

# Role of various types of shape-selectivity in catalysis, exemplified by diisopropylnaphthalene isomers

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## Introduction

Reactions of diisopropylnaphthalene (DIPN) synthesis are excellent examples how we can control isomeric composition of the product by exploiting shape-selectivity phenomenon and selecting proper reaction conditions. Moreover, these reactions are excellent examples illustrating main types of shape selectivity, such as substrate selectivity, product selectivity or transition state selectivity and also they prove an important role of the external surface of crystals and pore entrances.

A mixture of DIPN isomers can be obtained e.g. by alkylation of naphthalene with propylene. Scheme of the reaction is shown in Figure 1. Initially naphthalene is alkylated to monoisopropylnaphthalene (IPN) and aromatic nucleus is preferentially alkylated in alpha-position to give 1-IPN. 2-IPN isomer is mainly formed by 1-IPN isomerization. It is caused by the fact that 1-IPN is kinetically preferred but 2-IPN is thermodynamically more stable. In the second step of the reaction IPN is alkylated to give DIPN isomers mixture.

There are possible 10 isomers of DIPN but 2,3-DIPN, 1,2-DIPN and 1,8-DIPN isomers are usually not detected in the products or are present in trace amounts due to steric hindrances caused by direct neighbourhood of bulky alkyl substituents.

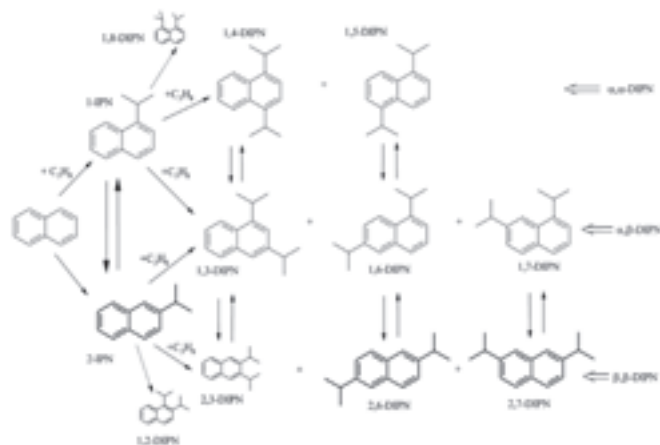


Fig. 1. Scheme of the reaction of naphthalene alkylation to IPN and DIPN isomers

Similar to IPN, DIPN isomers with substituents at alpha-positions are kinetically preferred but those with both substituents at beta-positions are thermodynamically favoured. So isomeric composition of DIPN mixture can be controlled by the selection of proper alkylation conditions. A kinetic product is formed at mild conditions and the DIPN mixture contains more than 50% of 1,4-DIPN and 1,5-DIPN (alpha,alpha-isomers). At more severe conditions (higher

temperature, longer reaction time, a catalyst more active for isomerization) DIPN product consists mainly of beta,beta-isomers. According to theoretical calculations and experimental data the thermodynamic product contains more than 40 % of 2,6-DIPN and more than 40% of 2,7-DIPN [1–3].

## Alkylation over mesoporous materials

A DIPN mixture is used as a high-quality solvent e.g. for carbonless copying papers, in agricultural chemistry, as a plasticizer [4–6]. A possibly lowest content of 2,6-DIPN isomer in such a product is advantageous due to its relatively high melting point.

Using of mesoporous materials with pore diameter above 2 nm as catalysts in alkylation of naphthalene is advantageous. Mesoporous catalysts such as MCM-41, MCM-48, SBA-15, and particularly SBA 1, with Al, Ga or other metals incorporated in the silica lattice favour obtaining DIPN product with very small content of 2,6-DIPN, even below 5% [7–10]. Such advantageous composition is a result of large available space inside catalyst pores and the presence of active sites on the catalyst surface with relatively weak acidity, that do not favour isomerisation but are strong enough to catalyse alkylation.

By the way, reports can be found in the literature where a very high 2,6-DIPN selectivity was described, e.g. even as high as 60% in the reaction carried out on MCM-41 and MCM-48 mesoporous catalysts but such observations resulted rather from improper DIPN isomer mixture analysis [11].

