Influences of solvents on the production of high purity 2,6-dimethylnaphthalene via catalytic isomerization and adsorptive separation

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Abstract

Influences of seven solvents – benzene, toluene, ethylbenzene (EB), *p*-diethylbenzene (*p*DEB), *o*-xylene, *m*-xylene, and *p*-xylene – on the production of high purity 2,6-dimethylnaphthalene (DMN) via catalytic isomerization and adsorptive separation of the 2,6-triad DMNs were investigated. The solvents act as a reaction media for the isomerization and a desorbent for the adsorption. From the catalytic testing in a batch reactor over a H-beta catalyst and the adsorption using a pulse test technique over Na-faujasite adsorbents, the results indicate that the solvent characteristics, e.g. dipole moment, relative π-electron basicity, play very important roles on both processes. And, the best catalytic isomerization and adsorption system can be demonstrated if an appropriate solvent is used. Among the employed solvents, appropriate solvents for either the isomerization or adsorption were identified in this study. However, only toluene shows a possibility for being used to produce high purity 2,6-DMN via the combination of the isomerization and adsorption technique.
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1. Introduction

2,6-Dimethylnaphthalene (DMN), a precursor to polyethylene naphthalate (PEN), is known as one of the major obstructions to produce PEN in a comparable price to those of other polyesters [1–7]. This is because of the large-scale production of 2,6-DMN needs a lot of energy and complicated systems to obtain acceptable throughput and purities. For example, most of many patented processes fail to produce 2,6-DMN with a high yield at low temperatures or without any side products formation [5–7]. Particularly when other DMN isomers are formed, the isolation of 2,6-DMN is very difficult. On one hand, the very close in boiling points of DMN isomers makes the use of conventional distillation methods not practical for an industrial requirement of 2,6-DMN purity [1,6,7]. On the other hand, the very high wettability of 2,6-DMN crystal and its

potential to form a eutectic mixture with other isomers lead to the difficulty in using crystallization to purify 2,6-DMN even it possesses a significant different freezing temperature from the others [6,7].

To alleviate such the problems, many attempts have been made to find the most selective and effective approach to produce 2,6-DMN with both lower energy utilization and side products formation. The largest commercialized process licensed by BP Amoco is one of the successful examples in the economic point of view. The process employs a complex liquid phase reaction-in-series with a use of toluene and butadiene as reactants. More importantly, the use of H-beta zeolite for the final 2,6-triad isomerization of the process, Eq. (1), is claimed to substantially suppress the DMN disproportionation and the isomerization across the triad, which is inevitably encountered when using other types of acidic or bi-functional catalysts [5–9]. As a result, such the separation difficulties can be significantly lowered since only the separation of 2,6-DMN from 1,5- and 1,6-isomers is required. Nevertheless, a rather low 2,6-DMN throughput as well as a high utility consumption are still the

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current major drawbacks of the process [1]:

(1)
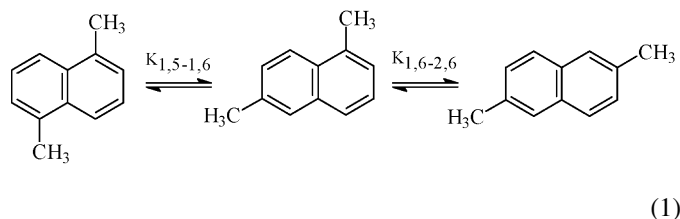
For the 2,6-triad isomerization, its high endothermicity and thermodynamic control result in a limit to which only 48 wt.% of 2,6-DMN can be produced at high equilibrium temperature [1–3]. This limitation is recently suggested by Kraikul et al. [4] to be better confronted by conducting such the isomerization in toluene media. They discover that the use of toluene would provide advantages on the improvement of the system mass transfer and modification of the isomerization thermodynamics besides facilitation the reaction for continuous operation in the liquid phase. Consequently, the maximum yield of 2,6-DMN at the high temperature can be accomplished at significant lower temperatures and also without any side reaction.

