CHAPTER VI

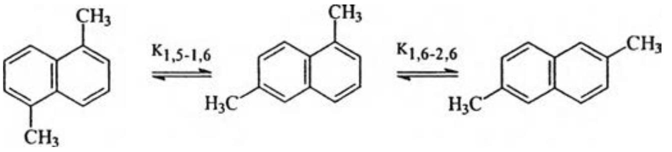
STUDY ON THE ADSORPTION OF 1,5-, 1,6- AND 2,6-DIMETHYLNAPHTHALENE ON A SERIES OF ALKALINE AND ALKALINE EARTH ION-EXCHANGED FAUJASITE ZEOLITES*

6.1 Abstract

Adsorption of the equilibrium mixture of 1,5-, 1,6- and 2,6-dimethylnaphthalene (DMN) was investigated over a series of alkaline and alkaline earth ion-exchanged faujasite zeolites using pulse test and breakthrough technique. It was found that the adsorption of the DMNs would proceed through a complex mechanism governing by at least molecular diffusion, acid-base interaction, preferential interaction with cation and molecular displacement. All ion-exchanged faujasite zeolites only provided rejective systems for 2,6-DMN and some of them were potential adsorbents for the 2,6-DMN purification.

6.2 Introduction

Large scale production of 2,6-Dimethylnaphthalene (2,6-DMN), a starting material for high performance engineering plastic and liquid crystal polymer, e.g. polyethylene naphthalene (PEN), currently encounters two major drawbacks that subsequently limit widespread utilization of the polymer. For instance, the largest commercialized process licensed by BP Amoco faces problems from the complexity of the synthesis and the thermodynamic limitation of the isomerization from 1,5-DMN to 2,6-DMN (Chem Systems, 2000) as shown in equation (1), which is called the 2,6-triad.



(1)

---

* Published in Adsorption (2006), 12, 317-327.

Besides the limitation of 2,6-DMN yield, thermodynamics also controls the composition of the isomerized product in a solvent-free system at 10%, 42%, and 48%wt of 1,5-, 1,6- and 2,6-DMN, respectively (Chem Systems, 2000; Kraikul *et al.*, 2005), which entails another separation problem.

Because DMN isomers have very close physical properties and molecular size, typical separation techniques cannot recover 2,6-DMN from the equilibrium mixture with high purity as industrial requirements (Chem Systems, 2000). In the process of BP Amoco, freeze crystallization was employed as a means for the 2,6-DMN purification (Smith *et al.*, 1999). However, energy intensive of the process entails the high production cost (Chem Systems, 2000) and draws many attentions to an adsorptive separation approach.

Selective adsorption of 2,6-DMN has been conducted over a wide range of adsorbent. L-zeolite (Verduijn *et al.*, 1992), activated carbon (Barger *et al.*, 1991) and ion-exchanged faujasite zeolites (Barger *et al.*, 1991; Inui and Pu, 1995; Maki *et al.*, 1988; Nakao *et al.*, 2004; Rota *et al.*, 1996) have been utilized as adsorbents in literatures. Most processes encounter the problem of 2,6-DMN purity; thus, a crystallization process is usually combined downstream to increase the product purity (Chem Systems, 2000; Maki *et al.*, 1988). For ion-exchanged faujasite zeolites, some adsorptive systems for 2,6-DMN have been reported using paraffins as a solvent. For example, Inui and Pu (1995) investigated the adsorption of 2,6-DMN and its isomers on NaY and LiY zeolites using cyclohexane as a solvent and reported that the difference in kinetic diameters between 2,6-DMN and other isomers creates the selective adsorption of 2,6-DMN. However, the study only investigated the binary DMN isomers system and the selectivity of 2,6-DMN respected to the other isomers in the 2,6-triad are still not effective for the separation purpose. Rota *et al.* (1996) also claimed the potential adsorptive system for 2,6-DMN using KX zeolite. However, the adsorption from the binary system was accomplished in n-octane with the total concentration of DMN at 8 wt%, which is not adequate for commercial applications.

Performing the adsorption in aromatic solvents seems to pronounce applicability due to a high solubility of the DMNs. However, only rejective systems can be demonstrated for 2,6-DMN (Barger *et al.*, 1991; Maki *et al.*, 1988; Nakao *et* *al.*, 2004) and the lower purity than the adsorptive system has been observed. For example, the 2,6-DMN rejective process patented by Barger *et al.* (1991) can produce only 69% of 2,6-DMN using KX zeolite as an adsorbent. Consequently, the raffinate needs to be processed through the 2nd adsorptive stage using activated carbon to enhance the 2,6-DMN purity up to 95.8%.