## Shape selectivity toward 2,6-DIPN and 2,7-DIPN

The other interesting direction of using DIPN is production of individual DIPN isomers, especially 2,6-DIPN. 2,6-Dialkylnaphthalenes can be oxidized to 2,6-naphthalenedicarboxylic acid or to 2,6-dihydroxynaphthalene or other products which can next be used for the production of high-quality polyester materials, e.g. polyethylene-2,6-naphthalate (PEN), polybutyl-2,6-naphthalate (PBN) or liquid-crystal polymers.

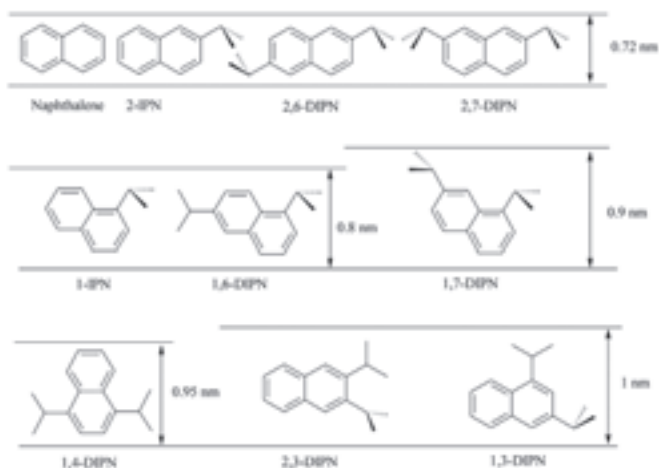


Fig. 2. Critical diameters of DIPN and IPN isomers

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Various positions of alkyl substituents in naphthalene nucleus lead to differences in size and shape of DIPN isomer molecules (Fig. 2), therefore shape selectivity effects can be expected in this case.

As can be deduced from Figure 2, using as catalysts wide pore zeolites, such as Y zeolite (FAU), with 0.74 nm diameter windows, leading to void  $\alpha$ -caves of 1.3 nm diameter, mordenite (MOR) with straight elliptical channels of 0.65–0.70 nm cross-section (channels 0.26–0.57 nm are not available to hydrocarbons) or beta zeolite (BEA) with sinusoidal channels of 0.66–0.67 nm cross-section and crosswise straight channels 0.56–0.56 nm [12], in reactions of DIPN synthesis should limit formation of DIPN isomers with critical diameter larger than 0.72 nm, i.e. the other than 2,6-DIPN and 2,7-DIPN. Formation and moving larger isomers inside pores of wide-pore zeolites is hindered or even impossible. Therefore, the main products of naphthalene alkylation on wide-pore zeolites are 2,6-DIPN and 2,7-DIPN, what was experimentally confirmed for many times. Moreover, DIPN products containing more than 70% of 2,6-DIPN and only ca. 25% 2,7-DIPN can be obtained by using high-silica mordenite as a catalyst [13–15].

Lately, a discussion appeared in the literature if such a high 2,6-DIPN selectivity in relation to 2,7-DIPN isomer is possible. On the one hand, articles were published where a very high 2,6-DIPN / 2,7-DIPN ratio was related for numerous catalysts of various types. However, in many cases the suggested high ratio resulted from incorrect GC analysis [11]. On the other hand, such a high 2,6-DIPN / 2,7-DIPN ratio was disbelieved, even in the case of mordenite catalysts, because critical sizes of both isomer molecules are very similar and both isomers are present in thermodynamic mixture in similar quantities [3]. However, at last these doubts were dispelled and in the case of mordenites the shape-selectivity effect and the very high 2,6-DIPN to 2,7-DIPN ratio was confirmed [16].

Beside mordenite, beta and Y zeolite, many other catalysts with various pore sizes and structures were tested in naphthalene alkylation. New zeolite structures with 12 MR and 14 MR pores were tested such as represented by *International Zeolite Association* [12] codes: MWW (ZSM-12), MSE (MCM-68), SSY (SSZ-60), CON (CIT-1) and AFI, ATS, IFR, CFI, DON, SFH, [17–21]. Among them only MWW and AFI zeolites revealed a relatively high 2,6-DIPN selectivity but the most selective catalyst was mordenite.

Investigations can also be found in the literature on developing shape selectivity by zeolite dealumination [22–24] or by modification (deactivation) of the external surface of zeolite crystallites by covering with e.g. ceria or other lanthanides [25].