In addition, Kraikul et al. [4] also reported the success of using an adsorption technique to purify 2,6-DMN from its isomeric mixture instead of using the energy intensive freeze crystallization as employed in the commercial process. With the use of toluene and some appropriate ion-exchanged faujasite zeolites (e.g. KX, CaX, LiY, NaY, KY, RbY, SrY, and BaY) as a desorbent and adsorbent, respectively, high purity 2,6-DMN fractions can be effectively recovered with purity close to 100 wt.% [10]. Based on their discovery, they proposed a new approach to produce high purity 2,6-DMN by integrating the catalytic isomerization to the adsorptive purification with the use of toluene as a media [11]. Therefore, high purity 2,6-DMN could be produced with a lower cost.

It seems that the use of solvent plays very important roles in the high purity 2,6-DMN production. And, the 2,6-DMN isomerization and separation could be significantly improved if an appropriate solvent is employed. Until now, no attention has been paid for this issue. Thus, in this work, seven solvents – benzene, toluene, ethylbenzene (EB), *p*-diethylbenzene (*p*DEB), *o*-xylene, *m*-xylene, and *p*-xylene – were studied for their influences on the catalytic isomerization of 1,5-DMN to 2,6-DMN over H-beta catalyst. The adsorption over selected faujasite adsorbents (NaX and NaY) were investigated and discussed.

2. Experimental

2.1. Catalytic isomerization experiments

Catalytic isomerization of 1,5-DMN along the 2,6-triad was batch-wisely conducted using an autoclave reactor. The reactant was prepared by dissolving 10 wt.% of a solid feedstock, 1,5-DMN (96% purity, Aldrich), into one of the employed solvents, which were benzene (99% purity, Fisher Scientific), toluene (99.9%, Fisher Scientific), ethylbenzene (EB) (99.8% purity, Aldrich), *p*-diethylbenzene (*p*DEB) (98% purity, Acros), *o*-xylene (99% purity, Sigma–Aldrich), *m*-xylene (99% purity,

Table 1
Solvents with their dipole moments, molecular sizes and relative basicity to benzene

Solvent	Dipole moment (D)[a]	Kinetic diameter $(A°)$	Relative basicity to benzene[g,h]
Benzene	0	5.85[b]	1.0
Toluene	0.36	5.85[c]	1.5
Ethylbenzene	0.59	6[d]	1.5
p-Diethylbenzene	0	7[e]	1.55
o-Xylene	0.62	6.8[f]	1.8
m-Xylene	0.33	6.8[f]	2.0
p-Xylene	0	5.85[b]	1.6

(a) from [12] values for 1,5-, 1,6- and 2,6-DMN are 0.07, 0.32 and 0.14 D, respectively. (b–f) from [13–17]. Values for 1,5-, 1,6- and 2,6-DMN are 7.7°, 7.7° and 7.2 A°, respectively. (g and h) from [18,19].

Sigma–Aldrich) and *p*-xylene (99% purity, Aldrich). Table 1 lists the employed solvents with their dipole moments, molecular sizes and relative basicity to benzene. All solvents were treated using silica gel prior to experiments, except benzene that was used as received. Then, a 20–40 mesh H-beta zeolite (24 SiO_2/Al_2O_3, 25% alumina binder, UOP LLC) was poured into the autoclave with a fixed amount of 5 wt.% with respect to the feed amount. After that, the autoclave was heated to desired temperatures and held for 2 h with periodical shaking. The products after the isomerization were quantitatively and qualitatively analyzed by a gas chromatograph (GC) equipped with an FID detector and the ULBON® PLC capillary column (Shinwa Chemical Industries Ltd., Japan) that can separate all isomers of DMN from each other.

2.2. Dynamic adsorption experiments

The pulse test technique was employed to study the influences of using such the solvents as desorbents to purify 2,6-DMN by means of adsorption. Firstly, the equilibrium mixture of 2,6-triad DMNs consisting of 8 wt.% 1,5-DMN, 43 wt.% 1,6-DMN and 49 wt.% 2,6-DMN was synthesized following the condition presented elsewhere [4]. Then, 10 wt.% of the DMNs equilibrium mixture was prepared using a desired desorbent and used as a feed. Five weight percent of *n*-nonane (99% purity, Aldrich) was also added into the feed as a tracer. Na-faujusite (FAU) zeolites obtained from UOP LLC (USA) were dried at 350 °C for 1 h before using as adsorbents.

