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Letter to the Editor

Polemic against conclusions drawn in "Shape-selective diisopropylation of naphthalene in H-Mordenite: Myth or reality?" (J. Catal., 270 (2010) 60–66)

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ABSTRACT

In the article mentioned in the title, the authors challenged the hypothesis on shape-selective formation of 2,6-diisopropylnaphthalene (2,6-DIPN) in isopropylation of naphthalene over H-MOR catalysts. They claimed it was a myth, and there was no need to explain the high 2,6-DIPN selectivity with shape selectivity because it was in the range predicted by kinetics and thermodynamics. They also suggested that improper analysis of DIPN products could be a reason of the high 2,6-DIPN selectivity observed in the literature. However, in the current article I proved that some experimental results cannot be explained by kinetics, thermodynamics and analytical errors; therefore, shape-selective diisopropylation of naphthalene over H-mordenite is still the reality.

1. Introduction

In the article published lately in the Journal of Catalysis, Bouvier et al. [1] presented their results of alkylation of naphthalene with isopropanol and isomerization of 2,6-diisopropylnaphthalene (2,6-DIPN) over H-USY and H-MOR catalysts. Reaction products were analysed using an improved analysis method, namely a comprehensive two-dimensional gas chromatography (GC–GC) [2]. The authors estimated also isomeric composition of DIPN mixture at thermodynamic equilibrium using molecular modelling methods and compared with experimental results [1]. Considering their own results, theoretical calculations and possible imperfections of analytical procedures used in some experiments demonstrated in the literature they concluded that "*shape-selective formation of 2,6-DIPN in H-MOR is a myth*" and "*there is no reason to use the shape-selectivity argument because the amount of 2,6-DIPN is well below the thermodynamic one*".

The discussed reaction system is very complicated and sometimes difficult to predict, and there are examples in the literature where improper analysis of DIPN isomers was applied, so their criticism is understandable and is very important to achieve the truth on the shape selectivity manifested by increased 2,6-DIPN formation over H-MOR. However, their conclusions are very astonishing, and they did not prove that the shape selectivity is impossible but simply they were not able to observe it. There are literature examples with correct DIPN analysis demonstrating shape selectivity and 2,6-DIPN yield higher than that at thermodynamic equilibrium. Therefore, on the basis of experimental data available in the literature and even those described in Ref. [1], I will prove that shape-selective formation of 2,6-DIPN over H-MOR is the reality and in some cases remains the best hypothesis.

2. Errors in DIPN analysis

To analyse products of naphthalene diisopropylation, Bouvier et al. [1] applied their innovative GC–GC gas chromatography method described in Ref. [2]. Their method has many advantages and certainly should be taken under consideration when developing analysis of DIPN isomers.

In their previous article, Bouvier et al. [2] compared the GC–GC method with other DIPN analysis methods available in the literature. They claimed that results of GC analysis on a non-polar column might be erroneous. This finding confirmed our previous observations that some catalytic experiments described in the literature were doubtful [3,4]. They also tested our DIPN analysis method using a polar column [5] and, as they claimed, analyses performed on polar columns were "*the best examples described in the literature*", though, they suggested that significant errors in the one column GC analyses were possible due to a poor separation of DIPN peaks [2]. However, Franke et al. [6] achieved a very good resolution of DIPN isomers using the one column GC method with a very polar column, and they also proved a very good concert of quantitative results obtained on the polar (Innowax) and the very polar GC column (CP-Sil 88, cyanopropylpolysiloxane). So, the literature results obtained with GC polar columns are good enough to be useful in the discussion on the shape selectivity.

