

CHAPTER II

LITERATURE REVIEWS

Beta zeolite is developing into a major catalyst in organic chemicals conversion, contribution to low waste technology. Beta zeolite was first synthesized by Wadlinger et al. [2] in the range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 10-200 in 1967. Then Beta zeolite was studied continuously.

Perez-Pariente et al. [6] studied the efficiency of the synthesis of Beta zeolite and the chemical composition of crystals. It was very difficult to effectively synthesize siliceous crystal of Beta zeolite. From aluminum-rich gels ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$), high yield of Beta zeolite could easily be obtained, whereas from siliceous gels ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 900$), Beta zeolite was found in small amount. And the crystals were enriched in aluminium. This synthesis insufficiency was due to the inefficiency use of silicon, the mother liquor always being exhausted in aluminium at the end of the crystallization. The incorporation of silicon in Beta zeolite could be improved by several means. When ethanol was kept in the system, when aluminium was excluded from the gel particles, or when the synthesis temperature was increased from 373 to 393 K, reasonable yields of siliceous Beta zeolite crystals were obtained.

Cambor and Perez-Pariente [7] studied the effect of Na and K ions in crystallization of Beta zeolite. The crystallization rate and crystal size of Beta zeolite made from K and Na containing gels had been shown to be dependent on the total alkali content and the molar fraction of each cation. The crystal size of final product increased with the K content of the gel. The surface of the crystal was shown to be enriched in aluminum because of the increasing of pH during crystallization.

Ramesh and Clearfield [8] studied the characterization of acid sites in Beta and ZSM-20 Zeolites. Beta ($\text{Si}/\text{Al} = 5-20$) and ZSM-20 zeolites with low Si/Al ratio had been synthesized using tetraethylammonium hydroxide as an organic template, and characterized by XRD, SEM, TGA and XPS. The acidic properties of these

zeolites were studied by temperature programmed desorption (TPD) of pyridine. TPD of pyridine revealed that the chemisorbed pyridine was desorbed at somewhat higher temperature from Beta zeolites as compared to ZSM-20 and/or HY zeolites.

Bellussi et al. [9] studied the catalytic performance of Beta zeolite in liquid-phase alkylation of benzene with ethylene and propylene to ethylbenzene and cumene (isopropylbenzene) respectively. They found that Beta zeolite was more active and more selective than phosphoric acid (PA), ultrastable Y zeolite (USY) and H-ZSM-5. Furthermore, they studied influence of Si/Al ratio and particle size of catalyst on activity and selectivity because intraparticle diffusion; they found that decreasing the framework Al content (by direct synthesis or by partial substitution of Al for B) produced a decrease in both conversion and selectivity in cumene and ethylbenzene. When USY used as catalyst, higher aromatics (triisopropylbenzene) increased because the presence of supercages.

Perego et al. [10] studied catalytic performance of Beta zeolite in the liquid phase alkylation of benzene with propylene compared with other zeolite: MOR, ERB-1, USY, MTW. The comparison is carried out both by catalytic tests and by computational evaluation of the energy barriers for diffusion of the product molecules and of the binding energies (BE's) of the same molecules. They found that among the zeolite studied here, Beta zeolite appeared to be one of the most efficient catalysts for liquid-phase alkylation of benzene with propylene. Under the same operating conditions Beta zeolite produced the smallest amount of propylene oligomers and shows the highest overall selectivity. The cumene obtained with Beta zeolite contained the smallest amount of *n*-propylbenzene, considering also the contribution to the formation of the latter during the consecutive transalkylation step of Diisopropylbenzenes (DIPBs). Most of the zeolites evaluated showed a significant alkylation activity: only USY zeolite was slightly less active. Besides, the high meta/para ratio of DIPBs, which was close to the equilibrium value, and the small amount of *o*-DIPB indicated high isomerization and transalkylation activity of Beta zeolite and MOR. Good agreement was found between the experimental

performances and the energy diffusion barriers and binding energies of cumene and DIPB isomers, in the different zeolite pore structures.

Jansen et al. [11] found that Beta zeolite has Brønsted-acid sites in the micropores and on the relatively large external surface. Lewis-acid sites, however, are predominantly present at the internal surface. They are related to local defects. These defects occur when a tertiary building unit (TBU) is rotated 90° around the *c* direction with respect to the neighboring TBUs in the same layer. The rotated TBU cannot connect properly with the adjacent layers. This resulted in T-atoms (Si or Al), which are not fully connected to the framework. The unique combination of optimal pore dimensions and Lewis-acid sites in the micropores of Beta zeolite resulted in the remarkably high stereoselectivity of Beta zeolite in the Meerwein-Ponndorf-Verley (MVP) reduction of 4-*tert*-butylcyclohexanone to the *cis*-alcohol. This result demonstrated the potential of Beta zeolite as Lewis acid catalyst in shape-selective organic conversions.

