging periods, the improved Na_2SiO_3 synthesis route (heated-ZSM-5) can produce more crystal nucleus which is also control ZSM-5 crystal size distribution[34] and reduce the particle size[32].

For the SEM images of Fig. 2c, although the crystal diameters of the sol-ZSM-5 zeolites are similar to that of heated-ZSM-5 zeolites, the morphology of the former are not as regular as the latter's. For different silica source, the oriented growth of crystal is also different. The TEOS-ZSM-5 crystals are hexagonal lath-shaped and the length/width of crystals is big (Fig. 2d). An interpretation of this phenomenon is that the filling manner of alcohols in the holes leads to the change of growth orientation of crystals[33]. It is worth noting that although the crystals of TEOS-ZSM-5 are perfect with no defects, the distribution of crystal diameters is broad. This can be explained that too much alcohol (alcohol/SiO_2 = 4) causes a part of crystals to aggregate to generate greater polymer and makes the particle sizes different[35]. It is obvious that the average crystal size increase in the following order: unheated-ZSM-5 > TEOS-ZSM-5 > heated-ZSM-5 > sol-ZSM-5.

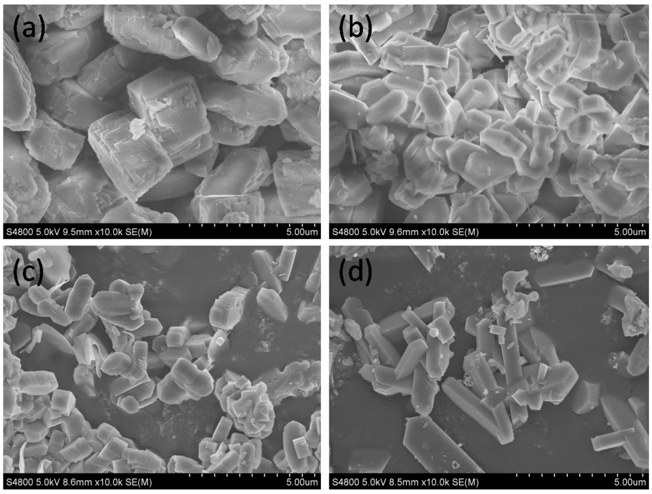

Fig. 2. SEM images of ZSM-5 zeolites (a) unheated-ZSM-5; (b) heated-ZSM-5; (c) sol- ZSM-5; (d) TEOS-ZSM-5

The BET area and pore volume of sol-ZSM-5 are the biggest among the ZSM-5 zeolites (Table-1). Both BET area and pore volume of heated-ZSM-5 are almost equal with that of sol-ZSM-5, but bigger than unheated-ZSM-5. It's easy to see that BET area and grain size are in inverse proportion: the larger the grain size, the smaller the BET area is. The pore volumes with BET areas change from small to big also have a rising process. All these facts show that changing the synthesis routes or silica sources leads to great change in the structural properties of the final product.

Fourier transform infrared studies: IR spectra (Fig. 3) of ZSM-5 zeolites in the range of 4000-450 cm^{-1} exhibited broad peak centered at 550 and 450 cm^{-1} which are attributed to the five-membered ring structures and the T-O bond of the SiO_4 and AlO_4 tetrahedron units, respectively[36-38]. The typical peaks for ZSM-5 zeolite at 850, 1100, 1220, 1633 and 3340 cm^{-1} are also observed. Additional evidence is the asymmetric stretch vibration of the T-O bond (at 1220 cm^{-1}, T is Al^{3+} or Si^{4+}), which has been assigned to external linkages (between TO_4 tetrahedron units)[39] and is a structure-sensitive IR band of ZSM-5 zeolites[25]. Moreover, the structural insensitive vibrations caused by internal asymmetric stretching vibrations of Si-O-T linkage of ZSM-5 were observed at 1100 cm^{-1}. As described in XRD and SEM patterns, FTIR data also gives verification that the structure of TEOS-ZSM-5 is weak intensity which corresponds to the relatively low crystallinity. In coherence with XRD and SEM data, it may be concluded that in the case without other templates, but presence of alcohol, TEOS is not an ideal silicon source.