Bouvier et al. [1] focussed mainly on their own results and the discussion on the literature results considering shape selectivity in diisopropylation of naphthalene over H-MOR was limited to several not very demonstrative examples. Probably assuming incorrect GC analysis, Bouvier et al. [1] did not discuss but only mentioned the most representative works of Sugi, Kim, Katayama, Horsley, Kikuchi and Song [7–20], where shape-selective formation

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of 2,6-DIPN over H-MOR was demonstrated. Although these investigations were based on analyses performed over GC columns with a rather low polarity (e.g. DB-17, TC-17), it is hard to believe that all these results were erroneous. Examples of DIPN analysis shown in the supplementary data to Ref. [21] revealed quite reasonable resolution of all DIPN isomers obtained on a TC-17 column. In the case of alkylation products obtained on the non-shape-selective catalysts, a significant quantities of all seven main DIPN isomers were detected, whereas in the literature reports on the shape selectivity [10–12,15,22] DIPN products obtained over high silica H-MOR catalysts contained >60% 2,6-DIPN, >25% 2,7-DIPN, 8–10% 1,6-DIPN and <5% of other isomers. Thus, the 2,6-DIPN selectivity was higher than the thermodynamic one, and the shape selectivity is the most reasonable explanation of such results.

3. Some comments on experimental results described in Ref. [1]

The hypothesis on the lack of shape selectivity in naphthalene alkylation over H-MOR was supported also by Bouvier et al.'s [1] own experimental results. They carried out alkylation of naphthalene with isopropanol in a batch-type microreactor in cyclohexane solution. As they claimed, a shape-selective formation of 2,6-DIPN was observed neither over the H-USY catalyst nor over H-MOR samples. Alkylation products obtained over H-USY were indeed compatible with kinetic and thermodynamic predictions and did not reveal shape selectivity but those obtained over H-MOR are not unambiguous and some doubts concerning experimental procedure can be formulated.

Bouvier et al. [1] examined two samples of mordenite, namely H-MOR (5.9) and H-MOR(24), but they did not test highly dealuminated mordenites. In the literature, the highest 2,6-DIPN selectivity was observed in alkylation over dealuminated H-MOR catalysts with SiO_2/Al_2O_3 ratio in the range 70–220 [10–20]. Furthermore, they did not test propylene as an isopropylating agent but only isopropanol; so, water was formed during alkylation. It is a common knowledge that high silica zeolites appear more hydrophobic than those with higher alumina content. Therefore, in the case of the relatively low silica zeolites, isopropanol and water might have been sorbed inside the pores, blocking access of naphthalene and other hydrocarbons to the interior of crystallites. Thus, the external surface of crystals could play a very significant role. This means that their conclusions might concern exclusively their own particular results. However, a careful analysis of their experimental results obtained over H-MOR indicates surprisingly that they do support but do not negate the shape selectivity.

4.Non-shape-selective catalysis vs. results obtained over H-MOR

In their article, Bouvier et al. [1] focused on the yield of 2,6-DIPN. They stated that DIPN mixtures obtained over H-MOR catalysts had a distribution in between that of a kinetic and a thermodynamic controlled mixture; therefore, there was no reason to use the shape-selectivity argument to explain composition of naphthalene diisopropylation product.

There are two aspects of shape-selective isopropylation of naphthalene in H-MOR. First is a high yield of β,β-DIPN isomers (>85%) [10–12,15,22], which is comparable with that for the thermodynamic product (80–90%) [1,23,24]. The second aspect is a high 2,6-DIPN content both in relation to the mixture of all DIPN isomers and in relation to the other slim β,β-isomer, namely 2,7-DIPN. For the thermodynamic DIPN mixture, 40–42% 2,6-DIPN can be predicted at temperature in the range of 200–250 °C [1], whereas more than 60% was reported in the literature on the shape selectivity [10–12,15,22].

The 2,6-DIPN/2,7-DIPN ratio can indicate shape selectivity, but unfortunately this issue was not considered by Bouvier et al. [1]. For the thermodynamic product, a high content of β,β-DIPN isomers can be expected, but the 2,6-DIPN/2,7-DIPN ratio is lower or close to 1. On the other hand, in the kinetic product the 2,6-DIPN/2,7-DIPN ratio is much higher than 1, but it contains very small quantities of β,β-DIPN isomers.

