Three-dimensional medium pore zeolites: Synthesis and Catalysis

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Introduction

Synthesis of zeolites plays an important role in the development of new technological processes in catalysis and simultaneously also in a better understanding of new inorganic materials. In spite of the fact that only around 10 structurally different zeolites are employed in large scale technologies, the number of new zeolites increases each year. Recently several novel zeolites possessing three-dimensional structure consisting of intersecting 10-ring channels have been successfully synthesized. Their structural features slightly differ from the most frequently used zeolite ZSM-5, which provides an interesting opportunity to compare their acidic properties and catalytic behavior with the standard commercial ZSM-5. These zeolites include TNU-9 [1] and SSZ-74 [2].

In this contribution synthesis of TNU-9 and SSZ-74 is discussed related to the acidic and catalytic behavior of these zeolites in toluene disproportionation and toluene alkylation with isopropyl alcohol.

Materials and Methods

Synthesis of zeolites TNU-9 and SSZ-74 is based on application of 1,4-bis(N-methylpyrrolidium)butane or 1,6-bis(N-methylpyrrolidium)hexane as structure-directing agents. The optimization of the synthesis conditions is presented together with the effect of aluminum source on the conditions of the synthesis and relevant acidity of the final zeolites.

Catalytic performance of both zeolites was tested in toluene disproportionation and toluene alkylation with isopropyl alcohol. Both reactions provide an important insight into the structural properties of these zeolites based on level of toluene conversion, shape-selectivity, selectivity to xylenes (cymenes) and also formation of n-propyl toluenes in the latter reaction.

Results and Discussion

Comparison of toluene conversions and selectivites to cymenes, n-propyl toluenes and para-selectivity in toluene alkylation with isopropyl alcohol over zeolties ZSM-5, SSZ-74 and TNU-9 is given in Table 1. SSZ-74 and ZSM-5 exhibit rather stable toluene conversion while a decrease in toluene conversion was observed over TNU-9 from 11.5 to 8.9 % during 180 min of T-O-S. The higher value of toluene conversion over TNU-9 is due to toluene disproportionation decreasing the selectivity to cymenes and n-propyl toluenes. Selectivity to cymenes increases in the order TNU-9 < ZSM-5 < SSZ-74 for 15 min of T-O-S while the following order was achieved after 180 min (ZSM-5 < TNU-9 < SSZ-74). The selectivity to cymenes over TNU-9 increases from 50 to 87 % mainly due to a particular decrease in the rate of toluene disproportionation. After 180 min of T-O-S the iso-/n-propyl toluene ratio is around 10-11 for SSZ-74 and TNU-9 while for ZSM-5 this ratio is close to 2. This difference is most probably due to a slightly larger size of channels of SSZ-74 and TNU-9 compared with ZSM-5. Based on the mechanism of this reaction [3] the cymene and toluene molecules are more flexible in the channel intersections of SSZ-74 and TNU-9 and the formation of the required bimolecular transition state is rather limited. Selectivity to *p*-cymene after 180 min increases in the sequence TNU-9 < SSZ-74 < ZSM-5. The highest *para*-selectivity over ZSM-5 corresponds well to the lowest iso-/n-propyl toluene ratio obtained over this zeolite. Limited movement of cymene molecules due to the channel size is reflected also in more pronounced differences in the diffusion coefficients.

Table 1 Toluene conversions and selectivity to cymene products over ZSM-5, SSZ-74 and TNU-9 in toluene alkylation with isopropyl alcohol. Reaction temperature – 250 ºC, WHSV = 10 h^{-1}, toluene/isopropyl alcohol molar ratio = 9.6.

	SSZ-74		TNU-9		ZSM-5	
T-O-S (min):	***15***	***180***	***15***	***180***	***15***	***180***
Toluene conversion (%)	9.0	9.1	11.5	8.9	7.4	7.5
Isopropyl alcohol conversion (%)	99.9	99.9	100.0	99.9	99.9	99.8
Selectivity to cymenes	86.8	85.0	26.7	79.8	41.3	45.1
Selectivity to propyltoluenes	7.8	7.4	23.7	7.6	28.9	26.6
Iso/n-propyl toluenes	11.1	11.4	1.1	10.5	1.4	1.7
Cymenes: meta	38.5	36.5	61.8	33.8	36.4	26.4
para	60.8	62.9	32.2	59.3	57.8	72.5
ortho	0.7	0.6	5.9	6.9	5.8	1.1
n-propyltoluenes: meta	66.7	66.3	63.7	39.5	58.1	52.7
para	32.8	33.1	31.1	59.5	41.4	47.0
ortho	0.6	0.5	5.2	1.0	0.5	0.3

Significance

This contribution discusses in detail the effect of the zeolite channel architecture (3-D channel system with 10-ring intersecting zeolites) on their catalytic properties in toluene disproportionation and alkylation with isopropyl alcohol. The understanding of the effect implies aspects of both fundamental research as well as industrial relevance.

References

1. Hong,S.B., Min,H.-K., Shin,C.-H., Cox,P.A., Warrender,S.J., Wright,P.A., *J. Am. Chem. Society*, 129, 10870 (2007).
2. Zones S.I., et al., US2007/0148086 A1.
3. Wichterlová B., Čejka J., *J. Catal.* 146 (1994) 523.