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Response to Letter to the Editor

## Reply to the letter of Robert Brzozowski concerning the conclusions drawn in "Shape-selective diisopropylation of naphthalene in H-Mordenite: Myth or reality?" [J. Catal. 270 (2010) 60-66]

In our publication [1] we questioned the involvement of molecular shape selectivity in diisopropylation of naphthalene over acid mordenite catalysts invoked in literature to explain the selective formation of 2,6-diisopropylnaphtalene (2,6-DIPN). Our arguments were based on catalytic experiments, advanced chromatographic analysis of DIPN isomers and computation of thermodynamic equilibria and transition states. In a letter to the editor of this Journal [2], Brzozowski argued against our conclusions. In this note we present our main reasons why we do not find these arguments in favor of shape selectivity effects sufficiently convincing to revise the conclusions of our paper.

In Fig. 1 of his letter, Brzozowski plotted the product ratio of 2,6-DIPN/2,7-DIPN against the content of 2,6-DIPN and 2,7-DIPN isomers in reaction products obtained on three different mordenite catalysts, SBA-15 and silica–alumina reference. The figure was produced using data from his earlier publications and our data. The data in Brzozowski's figure can be summarized as follows. Over SBA-15 and silica–alumina, at 10% "2,6-DIPN and 2,7-DIPN in the products" the 2,6-DIPN/2,7-DIPN ratio is 2.3 and decreases rapidly. At ca. 20% "2,6-DIPN and 2,7-DIPN in the products", the reaction product ratio of 2,6-DIPN/2,7-DIPN is ca. 1.4. At this stage, mordenites and mesoporous catalysts behave similarly. At 25–60% "2,6-DIPN and 2,7-DIPN in the products" the ratio of 2,6-DIPN/2,7-DIPN on the mordenite catalysts is increased to ca. 1.8 at the maximum, compared to 1.2 on the references. At higher contents of "2,6-DIPN and 2,7-DIPN in the reaction products" all catalysts behave similarly again and the internal thermodynamic equilibrium between 2,6-DIPN and 2,7-DIPN isomers is obtained. The high 2,6-DIPN/2,7-DIPN ratio of ca. 1.8 at medium content of 2,6-DIPN and 2,7-DIPN in the products obtained on mordenites led Brzozowski to conclude that mordenites are shape selective. It is surprising that shape selectivity would only occur at medium conversion, but not at low.

Based on our own experience, we think that the difficulty of DIPN product analysis as well as the representation of the results can lead to ambiguity. In a previous publication [3] we compared analyses of DIPN mixtures using a single GC column as done by Brzozowski [2] and GC * GC analysis. The problem with single column GC analysis is the important overlap of chromatographic peaks which together with baseline uncertainty can introduce substantial error in the quantification of individual isomers in DIPN mixtures. A further problem is that the quality of the DIPN isomer analysis on a single GC column is dependent of the content of 2,6-DIPN and 2,7-DIPN in the DIPN isomer mixture being analyzed. The analytical problem is illustrated in Table 1. At 20.8% naphthalene conversion on mordenite catalyst the reaction products contain 17.2% IPN and 1.1% DIPN. At this very low yield of DIPN of 1.1%, the "amount of 2,6-DIPN and 2,7-DIPN in the products" is already 25.2% and within the range where Brzozowski claimed shape selectivity [2]. The absolute content of 2,6-DIPN and 2,7-DIPN in this reaction mixture is very low however, viz. 0.15% and 0.10%, respectively. The analytical error on such small quantities given the difficulties of this particular GC analysis on a single column will be of the order of 0.03% [3]. The use of a yield ratio of these two isomers (2,6-DIPN/2,7-DIPN) as proposed by Brzozowski will amplify the error and make the ratio unreliable. In the example of Table 1 the 2,6-DIPN/2,7-DIPN ratio is 1.5 ± 0.6. This example illustrates that a ratio of 2,6-DIPN/2,7-DIPN of 1.8 at low content of DIPN compared to 1.2 in a mixture with high DIPN content claimed by Brzozowski to be important might be within the analytical error margin. Arguments in favor of molecular shape selectivity based on a plot of "2,6-DIPN/2,7-DIPN" against "2,6-DIPN + 2,7-DIPN in reaction products" are little convincing.

**Table 1**
Example of reaction product analysis [1].

| Catalyst | H-Mor 5.9 | |
|---|---|---|
| Reaction $T$ (K), $t$ (h) | 373, 20 | |
| Compound | Y[a] (%) | ID[b] (%) |
| Naphthalene | 79.2 | |
| 1-IPN | 17.2 | 47.3 |
| 2-IPN | | 52.7 |
| 1,2-DIPN | 1.1 | 0.0 |
| 1,3-DIPN | | 13.6 |
| 1,4-DIPN | | 18.0 |
| 1,5-DIPN | | 8.8 |
| 1,6-DIPN | | 15.5 |
| 1,7-DIPN | | 16.8 |
| 1,8-DIPN | | 0.0 |
| 2,3-DIPN | | 2.1 |
| 2,6-DIPN | | 15.1 |
| 2,7-DIPN | | 10.1 |
| PIPNs | 0.4 | |
| 2,6 + 2,7-DIPN content in reaction products | | 25.2% |
| 2,6-DIPN/2,7-DIPN | | 1.5 |

[a] Yield.
[b] Internal distribution.

## References

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[3] C. Bouvier, N. Reumkens, W. Buijs, J. Chromatogr. A 1216 (2009) 6410.

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