In order to understand how the 2,6-DIPN/2,7-DIPN ratio changes in a non-shape-selective DIPN product in the range from the kinetic product to the thermodynamic one, a relationship of the 2,6-DIPN/2,7-DIPN ratio on the sum of 2,6-DIPN and 2,7-DIPN in products obtained in alkylation of naphthalene with propylene over amorphous and mesoporous SBA-1 alumina-silicates is depicted in Fig. 1. Data were implanted from Ref. [25–27]. The sum of 2,6-DIPN and 2,7-DIPN was used as an operand to show in which area of the kinetic–thermodynamic range was a product composition. The kinetic product is poor in β,β-isomers, whereas they are the main isomers in the thermodynamic product. Such a plot can be used for a wide range of alkylation parameters and is relatively insensitive to the reaction conditions such as temperature, contact time, reactants proportions and pressure.

For the kinetic product the 2,6-DIPN/2,7-DIPN ratio was even higher than 2 (see Fig. 1) and decreased below 1 when was approaching thermodynamic equilibrium. The relationship for the non-shape-selective catalysts can be approximated by the bold line shown in Fig. 1. A value found for the alkylate obtained over H-USY zeolite at 100 °C [1] (grey square) is also in a good agreement with this relationship. However, points depicted for mordenites both from our [25,26] and Bouvier's et al. [1] experimental results diverge significantly from the relationship predicted for the non-shape-selective catalysts and the 2,6-DIPN/2,7-DIPN ratio is much higher. The literature results obtained over highly dealuminated mordenites [10–12,15,22] (not shown in Fig. 1) would be even more distinct.

The simplest explanation of such a relationship is shape selectivity, but another two potential possibilities must also be considered. The first one is an overestimation of 2,6-DIPN isomer during GC analysis that would also be expected in experiments performed on catalysts other than H-MOR and it was previously excluded. The second one is an unusual ability of H-MOR to differentiate rates of isomerization and alkylation in comparison with other catalysts.

There are possible two mechanisms of DIPN isomerization, namely intramolecular and intermolecular. The intermolecular isomerization, i.e. dealkylation/re-alkylation or disproportionation/transalkylation, can change the DIPN distribution in a free way bringing it closer to that of thermodynamic equilibrium; therefore, any unusual isomerization increasing the 2,6-DIPN/2,7-DIPN ratio can be expected in the case of the intramolecular mechanism. If we assume that isomerization between 2,6-DIPN and 2,7-DIPN is not significant (it also leads to the conventional kinetic–thermodynamic product), then the intramolecular isomerization occurs inside 3 groups of isomers: the group of 2,6-DIPN (1,5-DIPN ↔ 1,6-DIPN ↔ 2,6-DIPN), the group of 2,7-DIPN (1,8-DIPN ↔ 1,7-DIPN ↔ 2,7-DIPN) and the group of 1,3-DIPN (1,4-DIPN ↔ 1,3-DIPN ↔ 2,3-DIPN and also 1,2-DIPN).

Fig. 2A and B compares distribution of the 2,6-DIPN group and the 2,7-DIPN group of isomers, respectively. Distribution of both groups increases when approaching thermodynamic equilibrium and for the group of 2,7-DIPN (Fig. 2B) is practically the same for non-shape-selective catalysts and for H-MOR. The correlation determined for the 2,6-DIPN group for the non-shape-selective catalysts (Fig. 2A) can be well approximated with a straight line but for H-MOR catalysts the content of the 2,6-DIPN group of isomers is significantly higher. This indicates a different relationship for H-MOR than for the non-shape-selective catalysts.

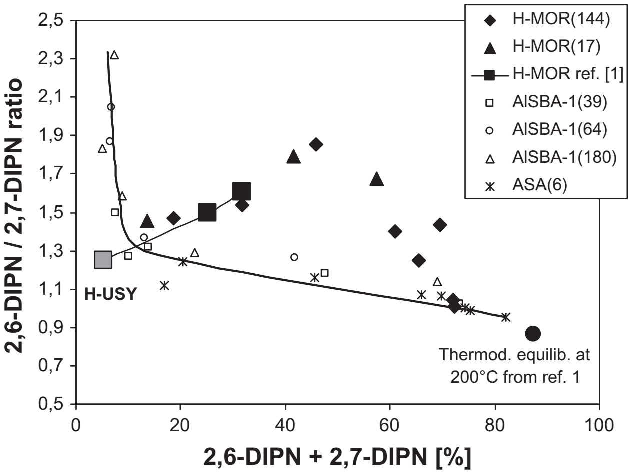

Fig. 1. 2,6-DIPN/2,7-DIPN ratio as a function of the sum of 2,6-DIPN and 2,7-DIPN in the products of alkylation obtained on non-shape-selective catalysts and H-MOR.