Experimental pulse testing was conducted by packing the adsorbent into a 70 mL stainless steel adsorber before subsequently filling with a selected desorbent of a 1.2 mL/min fixed flow rate, equivalent to 1 h^{-1} LHSV. After the system reached a desired temperature and pressure of 180 °C and 500 psi, respectively, 5 mL of a feed mixture was pulsed into the adsorber. The effluent was collected using a fraction collector for quantitative analysis using a GC equipped with an FID detector and the ULBON® PLC capillary column. The elution profile was then plotted between the composition and the retention volume of the effluent. By comparing the retention volume of the tracer to those of the DMNs, the net retention volumes (NRVs) were obtained. Relative adsorption selectivity of the species was then calculated using the ratio between the NRVs of the two interesting species.

3. Results and discussion

3.1. Influences of solvents on the 2,6-triad catalytic isomerization

The catalytic isomerization of dimethylnaphthalene (DMN) along the 2,6-triad was batch-wisely conducted in an autoclave reactor using 10 wt.% of 1,5-DMN and H-beta zeolite as a feed and catalyst, respectively. Fig. 1(a) shows the percent of 1,5-DMN conversion from different solvents at 220 °C with the solvent basicity and dipole moment. By considering the conversion of 1,5-DMN, it was found that the use of benzene, toluene and m-xylene as the solvent media can better expedite the isomerization than the others. Similar to the discussion by Kraikul et al. [4] for the 2,6-triad isomerization, the results in this study also stress the importance of the solvation effect on the production of 2,6-DMN, particularly for the toluene and m-xylene system that the solvents possess very close dipole moments to that of the intermediate species (1,6-DMN). Consequently, toluene and m-xylene would modify the thermodynamic of the isomerization more than the other solvents. On the other hand, it seems that either the very close dipole moments of pDEB and p-xylene to that of the feed (1,5-DMN) or the significantly different dipole moments of EB and o-xylene to those of the 2,6-triad DMNs lead to an inappropriate solvation and lower a potential of the solvents to facilitate the isomerization under the testing condition. Nevertheless, the 1,5-DMN conversion of the benzene system is the highest even the solvent possesses a dipole moment close to that of 1,5-DMN. This indicates that there should be other properties of the solvents influencing the isomerization besides their dipole moments.

By considering the relative π-electron basicity of the solvents, Fig. 1(a), it is believed that the lowest π-electron basicity of benzene would be one of the possible factors influencing the isomerization. For instance, the molecule of benzene that has the lowest π-electron basicity would interact with the zeolite surface the least. Thus, the adsorption of the DMN molecules on the acid sites would be barely competed by the solvent, leading to the highest 1,5-DMN conversion.

Fig. 1(b) shows the amount of side products generated from the different solvent systems and with or without 1,5-DMN. It is noted that the term "side products" is referred to the species created from disproportionation of the solvent molecules, e.g. benzene and pDEB from EB disproportionation, toluene, and timethylbenzene (TMB) from xylene disproportionation as suggested by GC. From the pure solvent results, the solvents themselves can also occupy the acid sites of the catalyst in competing with the DMN species. The results indicate that only benzene and toluene act as inert solvents over the H-beta zeolite under the testing condition. This would explain why benzene can facilitate the isomerization the best since its basicity is the lowest; so, the competitive adsorption would be lower than the others. Based on the results, it implies that the solvent basicity is another important property that influences the isomerization. In conclusion, we believe that the dipole moment would influence on the isomerization thermodynamics while the basicity would play a role on the turnover frequency (TOF) of the DMNs on the catalyst surface.