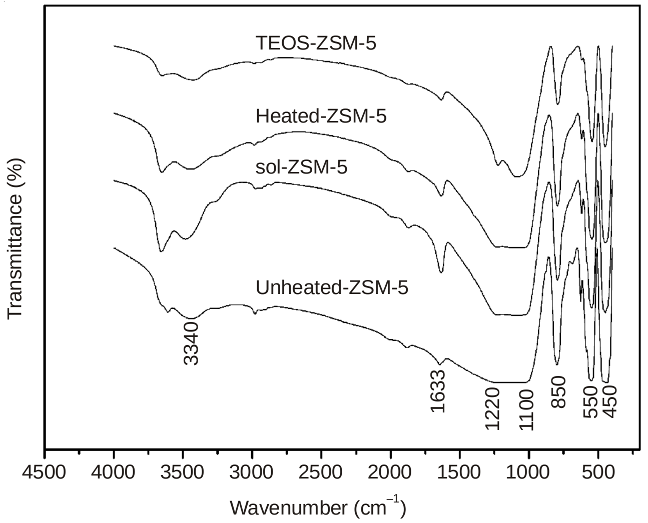

Fig. 3. IR spectra of different ZSM-5 zeolite samples

NH_3-Temperature programmed desorption: In the NH_3-TPD curves of ZSM-5 zeolites shown in Fig. 4, peaks are generally observed in two temperature regions, indicating the existence of at least two types of acid sites. However, the NH_3-TPD method can only distinguish acidic sites by sorption strength. Generally, the peaks in the low temperature (LT) region can be attributed to weak acidic sites, while those in the high temperature peaks are ascribed to the strong acidic sites. The high temperature peaks can be assigned to desorption from strong B and L acidic sites which are related to framework Al atoms charge compensated by acidic protons and to extra-framework Al atoms, respectively[20]. These strong B and L acidic sites also play a major catalytic role in the cyclohexene hydration reaction[40]. The low temperature peaks were ascribed to the weak L acidic sites which were from some extra-framework Al species, such as $Al(OH)_2^+$ and $Al(OH)^{2+}$ and also some framework Al species[41]. While Igi *et al.*[42] attributed the low temperature peaks to the release of NH_3 hydrogen-bound to NH_4^+ cations.

The total acidities of four ZSM-5 samples were calculated from the peak area and the results are listed in Table-1. Compared with unheated-ZSM-5, the total acidity of heated-ZSM-5 increased by 74.3 %. Clearly, both weak and strong acidity increase remarkably from 0.481 to 0.741 mmol NH_3/g (about 54 %) and from 0.529 to 1.02 mmol NH_3/g (about 93 %). It is also noted that although the total acidity of sol-ZSM-5 is similar to that of heated-ZSM-5, the strong acidity is lower than the latter. Therefore, the improved Na_2SiO_3 synthesis route (heated-ZSM-5) may be beneficial to improve the strong acidic site concentration. It is interesting to find that the NH_3-TPD spectra of TESO-ZSM-5 show three peaks. As suggested by Loc[43], the first desorption peak is believed to be associated with physically adsorbed or weakly chemically adsorbed ammonia molecules; the middle peak is NH_3 molecules adsorbed on zeolite hydroxyl groups and the high temperature peak is associated mainly with dehydroxylation, strong B and L acid sites. It is suggested that the silicon source not only can affect the morphologies of ZSM-5 zeolites, but can also be responsible for the distribution of acidic sites. The total acidic sites, especially the strong acidic sites, of the ZSM-5 samples decrease in the order of heated-ZSM-5> sol-ZSM-5> unheated-ZSM-5> TEOS-ZSM-5. As will be shown later, this result is also in line with the catalysis performance of the ZSM-5 zeolites in the cyclohexene hydration reaction.