The increased 2,6-DIPN/2,7-DIPN ratio could also be observed if the intramolecular isomerization within the 2,6-DIPN group leading to 2,6-DIPN at the expense of 1,5-DIPN and 1,6-DIPN was accelerated over H-MOR in comparison with non-shape-selective catalysts or that leading to 2,7-DIPN within the 2,7-DIPN group was suppressed. To verify this hypothesis, a distribution of 2,6-DIPN and 2,7-DIPN isomers inside their relevant groups is depicted in Fig. 3A and B, respectively. In both isomer groups, the relationship is the same for non-shape-selective and H-MOR catalysts. So, isomerization rates inside both groups were similar for all catalysts and did not influence the 2,6-DIPN/2,7-DIPN ratio. Therefore, the shape selectivity is the most reasonable explanation of the increased 2,6-DIPN selectivity over H-MOR catalysts.

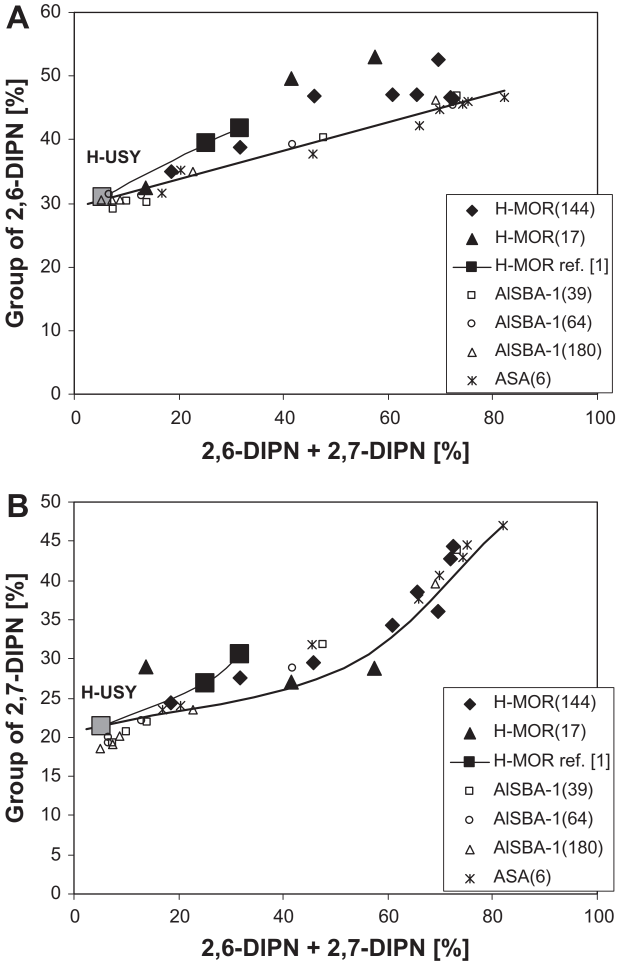

Fig. 2. Distribution of the 2,6-DIPN (A) and the 2,7-DIPN group of isomers (B) in the products of naphthalene alkylation over non-shape-selective catalysts and H-MOR as a function of the sum of 2,6-DIPN and 2,7-DIPN.

5. Reasons of shape selectivity over H-MOR

Two fundamental questions arise when considering the increased 2,6-DIPN/2,7-DIPN ratio in alkylation of naphthalene over H-MOR catalysts. Why is 2,6-DIPN preferred than 2,7-DIPN? And why is a DIPN product obtained over H-MOR rich in the bulky α,α- and α,β-isomers?