A comparison between the amount of side products formation with and without 1,5-DMN is also illustrated in Fig. 1. Obviously, the side products are formed in a higher extent with 1,5-DMN dissolved in the solvent systems. This implies that the solvents can also better react with the presence of 1,5-DMN,
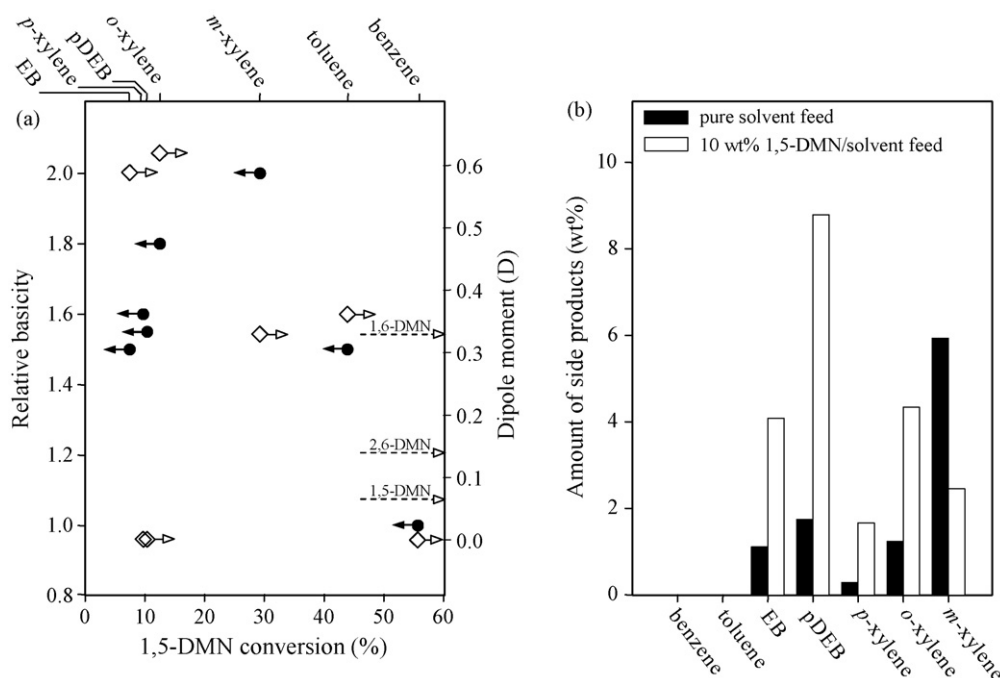

Fig. 1. Results from catalytic isomerization of 1,5-dimethylnaphthalene (1,5-DMN) over the H-beta zeolite at 220 °C (a) %conversion with the solvent basicity and dipole moment and (b) amount of side products formation from different solvent systems.

probably due to the modification of the system thermodynamics, or even react with the DMN species over the catalyst. Interestingly, despite of the highest basicity of *m*-xylene, the amount of the side products of the *m*-xylene system is significantly lower if 1,5-DMN is present. Therefore, this suggests that the appropriate solvation between the solvent and the DMNs would lower the possibility of the solvent to react on the catalyst.

All in all, the results show that both the dipole moment and basicity of a solvent play roles on the catalytic isomerization of 2,6-DMN. An appropriate solvent should have a very close dipole moment to that of the DMN intermediate, 1,6-DMN. Ability to suppress any side products formation during the isomerization is another important characteristic of the solvent needed to be considered. The solvent should not be used even it can better facilitate the isomerization than the others if it also creates some undesired products. Thus, only benzene and toluene that possesses a relative low basicity are suitable for such the interested application among the employed solvents.

3.2. Influences of solvents on the dynamic adsorption of 2,6-triad DMNs

The adsorption of the synthesized 2,6-triad DMN isomers was carried out over the commercial NaX ($SiO_2/Al_2O_3 = 2.5$) and NaY ($SiO_2/Al_2O_3 = 5.0$). The seven solvents were now used as desorbents for the separation. To make the profile of 1,5-DMN become clearer, pure crystals of the isomer was added into the DMN mixture to increase its concentration to 5 wt.% in the systems with EB, *p*DEB, toluene, *o*-xylene as desorbents and NaX

as an adsorbent. The elution profiles of 1,5-, 1,6- and 2,6-DMN are illustrated in Fig. 2. For most systems, the NRV magnitude follows the order of 1,5-DMN > 1,6-DMN > 2,6-DMN; thus, the separation of 2,6-DMN can be accomplished only in a rejective system as discussed by Kraikul et al. [9]. Though a separate peak of 2,6-DMN from *p*DEB and *p*-xylene desorbents over NaX and EB, toluene and *p*DEB desorbents over NaY suggests a possibility of 2,6-DMN purification from its equilibrium mixture.

