Journal of Catalysis 279 (2011) 231

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Response to Letter to the Editor

Reply to the "Comments on Shape-selective diisopropylation of naphthalene in H-mordenite: Myth or reality?" by Gyula Tasi and István Pálinkó

The comments by Tasi and Pálinkó [1] on our recent publication [2] are related to the estimation of the cross sectional area of diisopropylnaphtanene (DIPN) positional isomers and, especially, of the dimensions of the slimmest isomers, viz. 2,6-DIPN and 2,7-DIPN. We found the differences in the estimated cross sectional dimensions of these two isomers to be insignificant [2], while Tasi and Pálinkó insisted on the difference [1]. According to Tasi and Pálinkó the 2,6-DIPN molecule would be the only DIPN isomer fitting inside the mordenite pore and, therefore, be formed preferentially.

Tasi and Pálinkó in Table 1 of their comment showed that the level of theory for estimating molecular dimensions (MP2 vs. B3LYP) matters at a level of precision of the order of 0.01–0.06 Å. We estimated 2,6-DIPN to be as big as 2,7-DIPN within a 0.05 Å margin. Furthermore we did some control calculations on the same B3LYP level on the idealized sizes of the windows of mordenite and found them also to be accurate within 0.05 Å compared to the estimates in the Atlas of Zeolite Structure Types. The effective pore width of the mordenite zeolite channels under reaction conditions is unknown however, and will deviate substantially from the estimate of 6.5 × 7.0 Å in the Atlas depending e.g. on deformation upon adsorption of molecules [3] and on aluminum content and aluminum atom positioning in the framework. In view of the uncertainties of the actual free diameters of zeolite pores, a very high level of computational precision for estimating DIPN isomer dimensions does not seem to be needed.

The interpretation in literature of naphthalene diisopropylation on mordenite being governed by molecular shape selectivity has been inspired by the high 2,6-DIPN selectivity observed at high conversion levels. In our publication [2] we provided experimental evidence that at low conversion levels, formation of 2,6-DIPN is suppressed instead of favored. For instance, at a yield of 1.1% of DIPN on mordenite catalyst, the 2,6-DIPN content of the DIPN fraction was 15.1% only, while other bulkier isomers such as 1,4-DIPN (18.0%), and 1,7-DIPN (16.8%) fitting less well in the pores according to any molecular size estimation were formed more abundantly. The preferential formation of 1,4-DIPN and 1,7-DIPN isomers can be explained by intrinsic kinetic preferences [2]. Upon increasing the conversion the composition of the DIPN product slate evolves towards the internal thermodynamic equilibrium of the DIPN isomers being enriched in 2,6-DIPN and 2,7-DIPN isomers.

Our argument against the thesis of molecular shape selectivity governing naphthalene diisopropylation in mordenite is based on experimental product distributions at low conversion, and does not rely on estimation of molecular dimensions of DIPN isomers. The molecular dimensions of the DIPN-isomers obviously cannot explain the experimental results at low conversion, whatever computational method applied.

References

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doi:10.1016/j.jcat.2011.01.006