Although performed for static but not for dynamic conditions, a comparison of sizes of DIPN molecules with 12-R pore size of H-MOR shows clearly that pores of H-MOR are generally not accessible for α,α-, α,β-isomers as well as for 2,3-DIPN and only molecules of 2,6-DIPN and 2,7-DIPN can be formed and diffuse inside the H-MOR pores. However, the 2,6-DIPN selectivity higher than that of 2,7-DIPN is still discussed and several hypotheses were proposed. Horsley et al. [8] suggested a diffusion difference of 2,6-DIPN and 2,7-DIPN inside mordenite pores. Steric requirement at the transi-

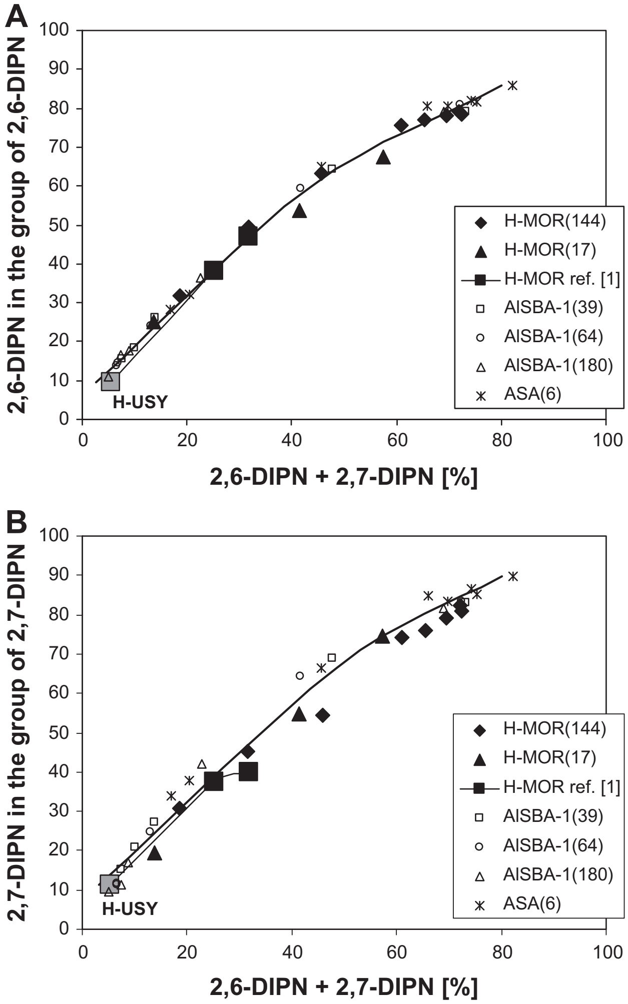

Fig. 3. Distribution of 2,6-DIPN in the group of 2,6-DIPN isomers (A) and 2,7-DIPN in the group of 2,7-DIPN isomers (B) obtained in alkylation over non-shape-selective catalysts and H-MOR as a function of the sum of 2,6-DIPN and 2,7-DIPN.

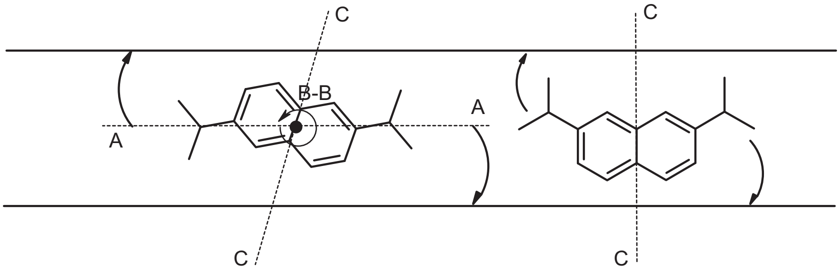

Fig. 4. Schematic representation of 2,6-DIPN and 2,7-DIPN molecules inside the H-MOR channel.