From Fig. 2, it was also observed that the adsorption of the DMNs for all solvent systems over NaX possesses more affinity than those of NaY. This reveals that the adsorbability of the DMNs somewhat evidently depends on the SiO_2/Al_2O_3 ratio of the adsorbent. One possible reason lines on the difference in the available adsorption sites corresponding to the difference in the SiO_2/Al_2O_3 ratio. As discussed by Kraikul et al. [10], preferential interaction between the DMNs and Na$^+$ cation seems to dominantly control the adsorption behavior for Na-FAU adsorbents. Thus, NaX that possesses more Na sites would provide more adsorption affinity than NaY, resulting in the higher NRVs for all DMN species and also all solvent systems. It should be noted that there is no profile of 1,5-DMN eluted from the NaX adsorber within the observed NRV range if benzene and *p*DEB are used as desorbents.

Different adsorption–desorption behaviors were also observed when using different types of desorbent. This suggests that a desorbent plays important roles on the adsorptive separation of these three DMN isomers. Also, this reveals the importance of the balance between the adsorptivity of
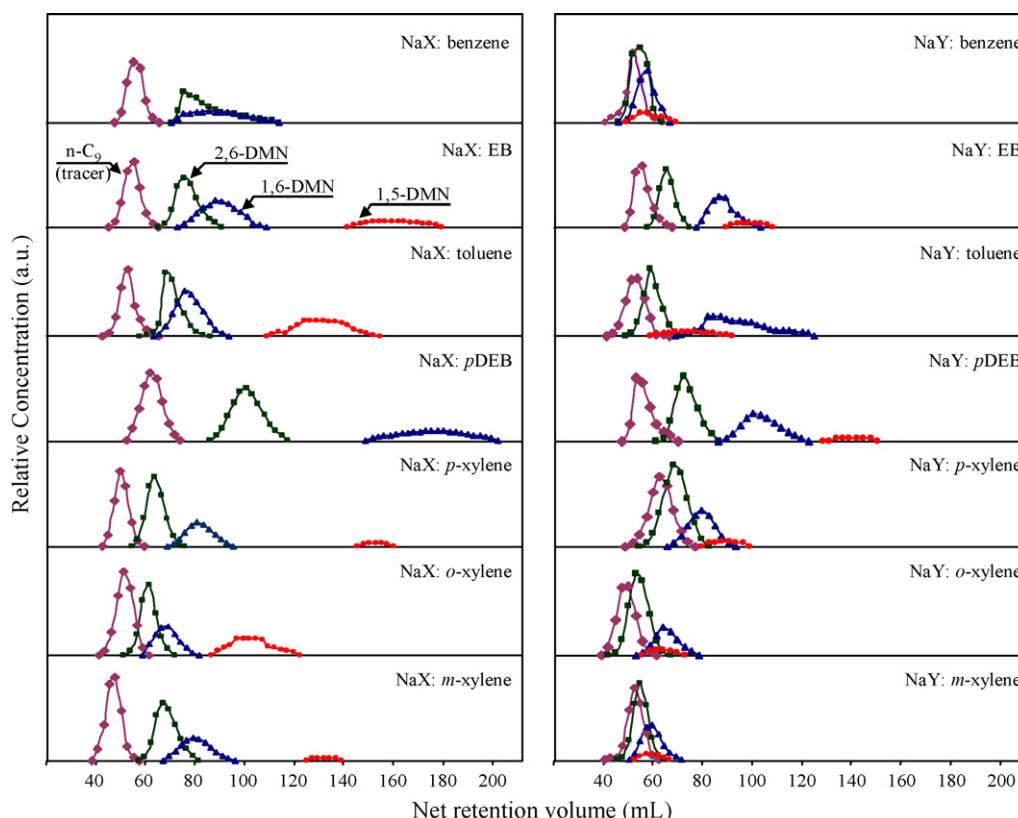

