

Novel *in situ* zeolite synthesis technique

Anne M. Gaffney* and Jan H. Koegler

Lummus Technology, 1515 Broad Street, Bloomfield, NJ 07003 USA

*agaffney@cbl.com

Introduction

Zeolites are important catalysts in many petrochemical and refining processes. The traditional method of zeolite synthesis starts by dissolving nutrients in caustic/template solution, followed by hydrothermal treatment, washing, ion exchange and calcination. Lummus Technology has developed a novel method for preparation of zeolite-based catalysts in which alumino-silicate precursor bodies, such as preshaped spray-dried particles or extrudates, are converted to zeolites while maintaining the morphology of the precursor [1,2]. Catalysts with special properties can be prepared, such as materials containing extremely small zeolite crystal sizes, and catalysts with hierarchical pore structures. The method was demonstrated for many zeolites, such as beta, ZSM-5, A, X, Y, L, and mordenite. The synthesis procedure offers higher product yields and higher productivity per reactor volume compared to conventional synthesis procedures. Zeolite beta catalyst particles obtained by this procedure showed better catalyst performance than commercial zeolite beta extrudates in benzene alkylation to ethylbenzene and cumene.

Materials and Methods

Commercially available silica particles were used as the precursors for the synthesis of zeolite beta, ZSM-5, Y, and mordenite. Spray-dried particles (Davison Sylopol 948) of 60 μm , a pore volume of 1.1 cm^3/g , and a surface area of 291 m^2/g were obtained from WR Grace. Silica extrudates (CS1030E) with a diameter of 2.5 mm, a pore volume of 1.1 cm^3/g , and a surface area of 300 m^2/g were obtained from PQ Corporation. Impregnation of the silica and silica-alumina precursors was carried out with a solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) in distilled water above the incipient wetness point of the precursor. XRD analysis of the samples was carried out on a Philips PW1840 diffractometer. N_2 porosimetry was carried out with a Micromeritics ASAP2010 at 77 K. In an effort to obtain very small zeolite Y crystals using our synthesis approach, a high-throughput synthesis project was carried out in cooperation with Avantium Technologies. The liquid phase alkylation of benzene with ethylene was carried out at 190°C and 350 psig (24.1 bar) in a differential recycle reactor with an internal diameter of 0.65 inch (1.65 cm). The circulation rate was set at 200 g/min. Between 0.60 and 1.00 g of the catalyst was loaded in the reactor between quartz wool and glass beads. The activity of commercial beta catalysts with a silica-to-alumina ratio of 23 and a size of -12/+20 mesh was measured as a reference.

Results and Discussion

Tables 1 and 2 show zeolite beta performance in benzene alkylation to ethylbenzene and cumene on a weight and a volumetric basis. All beta samples from the *in situ* conversion had a SAR of 30. The samples from the *in situ* procedure showed up to 80% higher volumetric performance than the best commercial sample. No differences in selectivity were observed. As expected, the volumetric activity goes up with increasing crystallinity. The improvement in

performance can be due to higher intrinsic activity of zeolite and to an increase in the effective diffusivity, leading to higher catalyst utilization.

Table 1. Zeolite beta features and activity in benzene alkylation to ethylbenzene.

Sample	Relative crystallinity (%)	$V_{\text{meso+macro}}$ (cm^3/g)	Relative k_{observed} by weight	Relative k_{observed} by volume	Relative amount of zeolitic Al	Average mesopore size (nm)
Commercial, 1	80	0.70	1.00	1.00	1.00	20
Commercial, 2	80	-	0.77	1.02	-	-
Beta, SD3 + 20% Al_2O_3	91	0.69	2.14	1.79	0.87	200
EX1	59	0.82	1.05	1.07	-	40
EX2	108	0.69	1.68	1.65	-	110
EX3	113	0.61	1.29	1.27	-	180

Table 2. Zeolite beta features and activity in benzene alkylation to cumene.

Sample	Relative crystallinity (%)	$V_{\text{meso+m}}^{\text{acro}}$ (cm^3/g)	Relative k_{observed} by weight	Relative k_{observed} by volume	n-propyl-benzene level
Commercial, 1	80	0.74	1.00	1.00	222
Beta, SD1	91	0.69	1.76	1.48	228

Considering the activity-pore dimension relationship, it is believed that at least to some extent, the increase in observed alkylation activity may be accounted for by enhanced mass transfer properties [3].

Significance

Advantages of the synthesis method compared to conventional zeolite synthesis methods are high nutrient utilization, elimination of the filtration step in the synthesis process, and elimination of zeolite extrusion. The principle was demonstrated for zeolite beta, ZSM-5, Y, mordenite and A. The synthesis procedure was demonstrated on kilogram-scale with spray-dried and extrudate precursor particles. Upon conversion, the average pore size of the precursor phase shifted from 10 nm to 100 nm for the extrudates, and from 20 nm to 200 nm for spray-dried particles. The method offers a route to zeolites with high product crystallinity, relatively small crystal sizes, and unique pore size distribution. Zeolite beta samples obtained by the novel procedure showed superior performance in aromatics alkylation compared to commercial zeolite catalysts.

References

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