Until now, no study has emphasized the adsorption of DMN on a complete series of alkaline and alkaline earth ion-exchanged faujasite zeolites, particularly for the equilibrium mixture of 1,5-, 1,6- and 2,6-DMN that is the product from the 2,6-DMN commercial production process. In this contribution, the adsorption of the equilibrium mixture on those zeolites was reported.

6.3 Experimental

The equilibrium mixture of DMNs was synthesized from catalytic isomerization of 1,5-DMN (96%, Aldrich, USA) in toluene (99.9%, Fisher Scientific, USA) over H-beta catalyst (24 SiO_2/Al_2O_3, 25% alumina binder, UOP LLC, USA) following our previous condition presented elsewhere (Kraikul *et al.*, In press). The total concentration of DMN was fixed at 10 wt%, which composes 8%, 43% and 49% of 1,5-, 1,6- and 2,6-DMN, respectively. It is remarked that the above equilibrium composition is slightly different from that of the solvent-free system as discussed in our regarding article (Kraikul *et al.*, In press). For all experiments, n-heptane (99%, Aldrich, USA) was added into the equilibrium solution as a tracer. The alkaline and alkaline earth ion-exchanged faujasite zeolites used as adsorbents were obtained from UOP LLC (USA) as listed with their chemical compositions in Table 6.1.

Experimental pulse test was conducted using the experimental apparatus as shown in Fig. 6.1. The adsorbent was packed into a 70 mL stainless steel adsorber before subsequently filled with toluene, which was a desorbent in this study. The flow rate of the desorbent was fixed at 1.2 mL/min, equivalent to 1 h^{-1} LHSV. After the system reached the desired temperature and a pressure of 500 psi, 5 mL of a feed mixture was then injected to the adsorber and the effluent was collected using a fraction collector for quantitative analysis by means of a gas chromatograph (GC) equipped with a Stabiwax-DB® capillary column and a FID detector. Relative adsorption selectivity of the species was then calculated using the ratio between the net retention volume (NRV) of the two interested species.