Besides naphthalene alkylation with propylene, a very high beta, beta-selectivity (even above 80%) was observed in disproportionation of isopropylnaphthalene on wide-pore zeolites [26, 27]. In the reaction carried out in the presence of mordenite catalyst also very high ratio of 2,6-DIPN to 2,7-DIPN was observed, namely 54% vs. 26% [26, 27], whereas on HY and H-beta zeolites the ratio was opposite and the reaction product contained significantly more 2,7-DIPN than 2,6-DIPN, even 67% in comparison to 23%, respectively. These changes in relation between both isomers are very good example illustrating transition state shape-selectivity [27]. Bimolecular complexes of IPN leading to the formation of 2,6-DIPN are more straight in shape, but those leading to the 2,7-DIPN have bent shape. As a result of better fit of the transition state complexes shapes to the straight channels of mordenite, 2,6-DIPN was the main product of the reaction, whereas in the case of pores of Y and beta zeolites which force bending of the transition state complexes, 2,7-DIPN was the main isomer detected in the product.

### Other types of shape selectivity

Besides classic types of shape selectivity such as substrate shape selectivity, product shape selectivity and transition state

shape selectivity, other types of shape selectivity were observed in the case of DIPN and wide-pore zeolites, concerning shape of the external surface, such as *pore mouth shape-selectivity* known also as *pore entrances shape-selectivity*. Important role of so called “nests” present on the external surface of a zeolite crystallites was proposed for naphthalene alkylation with methanol in the 80s of the 20<sup>th</sup> century [28, 29]. The idea of pore mouth shape selectivity was proposed several years later by Martens and co-workers [30].

In naphthalene alkylation on wide pore zeolites at some particular reaction conditions it was possible to obtain DIPN product containing mainly bulky 1,4-DIPN and 1,3-DIPN isomers. In the reaction carried out in a flow reactor on CaREY zeolite (Y zeolite modified with Ca and a mixture of lanthanides) at temperature 200°C, a DIPN isomer mixture was obtained containing more than 56% 1,4-DIPN and 1,3-DIPN [31], namely isomers with critical dimension evidently larger than the diameter of zeolite windows. Assuming the reaction occurred on the external surface of zeolite crystals, such a large selectivity toward these isomers could be explained neither by kinetics nor by thermodynamics. Therefore, it was proposed that in this case the reaction run mainly in pore entrances and only the part of naphthalene ring being out of the pore was alkylated. So 1,4-DIPN and 1,3-DIPN were formed, namely isomers with both alkyl substituents linked to one and the same naphthalene ring.

Further examples that confirm important or even dominating role of pore entrances in the reaction of naphthalene alkylation with propylene can be found in the literature [32]. For instance in the reaction carried out on HY-7 zeolite (silica/alumina ratio 7) at 160°C a product containing 40% of 1,4-DIPN was obtained and summary amount of 1,4-DIPN and 1,3-DIPN was 55% [13, 33]. In the same reaction conducted at the same conditions on the wide-pore HL-6 zeolite (LTL) both isomers constituted 57% of DIPN isomers, including 40 % of 1,4-DIPN. A relatively high content of 1,4-DIPN and 1,3-DIPN (30%) was even observed in the case of mordenite with silica modulus 10 [34].

One more example of domination of reactions that occurred in pore entrances but not inside pores or on the non-selective external surface was observed for isomerization of DIPN [35]. Intramolecular isomerization of 2,6-DIPN to 1,6-DIPN was faster on beta and mordenite zeolites than that to 2,7-DIPN, although the latter isomer is slimmer and is thermodynamically more preferred. For 20% conversion of 2,6-DIPN selectivity of isomerization to 1,6-DIPN was twice of that to 2,7-DIPN, 62–63% vs. 26–30%, respectively. Under the same conditions but on other catalysts, i.e. Y zeolite and amorphous silica-alumina, selectivity toward both isomers was similar. This proves that in the presence of mordenite and beta zeolite isomerization of 2,6-DIPN took place mainly in pore entrances, and share of the reactions occurring inside pores and on the non-selective external surface was significantly smaller.

An additional prove of the important function of pore entrances in DIPN isomerization was a comparison of isomerization rates of 2,6-DIPN and 1,7-DIPN [35]. Isomerization of 2,6-DIPN on beta and Y zeolites was significantly slower than that of 1,7-DIPN, although, opposite to 2,6-DIPN, 1,7-DIPN was not able to react inside pores because of its molecule size. On the other hand, reaction velocities of both isomers were similar on amorphous silica-alumina, and even on mordenite 2,6-DIPN isomerized faster than 1,7-DIPN. The most convincing explanation of such observations was the assumption that 1,7-DIPN molecule better accommodated to pore entrances in Y and beta zeolites than 2,6-DIPN and the reaction occurred there very fast. A significant role of the shorter diffusion path of 1,7-DIPN molecules to pore entrances and products from pore entrances than that of 2,6-DIPN substrate to and 2,7-DIPN product from the pores interior can also be expected.

