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Synthesis of ZSM-5 Zeolite with Small Crystallite and its Application in Aromatization of Propane

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Abstract: By optimizing the crystallization condition, a procedure for the synthesis of small crystallite zeolite ZSM-5 was developed. Compared with the larger crystallite ZSM-5, the smaller one exhibits higher catalytic performance in aromatization reaction of propane.

Keywords: ZSM-5 zeolite, small crystallite size, aromatization, propane.

Recently, great interests were put on the nano-sized materials. It was found that zeolite ZSM-5 with small or nano-sized crystallite could achieve excellent catalytic performance in certain reactions[1-3]. However, most publications concerning the synthesis of ZSM-5 with small crystallite always use the costly TPAOH/Br as organic templates. We reported here the method using much cheaper ethylamine as template and the products were applied to aromatization of propane in which the stability of catalyst was improved without using costly Pt[4]or Pd[5] as stabilizer. Synthesis of small crystallite ZSM-5 were developed starting from the procedure described by Qin *et al* [6] by reacting a mixture having molar composition: Al_2O_3: 84 SiO_2: 32.6 ethylamine: 9.6 Na_2O: 3360 H_2O: 60 NaCl in an autoclave equipped with stirrer. The mixture was crystallized statically at 378 K for 24 h, then starting the stirrer at 300 r/min with raising temperature to 388 K and crystallized for another 62 h. The product was identified as highly crystallized ZSM-5 by XRD with crystallite size 0.1 μm by SEM. Chemical analysis showed the SiO_2/Al_2O_3 of the product was 49. Another sample with crystallite size 2~6 μm from Catalyst Plant of Nankai University was chosen as reference sample with SiO_2/Al_2O_3=50.

The zeolite samples were converted to H-form by calcination and ion-exchange. ZnHZSM-5 was prepared by impregnating the H-form into zinc nitrate solution, followed by drying at 353 K and calcination at 823 K for 4 h. A fixed bed continuous flow reactor was used by packing it with 1g of self supported binder-free pellets (60-80mesh) of the catalyst samples. The products were analyzed using gas chromatography. The results are summarized in **Table 1**.

Table1* Aromatization of propane over ZSM-5 zeolites with different crystallite sizes

time on stream(h)	conversion (%)	yield of aromatics(%)	Selectivity to aromatics(%)	selectivity to C_1+C_2(%)	selectivity to $C_2^=+C_3^=$(%)
2	67.8	34.4	50.7	58.8	6.8
	59.1	30.2	51.1	44.2	4.7
3	67.3	34.3	51.0	57.9	7.8
	49.0	26.3	53.7	37.6	8.7
4	65.6	33.9	51.7	57.3	8.8
	36.7	20.6	56.1	31.1	12.8
5	60.0	31.0	51.7	59.9	9.1
	25.9	14.4	55.6	26.8	17.6

*Reaction conditions: Temp = 823 K, WHSV = 6.5 h^{-1}, Zinc content = 2%wt. The upper and the lower of each data pair are related to the results over ZSM-5 zeolite with crystallite size 0.1μm and 2~6μm, respectively.

As shown in **Table 1**, the conversions of propane from 2 to 5 h on stream decreased over small crystallite ZSM-5 and the larger one is 7.8 and 33.2%, respectively. The selectivity to aromatics, C1+C2, $C2^=+C3^=$ almost keep constant over small crystallite one. The smaller the crystallite is, the shorter of the diffusion path and the more pore mouth are. Thereby, the diffusions of reactants and products inside the small crystallite are easier than those inside larger ones, coke or its precursors will accumulate more slowly over small crystallite ZSM-5. As we know the loss of metal species from zinc containing zeolite is due to the formation of strong reducing agent (hydrogen or carbon) which can convert zinc oxide into metal, therefore, the less the coke formed, the slower the zinc ran off, thus higher stability was maintained over small crystallite ZSM-5.

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References

1. M. Sugimoto, H. Katsuno, K. Takatsu, N. Kawata, *Zeolites*, **1987**, *7*, 503.
2. S. P. Bu and T. Inui, *Zeolites*, **1996**, *17*, 334.
3. M.V. Landau, N. Zaharur, M. Herskowitz, *Applied Catal.* **1994**, *A: General, 115*, L4-L15.
4. T. Inui, *Stud. Surf. Sci. Catal*., **1989,** *44*, 189.
5. D. Seddon, *Catalysis Today*, **1990,** *6*, 351.
6. G. L. Qin, C. C. Wu, R. H. Mu, *Shi You Lian Zhi*, **1978**, *11-12*, 85.

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