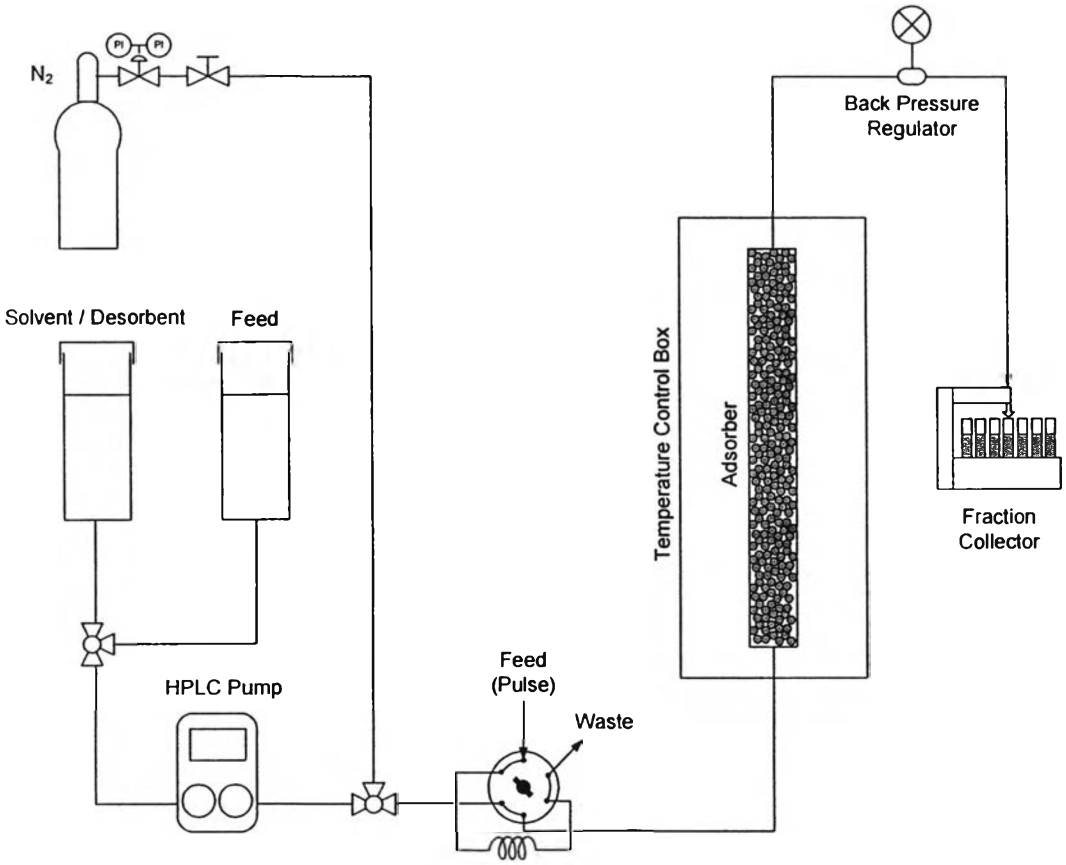


Figure 6.1 Experimental setup for the pulse test and breakthrough study.

For studying the effect of temperature, the pulse test experiments were carried out at 40, 100, 160, 180 and 200°C for NaY. Effects of exchanged cation on the DMNs adsorbability on the employed faujasite zeolites were also investigated at a fixed temperature of 180°C. The correlation between the adsorption affinity of the DMNs and the strength of the adsorbent acidity was then made. In this contribution, the Sanderson's intermediate electronegativity of the adsorbents (S_{int}) was calculated as a representative to the strength of the adsorbent acidity following the equation,

$$S_{\text{int}} = \left(\prod_i S_i^{n_i}\right)^{1/\left(\sum n_i\right)} \qquad (1)$$

where S_i is the Sanderson's electronegativity of the atom, and n_i is the stoichiometric of the atom in a unit cell of adsorbent (Dixit and Rao, 1996).

For the ion-exchanged zeolites with a formula of $Na_pM_q(SiO_2)_r(AlO_2)_s$, the S_{int} can be calculated by,

$$S_{\text{int}} = \left(S_{Na}^{p} S_{M}^{q} S_{Si}^{r} S_{Al}^{s} S_{O}^{2(r+s)}\right)^{1/[p+q+r+s+2(r+s)]} \qquad (2)$$

The calculated S_{int} of the employed adsorbents are listed in Table 6.1. The higher S_{int} indicates high electron-accepting ability and strong adsorbent acidity (Mortier, 1978; Barthomeuf, 1991; Barthomeuf, 1996).

The adsorbents providing a high potential for being used in 2,6-DMN separation were also identified from the experimental pulse test results. After that, the high concentration study was performed using the breakthrough technique. In this study, the feed was not diluted by the solvent as in the case of the pulse test; thus, the effect of feed concentration would be observed. The experiment was performed following the same procedure as for the pulse test, except the equilibrium mixture was continuously pumped to the adsorber. After a 100 mL of the feed had been pumped into the adsorber, the desorbent was then fed to desorb the DMNs from the column. Adsorption capacity and selectivity of the selected adsorbents were calculated. Comparison between those from the low concentration study (pulse test) and high concentration study (breakthrough test) was then made.

Table 6.1 Chemical composition, ionic radius and Sanderson's intermediate electronegativity (S_{int}) of the alkaline and alkaline earth exchanged faujasite zeolites used as adsorbents

Adsorbent	Chemical Composition	Ionic Radius (A°)	Sanderson's intermediate electronegativity (S_{int})[a]
LiX	$Li_{20}Na_{64}(AlO_2)_{84}(SiO_2)_{108}$	0.76	3.284
NaX	$Na_{84}(AlO_2)_{84}(SiO_2)_{108}$	1.02	3.278
KX	$K_{82}Na_2(AlO_2)_{84}(SiO_2)_{108}$	1.38	3.076
RbX	$Rb_{71}Na_{13}(AlO_2)_{84}(SiO_2)_{108}$	1.52	3.052
CsX	$Cs_{73}Na_{11}(AlO_2)_{84}(SiO_2)_{108}$	1.67	2.962
MgX	$Mg_{30}Na_{24}(AlO_2)_{84}(SiO_2)_{108}$	0.72	3.705
CaX	$Ca_{40}Na_4(AlO_2)_{84}(SiO_2)_{108}$	0.99	3.754
SrX	$Sr_{41}Na_2(AlO_2)_{84}(SiO_2)_{108}$	1.12	3.732
BaX	$Ba_{41}Na_2(AlO_2)_{84}(SiO_2)_{108}$	1.35	3.657
LiY	$Li_{22}Na_{31}(AlO_2)_{53}(SiO_2)_{139}$	0.76	3.587
NaY	$Na_{53}(AlO_2)_{53}(SiO_2)_{139}$	1.02	3.580
KY	$K_{51}Na_2(AlO_2)_{53}(SiO_2)_{139}$	1.38	3.435
RbY	$Rb_{47}Na_6(AlO_2)_{53}(SiO_2)_{139}$	1.52	3.409
CsY	$Cs_{49}Na_4(AlO_2)_{53}(SiO_2)_{139}$	1.67	3.334
MgY	$Mg_{20}Na_{13}(AlO_2)_{53}(SiO_2)_{139}$	0.72	3.907
CaY	$Ca_{23}Na_7(AlO_2)_{53}(SiO_2)_{139}$	0.99	3.890
SrY	$Sr_{24}Na_5(AlO_2)_{53}(SiO_2)_{139}$	1.12	3.883
BaY	$Ba_{24}Na_5(AlO_2)_{53}(SiO_2)_{139}$	1.35	3.836