Further examples of the pore entrances importance in reactions of isopropylated naphthalene can be found in the literature [32]. In tests of 2,6-DIPN isomerization carried out on mordenite catalysts under propylene pressure bulky DIPN isomers were more abundant in the products than the expected 2,7-DIPN [25, 36]. For example, in the reaction carried out on mordenite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 14, at 200°C and at propylene / 2,6-DIPN ratio of 1/2 the product contained 1.1% of 2,7-DIPN and 4.6% of other DIPN isomers. Alkylation products obtained during the test also confirmed the more significant influence of pore entrances than that of the external surface (alkylation products could not be formed inside pores). Despite of 4-times stoichiometric excess of propylene the product contained 10 times more triisopropyl naphthalenes than tetraisopropyl naphthalenes. For such a high propylene excess more tetraisopropyl naphthalenes than triisopropyl naphthalenes can be expected. This can be only explained if we assume that alkylation of 2,6-DIPN molecule (or 2,7-DIPN formed from its) occurred in pore entrances and only the naphthalene ring being out of the zeolite pore was alkylated. This reaction was more important for the product composition than the alkylation of triisopropyl naphthalenes occurring only on the non-selective external surface of crystallites.

### Summary and conclusions

Proper choice of catalyst and reaction conditions enables to synthesize DIPN mixtures with significantly different isomeric composition. Naphthalene alkylation and IPN disproportionation carried out on high-silica mordenite catalysts lead to the 2,6-DIPN rich product. On the other hand, 2,7-DIPN is the most abundant product of IPN disproportionation on beta or Y zeolite.

In alkylation of naphthalene with propylene over wide-pore zeolites is also possible to obtain DIPN rich in 1,4-DIPN (>40%) and 1,3-DIPN isomer (summary 56%).

Alkylation of naphthalene with propylene over mesoporous materials can be used to prepare DIPN mixture with small 2,6-DIPN and 1,5-DIPN content that can be used as a high-quality solvent.

DIPN synthesis reactions or reactions involving DIPN molecules are excellent to illustrate not only basic types of shape selectivity such as substrate, product and transition state shape selectivity but also prove a very important role of pore entrances in catalysis.

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## Aktualności z firm

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### RYNEK

#### Po świetnym pierwszym kwartale, LANXESS podnosi prognozy na 2016 r.

Po dobrym pierwszym kwartale koncern LANXESS, producent specjalistycznych środków chemicznych, podniósł prognozę zysku za rok obrotowy 2016 r. Obecnie spółka spodziewa się, że EBITDA z wyłączeniem pozycji nadzwyczajnych wyniesie od 900 do 950 mln EUR. Poprzednie prognozy LANXESS zakładały zysk w granicach od 880 do 930 mln EUR. W pierwszym kwartale 2016 r. EBITDA z wyłączeniem pozycji nadzwyczajnych zwiększył się o ok. 14%, do 262 mln EUR, w porównaniu z 229 mln EUR w analogicznym okresie poprzedniego roku. Ten pozytywny trend należy przypisywać przede wszystkim zwiększeniu wolumenu sprzedaży, poprawie wykorzystania możliwości produkcyjnych, korzystnym wahaniom kursowym oraz nieobecności kosztów, które zostały poniesione w pierwszym kwartale 2015 r. w związku z uruchomieniem w Azji nowego zakładu produkcji kauczuku. Marża EBITDA z wyłączeniem pozycji nadzwyczajnych wzrosła o 13,6% w porównaniu do 11,2% rok wcześniej, utrzymując się na dobrym poziomie. Zysk netto istotnie się zwiększył, osiągając 53 mln EUR, w porównaniu do 22 mln EUR w pierwszym kwartale 2015 r. Zysk na akcję wyniósł 0,58 EUR, podczas gdy rok wcześniej wynosił 0,24 EUR. Wartość sprzedaży spadła zaledwie o niecałe 6%, z 2,04 mld EUR do 1,92 mld EUR. Było to częściowo spowodowane korektą cen sprzedaży uwzględniającą spadek cen surowców. W pierwszym kwartale 2016 r. zobowiązania finansowe netto utrzymały się na praktycznie niezmiennym poziomie 1216 mld EUR, w porównaniu do 1211 mld EUR na zakończenie 2015 r. (kk)