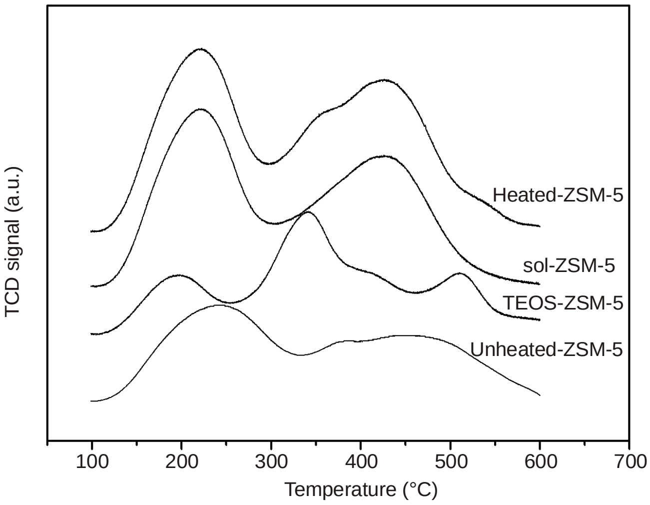

Fig. 4. NH_3-TPD curves of ZSM-5 zeolites from different silica sources and synthesis routes

Thermal gravimetric analysis: Thermogravimetric/DTG profiles of the studied materials are presented in Fig. 5. Some well-defined thermogravimetric effects indicated that the samples of heated-ZSM-5, unheated-ZSM-5 and sol-ZSM-5 only have one weight loss zone from room temperature to 200 °C which are assigned to the dehydration of physically adsorbed water. From Fig. 5 (DTG), the loss rate of adsorbed water reached the maximum at 100 °C. After adsorbed water was absolutely lost, the qualities of samples were constant regardless of temperature change. The total weight loss for the above three samples are about 5.57, 6.27 and 5.98 % from room temperature to 800 °C, respectively. In addition, different with other synthesis system using organic templates, the ZSM-5 from template-free synthesis systems have no organic decomposition in the heating process[44].

The TG/DTG studies also show a difference in TEOS-ZSM-5 sample. There are two sharp peaks in the temperature ranges from 50-200 °C and 350-450 °C. The first peak can be assigned to desorption of water and methanol which adsorbed on the outer surfaces of crystals. The second peak was observed only in the TG/DTG curves of TEOS-ZSM-5 although large molecules like TPA^+ were not used. Kalipcilar and Culfaz[29] used colloidal silica sol stabilized with methanol as silica source for ZSM-5 synthesis and similar TG/DTG result was observed. According to this observation, the second peak can be assigned to the methanol remain in the crystal holes until desorption