tion state composed of the substrate and acid sites inside the pores was also postulated to be the origin of shape selectivity [7,9,11]. Tasi et al. [24] suggested smaller dimensions of 2,6-DIPN conformers than those of 2,7-DIPN; however, this suggestion was not confirmed by Song et al. [16,20] and Bouvier et al. [1]. Song et al. [16,20] proposed that different frontier electron densities at positions 6 and 7 of the 2-IPN aromatic ring in the spatially restricted environment inside the H-MOR pores favoured formation of 2,6-DIPN. Such a difference in electron density of 2-IPN was not confirmed by calculations of Tasi et al. [24] and Bouvier et al. [1]. Therefore, the last two hypotheses can be rejected. The most probable hypotheses are spatial restrictions of the transition states and hindrances during diffusion of the reaction products. Fig. 4 shows schematically molecules of 2,6-DIPN and 2,7-DIPN inside the H-MOR channel. If we consider possibilities of tilt and rotation, the diffusion of the molecule along the H-MOR channel seems easier for 2,6-DIPN than for 2,7-DIPN. Easy rotation of the 2,6-DIPN molecule around the A–A axis is possible, whereas the 2,7-DIPN molecule does not reveal such possibility. Therefore, rotation inside the pore is less hindered for the 2,6-DIPN than for the 2,7-DIPN molecule and demands less energy. Similarly, swinging DIPN molecule inside the pores, as shown by arrows in Fig. 4, seems easier for 2,6-DIPN than for 2,7-DIPN (more evenly distributed mass around the B–B axis) and the 2,6-DIPN molecule can fit a free space inside the H-MOR pore easier than the 2,7-DIPN molecule. Fig. 4

Therefore, explanations of the increased 2,6-DIPN/2,7-DIPN ratio such as proposed by Horsley et al. [8] and by Katayama, Sugi, Kim and their co-workers [7,9,11] seem to be the most reasonable. A better fitting of the intermediate complex to the H-MOR pores was also proposed for disproportionation of 2-IPN to 2,6-DIPN and naphthalene [28].

A relatively high abundance of bulky α,α-DIPN and α,β-DIPN isomers in the products obtained over H-MOR and simultaneous observations suggesting shape selectivity can be explained with help of catalysis on the external surface of zeolite crystallites or on non-shape-selective admixtures usually present in zeolite samples. A total product obtained in alkylation of naphthalene over H-MOR can consist of various proportions of partial products both the shape-selective one formed inside the pores and a non-shape-selective DIPN product. Composition of the non-shape-selective DIPN product changes with reaction conditions and is closer to the kinetic one at mild conditions or to the thermodynamic one at sever conditions. To challenge the shape selectivity, Bouvier et al. [1] used an argument that the amount of 2,6-DIPN in their products was always below the thermodynamic one. If we assume that composition of the shape-selective product was constant and independent of reaction conditions, then the 2,6-DIPN content in the resultant product obtained at thermodynamic conditions should be higher than that predicted for the thermodynamic mixture. However, such a postulation is doubtful and a composition of the shape-selective product also approaches the thermodynamic one. Fig. 1 can confirm this hypothesis because the 2,6-DIPN/2,7-DIPN ratio observed for H-MOR decreases to ca. 1 when approaching thermodynamic conditions. Thus, besides a suitable catalyst, an adequate reaction conditions are necessary to achieve high 2,6-DIPN selectivity.

At mild conditions, diffusion of hydrocarbons from the pores becomes slower and the non-shape-selective product from the external surface appears more significant. Moreover, it is enriched in α,α- and α,β-isomers. Although the external surface of the zeolite crystal is relatively small in comparison with the internal surface, a path of the reaction products to the reaction bulk is very short. Therefore, at very mild conditions, both product composition and the 2,6-DIPN/2,7-DIPN ratio are similar to those of the kinetic product.

To sum up, the composition of the DIPN product obtained over H-MOR was at mild conditions similar to the kinetic one and at severe conditions to the thermodynamic one but at intermediate conditions diverged significantly from that predicted for the non-shape-selective products.

6. Conclusions

There are many attempts to explain the high 2,6-DIPN selectivity in isopropylation of naphthalene over H-MOR catalysts. DIPN products are sometimes very complex and difficult to interpret because they are frequently a resultant mixture of various partial products, the shape-selective one and non-shape-selective ones. A criticism of Bouvier et al. [1] is understandable and very important to find the truth on the shape-selective diisopropylation of naphthalene over H-MOR. They are right that usually the 2,6-DIPN yield is in the range predicted by the kinetics or thermodynamics, but a careful consideration of the 2,6-DIPN/2,7-DIPN ratio leads to the conclusion that the shape-selective reaction occurs inside the H-MOR pores.