(Komunikat prasowy LANXESS, 16.05.2016)

#### Polska Grupa Górnicza: jest porozumienie inwestorów i banków

26 kwietnia br. zawarto porozumienie w sprawie rozpoczęcia działalności Polskiej Grupy Górniczej (PGG). Inwestorzy angażują się w PGG na warunkach rynkowych i będą konsekwentnie nadzorować realizację biznesplanu spółki. Przeprowadzone analizy wskazują, że inwestycja generuje dodatnie stopy zwrotu dla inwestorów. Stronami porozumienia są Grupa Energa, Grupa PGE, Grupa PGNiG, Węglkokoks, Towarzystwo Finansowe „Silesia” (TFS), Fundusz Inwestycji Polskich Przedsiębiorstw (FIPP) FIZAN, a także banki – obligatariusze Kompanii Węglowej – Alior Bank, BGK, BGŻ BNP Paribas, PKO BP, Bank Zachodni WBK oraz 13 organizacji związkowych Kompanii Węglowej.

Spółka PGG, która stanie się największym producentem węgla kamiennego w Polsce i w Europie, zostanie utworzona z 11 kopalń, 4 zakładów oraz części centrali wydzielonych z Kompanii Węglowej. Zaangażowanie w PGG daje udziałowcom z sektora energetyki dostęp do bogatych zasobów węgla energetycznego o parametrach dopasowanych do potrzeb istniejących i planowanych jednostek wytwórczych, co wpisuje się w cele strategiczne grup energetycznych. Ponadto współpraca sektora wytwarzania z sektorem wydobywczym gwarantuje odbiorcom usług energetycznych możliwość pozyskania stabilnych partnerów zapewniających nieprzerwane dostawy energii elektrycznej i ciepłej po przewidywalnej cenie. (kk)

(<http://www.gkpgge.pl/>, 26.04.2016)

#### Grupa PCC EXOL – I kwartał 2016 r. na dużym plusie

Grupa Kapitałowa PCC EXOL po raz kolejny wypracowała wyniki finansowe na bardzo dobrym poziomie. Zysk EBITDA wyniósł 11,8 mln PLN i wzrósł o 13,5%, a zysk netto odnotował ponad 65% wzrost w stosunku do I kwartału minionego roku, osiągając wartość 5,2 mln PLN. Marża na sprzedaży wyniosła 17,7% i wzrosła o 2,0 p.p. w porównaniu do ubiegłorocznego I kwartału. Przychody ze sprzedaży wyniosły 133 mln PLN, poprawiając zeszłoroczną wartość o 1,5 mln PLN, tj. o 1,1%. Osiągnięty poziom zysku netto wynikał przede wszystkim ze zwiększenia marży na sprzedaży oraz obniżenia o ponad 30% kosztów finansowych. Wynik finansowy przełożył się również na wzrost podstawowych wskaźników rentowności. (kk)

(<http://www.pcc-exol.eu/>, 13.05.2016)

#### PCC EXOL wśród spółek giełdowych wypłacających dywidendę

16 maja br. Walne Zgromadzenie, zgodnie z wcześniejszymi rekomendacjami Zarządu i Rady Nadzorczej Spółki, podjęło uchwałę o przeznaczeniu blisko połowy zysku netto za 2015 r. na dywidendę. Środki zostaną wypłacone akcjonariuszom proporcjonalnie do liczby posiadanych akcji, w wysokości 0,04 PLN na jedną akcję. W minionym roku Grupa PCC EXOL odnotowała najwyższe w swojej historii zyski. Skonsolidowany zysk EBITDA osiągnął poziom 40,3 mln PLN (wzrost o 42%), a skonsolidowany zysk netto wzrósł ponad trzykrotnie i wyniósł 14,7 mln PLN netto. Również I kwartał br. zamknęła mocno poprawionymi, w stosunku do ubiegłorocznych, wynikami, osiągając ponad 65% wzrost zysku netto (5,2 mln PLN), 13,5% wzrost zysku EBITDA (11,8 mln PLN) i poprawę marży o 2 p.p. do poziomu 17,7%. (kk)

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