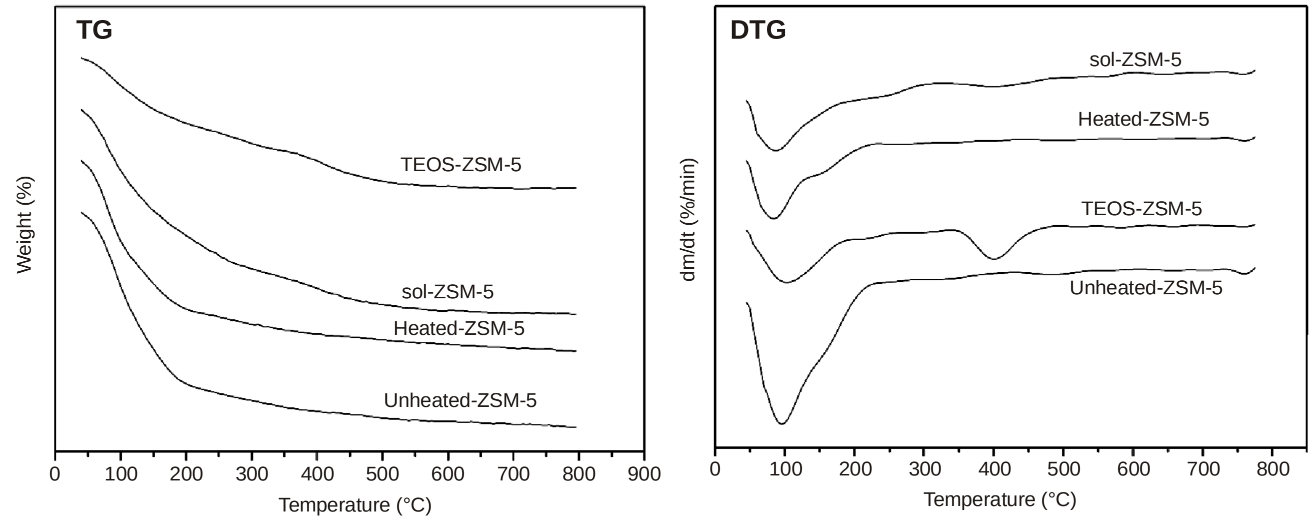

Fig. 5. TG/DTG curves of ZSM-5 zeolites

above 350 °C. The sample lost 2 % of its weight at around 100 °C and 1.8 % of its weight from 350 to 450 °C. All the TG/DTG data imply that although ZSM-5 crystallization systems are different, their framework rigidity and structural stability are almost the same.

Catalyst testing: In present work, the four as-synthesized ZSM-5 catalysts were studied for the hydration of cyclohexene and the results are compared in Fig. 6. It is evident that heated-ZSM-5s have the best catalytic activity among all the catalysts and they offer 3 fold increases in the conversion of cyclohexene compared with that using unheated-ZSM-5s. The particle size and acidic sites on the external surface of the ZSM-5 catalyst are identified as critical parameters in determining catalytic activity[6]. The activity of ZSM-5 catalyst increases with the decrease of the crystal size. When fine particles are used, the activity is directly proportional to the acidity[23]. That is why the crystal sizes are similar between sol-ZSM-5 and heated-ZSM-5, but the catalytic activity of former (12.5 %) is slightly lower than that of latter (10.9 %). The TEOS-ZSM-5 with big crystal size and less acidic sites exhibited the lowest activity of only 3.8 %.

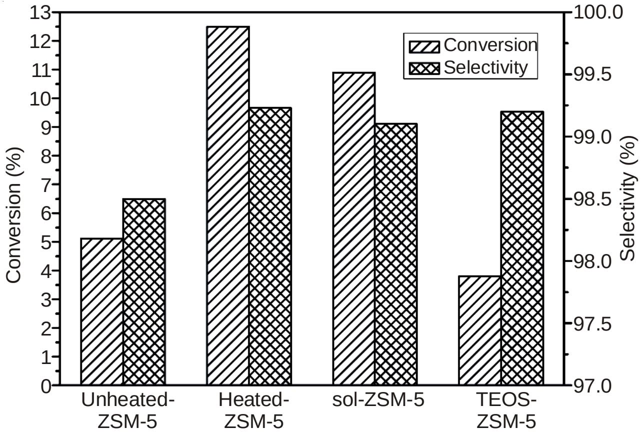

Fig. 6. Activities of cyclohexene hydration reaction over different ZSM-5 zeolites

Although there is a big difference in the conversion of cyclohexene, all ZSM-5 zeolites have an extremely high selectivity (>99 %) for cyclohexanol. This high selectivity can be understood as a result of the shape selectivity of the zeolites. ZSM-5 zeolites are MFI structure with 10-membered ring (0.54 × 0.56 nm) channels which allow cyclohexene (0.6 nm) and cyclohexanol to opt the pores freely. Meanwhile, the bulky by-products such as 2-cyclohexenyl cyclohexanone, dicyclohexyl ether[31] are difficult to form due to the strong geometric limitation.

By comparing the activity and selectivity of different ZSM-5 catalysts, it is found that the improved Na_2SiO_3 synthesis route (heated-ZSM-5) is probably more suitable for the synthesis of ZSM-5 catalysts.

Conclusion

The template-free ZSM-5 zeolites have been successfully fabricated by using tetraethyl orthosilicate, sodium metasilicate and silica sol. It was shown that ZSM-5 zeolites exhibited an extremely high selectivity (> 99 %) for cyclo-hexanol because of the shape selectivity of the zeolites and the activities increased in the following order: TEOS-ZSM-5< unheated-ZSM-5< sol-ZSM-5< heated-ZSM-5. In addition, the results suggested that the improved Na_2SiO_3 synthesis route (heated-ZSM-5) provides a possibility for synthesis of high quality ZSM-5 zeolites from sodium metasilicate synthesis mixture, which has several unique advantages such as low cost, well-defined crystalline structure and high activity. Furthermore, this method can be extended to zeolites synthesis fields for industrial production.

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