Fig. 2. Elution profiles of 1,5-, 1,6- and 2,6-DMN on the NaX and NaY zeolites at $1\,h^{-1}$ LHSV, 180 °C from different desorbent systems.
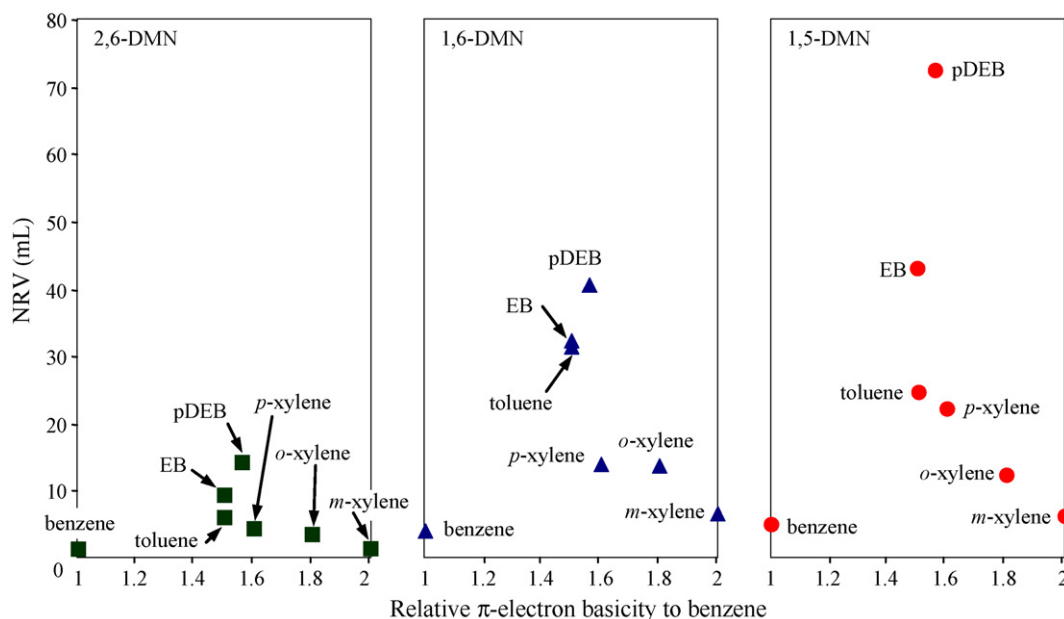
Fig. 3. Correlation plot between relative π-electron basicity to benzene and the NRVs of DMNs on the NaY zeolite at 1 h^{-1} LHSV, 180 °C from different desorbent systems.

adsorbates (DMNs) and desorbent as discussed by Morbidelli et al. [20] and Kulprathipanja [21]. To preliminarily illustrate roles of the desorbents on the adsorbability of each DMN on Na-FAU adsorbents, their NRVs are plotted as a function of relative π-electron basicity as exhibited in Fig. 3 for the case of NaY. The result shows that the basicity of the desorbents affects the DMNs' adsorbability in a different degree. Generally, the desorbent with a high basicity would strongly bind on acidic sites of the adsorbent, resulting in lower available sites for DMN species to competitively adsorb with. For example, it seems that the interaction of m-xylene over the zeolite surface is too strong; thus, no separation of the DMNs can be observed. The same is also the case for p- and o-xylene, i.e. the decrease in their relative basicity shows the reduction of the adsorption affinity of the desorbents over NaY, substantiating our hypothesis as beforehand discussed. The further decrease of the desorbent basicity to EB and toluene creates a weaker desorption of the DMNs on NaY adsorbent as expected.

However, other parameters are needed to be considered for the adsorption–desorption behavior besides the acid–base interaction in the pDEB and benzene systems. A very high adsorption affinity of the DMNs over NaY was observed from the high NRVs for the case of using pDEB as a desorbent. The desorption of DMNs is somewhat difficult and then needs a higher desorbent volume for the desorption. We believe that the desorbent molecular structure would be one of the possible reasons for the desorption behavior. The bulky structure of pDEB with its diethyl-substituted groups would create a steric hindrance and deter its interaction not only with the zeolite but also with the adsorbed DMN species. The result from the benzene system is clearly one of the important examples to our mentioned hypothesis as it is widely known that at a high loading, benzene preferentially adsorbs on the 12R oxygen framework of the FAU structure [18]. Thus, the accessibility to the cation sites of the

DMNs as well as its adsorption onto the sites would be diminished, resulting in the very low NRVs or even no separation of the DMNs.