[a] Calculated using equation 1.

6.4 Results and Discussion

6.4.1 Effect of Temperature

The pulse test was conducted over a range of temperature from 40°C to 200°C on NaY adsorbent. Fig. 6.2 shows the pulse test results from different testing temperatures of the 1,5-, 1,6- and 2,6-DMN over NaY using n-heptane and toluene as a tracer and desorbent, respectively. It was found that all DMNs were eluted at the same time as the tracer at 40°C, which suggests that there is no adsorption of the DMNs on NaY at this temperature. Improvements on the DMNs adsorption can be observed with increasing temperature. This indicates that the species need external energy to promote their diffusion through the zeolite pore since their molecular sizes (as listed in Table 6.2) are very close to that of FAU pore aperture (7.4 A°). The elution profiles of the DMNs also become sharper as a function of temperature due to the increment of the diffusion rate of 2,6- and 1,6-DMN.

Fig. 6.3 shows the variation of the calculated adsorption selectivities with temperature. Interestingly, it was found that the selectivities increase with the increase in the temperature and decrease with the temperature higher than 160°C. This result could be explained by the improvement on both the DMNs diffusion and the diffusion rate by thermal energy as previously discussed. More diffusion of the 1,5- and 1,6-DMN through the FAU pore than 2,6-DMN would provide the higher seletivities, which can also be suppressed by the higher diffusion rate of the two species at the high temperature region.

All in all, it seems that the adsorption of the DMNs on NaY is controlled by the molecular diffusion, called as the rate-selective mechanism. However, it was observed that the elution order of the DMNs does not agree well with that of the calculated barrier energy of diffusion through FAU (Millini *et al.*, 2003) as listed in Table 6.2. Generally, the molecule that has the lowest diffusion energy would deliberately diffuse through the zeolite pore slower than that with the higher diffusion energy resulting in the higher NRV as observed in the cases of n-paraffins adsorption (De Meyer *et al.*, 2003; Wei, 1994; Gorring, 1973). However, it was revealed from the study that the diffusion of 2,6-DMN through FAU pore is the fastest even though it has the lowest barrier energy of diffusion. Therefore, it can be concluded that the adsorption would not only be dominated by the rate-selective mechanism.