Moreover, they are also right that some literature data (especially analytical procedures) need careful revising. However, there are literature examples with trustworthy analyses where the 2,6-DIPN selectivity higher than the thermodynamic one was achieved [10–12,15,22].

Experiments performed by Bouvier et al. [1] were doubtful and did not prove lack of shape selectivity. To test their hypothesis, they should repeat experiments with propylene as an alkylating agent and with high silica mordenites as catalysts. Therefore, considering available literature data, I must emphasise that the shape selectivity in diisopropylation of naphtahlene over H-MOR is the reality.

References

[1] C. Bouvier, W. Buijs, J. Gascon, F. Kapteijn, B.C. Gagea, P.A. Jacobs, J.A. Martens, J. Catal. 270 (2010) 60.
[2] C. Bouvier, N. Reumkens, W. Buijs, J. Chromatogr. A 1216 (2009) 6410.
[3] R. Brzozowski, Appl. Catal. A 272 (2004) 215.
[4] R. Brzozowski, A. Vinu, T. Mori, Catal. Commun. 8 (2007) 681.

[5] R. Brzozowski, W. Skupinski, M.H. Jamroz, M. Skarzynski, H. Otwinowska, J. Chromatogr. A 946 (2002) 221.
[6] S. Franke, J. Grunenberg, J. Schwarzbauer, Int. J. Environ. Anal. Chem. 87 (6) (2007) 437.
[7] A. Katayama, M. Toba, G. Takeuchi, F. Mizukami, S. Niwa, S. Mitamura, J. Chem. Soc. Chem. Commun. (1991) 39.
[8] J.A. Horsley, J.D. Fellmann, E.G. Derouane, C.M. Freeman, J. Catal. 147 (1994) 231.
[9] Y. Sugi, M. Toba, Catal. Today 19 (1994) 187.
[10] Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim, X. Tu, M. Matsumoto, Stud. Surf. Sci. Catal. 90 (1994) 397.
[11] J.-H. Kim, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, Micropor. Mater. 5 (1995) 113.
[12] J.-H. Kim, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, S. Nakata, A. Kato, Appl. Catal. A 131 (1995) 15.
[13] Y. Sugi, K. Nakajima, S. Tawada, J.-H. Kim, T. Hanaoka, T. Matsuzaki, Y. Kubota, K. Kunimori, Stud. Surf. Sci. Catal. 125 (1999) 359.
[14] Y. Sugi, J.-H. Kim, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, Stud. Surf. Sci. Catal. 84 (1994) 1837.
[15] E. Kikuchi, K. Sawada, M. Maeda, T. Matsuda, Stud. Surf. Sci. Catal. 90 (1994) 391.
[16] C. Song, C.R. Acad. SciSer. IIc 3 (2000) 477.
[17] C. Song, S. Kirby, Micropor. Mater. 2 (1994) 467.
[18] A.D. Schmitz, C. Song, Catal. Today 31 (1996) 19.
[19] A.D. Schmitz, C. Song, Catal. Lett. 40 (1996) 59.
[20] C. Song, X. Ma, A.D. Schmitz, H.H. Schobert, Appl. Catal. A 182 (1999) 175.
[21] T. Shibata, H. Kawagoe, H. Naiki, K. Komura, Y. Kubota, Y. Sugi, J. Mol. Catal. A 297 (2009) 80.
[22] Y. Sugi, H. Maekawa, Y. Hasegawa, H. Naiki, K. Komura, Y. Kubota, Catal. Today 132 (2008) 27.
[23] R. Brzozowski, J.C. Dobrowolski, M.H. Jamroz, W. Skupinski, J. Mol. Catal. A 170 (2001) 95.
[24] G. Tasi, F. Mizukami, I. Palinko, M. Toba, A. Kukovecz, J. Phys. Chem. A 105 (2001) 6513.
[25] R. Brzozowski, W. Tecza, Appl. Catal. A 166 (1998) 21.
[26] R. Brzozowski, W. Skupinski, J. Catal. 210 (2002) 313.
[27] R. Brzozowski, A. Vinu, B. Gil, Appl. Catal. A 377 (2010) 76.
[28] R. Brzozowski, W. Skupinski, J. Catal. 220 (2003) 13.

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