In addition, the desorbent dipole moment is also believed to affect the adsorption behavior of DMNs over Na-FAU adsorbents. For instance, toluene that possesses the very close dipole moment to those of the DMNs than EB would create thermodynamically favorable interaction to the adsorbed species, leading to a lower NRV required for the desorption process even toluene and EB posses the same relative basicity. In other words, a suitable desorbent–DMNs interaction would be able to facilitate the DMNs elution. It should be noted that the results from the NaX systems are somewhat similar to those of NaY but the correlation is not plotted in this article due to a problem that 1,5-DMN is not desorbed from the benzene and pDEB systems.

From the above discussion, it is clearly evident that there are many parameters governing the adsorption of DMNs on the faujusite zeolites. Apparently, the Na-cation of FAU offers the preferential adsorption sites for DMNs. Besides, the desorbent–DMNs interaction and the desorbent characteristics have also revealed their importance in some adsorptive separation systems, i.e. toluene and pDEB desorbents. All of these parameters need to be balanced in order to achieve a good system for 2,6-DMN purification.

The separation efficiency of 2,6-DMN is considered from the selectivity parameters. The plot between the selectivity of 1,5- and 1,6-DMN with respect to 2,6-DMN and the relative π-electron basicity is illustrated in Fig. 4. As expected, the difficulty in accessing the Na sites of DMNs in the benzene system results in the lowest selectivity. As o- and m-xylene desorbents, their strong interaction corresponding to their high basicity creates poor separation efficiency. On the contrary, dissimilarity between the selectivity of 1,5- and 1,6-DMN with respect to 2,6-DMN was observed for the other desorbents. This
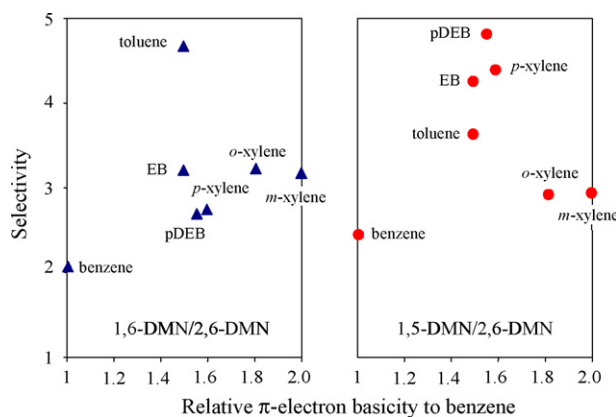
Fig. 4. Correlation plot between relative π-electron basicity to benzene and the adsorption selectivity over the NaY zeolite at $1\,h^{-1}$ LHSV, $180\,°C$ from different desorbent systems.

substantiates that not only the desorbent basicity governs the separation efficiency of 2,6-DMN, but the other characteristics of the desorbents (e.g. dipole moment and molecular size) and the basicity of the DMNs themselves also do as previously discussed. Again, the best system could be demonstrated if those parameters are balanced.

In conclusion, the results in this study suggest that the performance of the process to produce high purity 2,6-DMN via catalytic isomerization and adsorptive separation strongly lines on a type of the solvent to be used. For the reaction point of view, the solvent should be inert under the desired operating conditions; thus, only benzene and toluene can be used. However, benzene is not suitable for an adsorption unit. Thus, only toluene is an appropriate one among the employed solvents for the production of high purity 2,6-DMN by the reaction-adsorption process as discussed by Kraikul et al. [4,10,11]. Nevertheless, the other adsorbent–desorbent systems, as previously discussed, can also be used if only the catalytic isomerization or adsorptive purification is of interest individually.

4. Conclusions

The influences of seven solvents – benzene, toluene, ethylbenzene (EB), *p*-diethylbenzene (*p*DEB), *o*-xylene, *m*-xylene and *p*-xylene – on the production of high purity 2,6-dimethylnaphthalene (DMN) via catalytic isomerization and adsorptive separation of the 2,6-triad DMNs are revealed in this contribution. The results show that the solvents play very important roles on both catalytic isomerization over H-beta catalyst and adsorptive separation over Na-FAU adsorbents. Under the studied condition, high purity 2,6-DMN can only be produced in a combination of the isomerization and adsorption if toluene is employed.

Acknowledgements

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