Rodriguez et al. [12] studied alkylation of benzene with propylene catalyzed by fluorinated alumina. They found that this alkylation reaction proceeded via a protonation of propylene by the acid sites to form the active species. The latter could react with benzene, producing cumene, or it could react with another propylene molecule producing a C₆ species. In their case, both reactions were observed, but the transformation of benzene was almost 100% selective toward benzene, and di- and trialkylbenzenes are not observed. Such a point is important for the gasoline reformulation in which the formation of heavy products has to be avoided. Their results also indicated that consumption of propylene by oligomerization was important enough, but that could be probably reduced by optimization of the propylene/benzene ratio.

Medina-Valtierra et al. [13] studied the alkylation of benzene with isopropanol to produce cumene by using a MCM-41 aluminosilicate as catalyst. They found that cumene was formed as the primary product of isopropylation, which does not easily react to form diisopropylbenzene (DIPB) due to the lower probability of further

reaction. Therefore, it was interesting to find that with MCM-41 catalyst, cumene was the main product. An important side reaction was the cumene disproportionation to give toluene + ethylbenzene or DIPB isomers in concentrations for lower than their thermodynamic equilibrium. In this case, the primary product of alkylation diffused into the broad channels when they react slowly. Since large molecules such as alkylnaphthalenes could diffuse easily in the mesopore channel of MCM-41, they concluded that the main products detected are those favored kinetically at the active sites. The cumene selectivity could be due to the low acid site concentration in the MCM-41, and the rapid diffusion of cumene in the broad channels of MCM-41.

Bandyopadhyay et al. [14] studied selective formation of cymene by transalkylation reaction of toluene with cumene and 1,4-diisopropylbenzene. The effect of various reaction parameters on the activity and selectivity is studied over H-Beta and results are compared with H-Y and H-ZSM-12. Cymene (isopropyltoluene) could be successfully and selectively formed by the transalkylation of toluene with cumene and 1,4-diisopropylbenzene. Transalkylation with diisopropylbenzene is advantageous due to the simultaneous formation of cumene along with cymene. In general, the reaction in large pore zeolites favors bimolecular pathway, and proceeds via a diphenylpropane type intermediate. Among the large pore zeolites considered in this study, H-Beta was more active and selective than H-Y and H-ZSM-12 for the trans alkylation reaction. Performance and the deactivation of the catalysts during the reaction could be attributed to their structural properties.

Camilot et al. [15] studied acidity of Beta zeolite with Si/Al ratios ranging from 18 to 33 by temperature programmed desorption (TPD) of ammonia and their catalytic behavior was evaluated by disproportionation of ethylbenzene. The acid strength of Beta zeolite determined by TPD of ammonia increases as the Si/Al ratio is increased from 18 to 33. Despite carrying out TPD measurements under very careful condition, the NH_3/Al ratios were always higher than unity and this result was probably a consequence of Lewis acid sites formed by structural defects present in H-Beta zeolite. The ammonia desorbed between 380°C and 600°C seemed to be very appropriate to quantify the number of Brønsted acid sites in this zeolite. The results

correlated very well with the catalytic behavior of this zeolite: the catalysts with stronger acid sites, determined by NH_3 -TPD, present also higher catalytic activity in the disproportion of benzene. The induction period of this reaction had 'no dependence on zeolite Si/Al ratio.

Perego et al. [16] studied the liquid-phase of toluene with propylene on two amorphous mesoporous silica-aluminas (MSA and MCM-41) and compared with the amorphous silica-alumina (ERS-8) and Beta zeolite. The catalytic activity, the selectivity to *o*-, *m*- and *p*-cymenes and the formation of polyalkylates are discussed as a function of acidic and porosity. The catalytic behavior of MSA, MCM-41, ERS-8 and Beta zeolite is also compared with data reported in the literature for traditional alkylation catalysts (AlCl_3 -HCl and supported phosphoric acid, SPA) and for other acidic zeolites. MSA and MCM-41 showed alkylation activities comparable with Beta zeolite, while their isomerization and transalkylation activities were lower than those of Beta zeolite and AlCl_3 -HCl, but similar to SPA. Such behavior was in agreement with the Brønsted acidity of materials studied.

From the reviews, Beta zeolite was widely used for transformation of aromatics includes cumene synthesis from benzene and isopropanol. It was shown that, the shape selective of Beta zeolite for cumene is better than ZSM-5 and Y-zeolite. Major by-product from this reaction is DIPB, which may be recycled to produce cumene by transalkylation with benzene or used for cymene production.