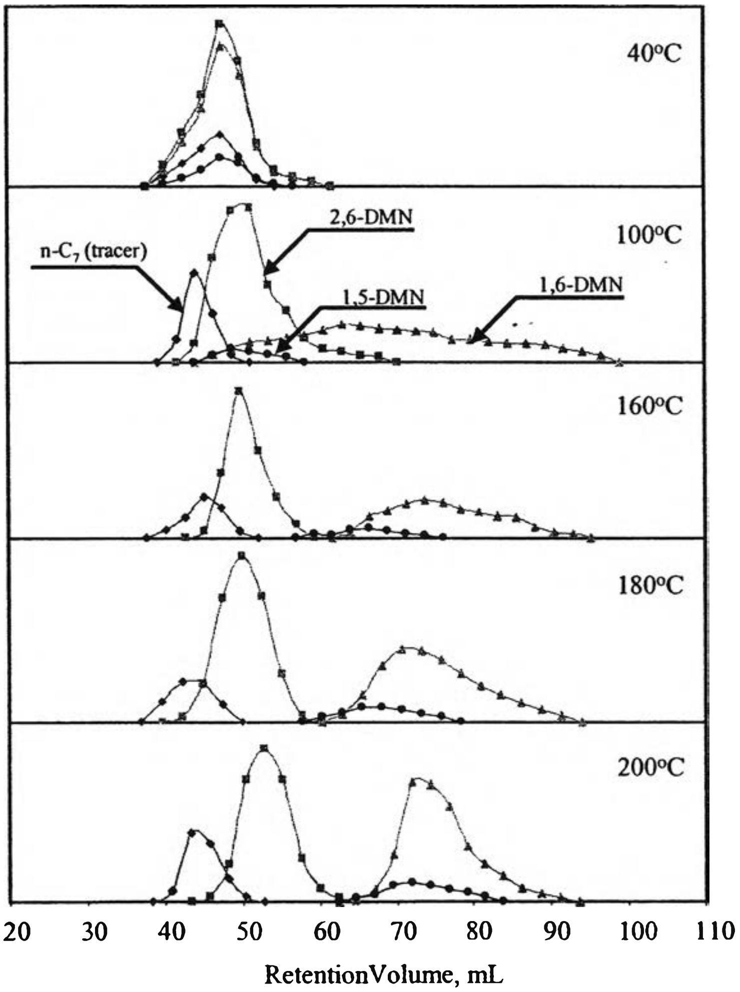


Figure 6.2 Pulse test results of 1,5-, 16,- and 2,6-DMN with their equilibrium composition on NaY, 1 h^{-1} LHSV at different temperatures.

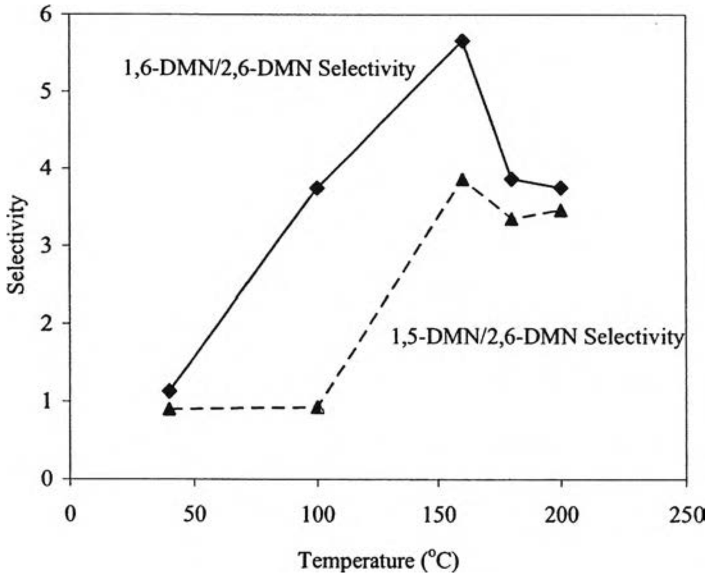


Figure 6.3 Adsorption selectivity of 1,6-DMN and 1,5-DMN respected to 2,6-DMN as a function of temperature on NaY, 1 h^{-1} LHSV.

Table 6.2 Kinetic diameter and barrier energy of diffusion through FAU pore of 1,5-, 1,6- and 2,6-DMN

DMN Isomer	Kinetic Diameter (A°)	Barrier Energy of Diffusion through FAU (kJ mol^{-1})*
1,5-DMN	7.7	34.3
1,6-DMN	7.7	38.9
2,6-DMN	7.2	21.3

* Millini *et al.* (2003).

6.4.2 Effect of Exchanged Cation of the Faujasite Zeolites

Adsorption of the DMNs on the alkaline and alkaline earth ion-exchanged faujasite zeolites (as listed in Table 6.1) was investigated using the pulse test technique at 180°C. The elution profiles of 1,5-, 1,6- and 2,6-DMN from the adsorbents are illustrated in Fig. 6.4. It was observed that 1,5- and 1,6-DMN can diffuse through the FAU pore better than 2,6-DMN as they possess the higher NRVs. On the other hand, it seems that all ion-exchanged faujasite zeolites tend to reject 2,6-DMN from the system when using toluene as the desorbent. This result also substantiates our previous hypothesis that the adsorption should not be controlled by only the molecular diffusion (rate-selective mechanism) since the elution order of 1,6- and 1,5-DMN varies among the employed FAU adsorbents while that of 2,6-DMN does not. As the results, it was suggested that the separation of 2,6-DMN could be accomplished only in a rejective system over some particular ion-exchanged faujasite zeolites. For instance, the rejective operation over KX, CaX, LiY, NaY, KY, RbY, SrY and BaY shows a clear separated profile of 2,6-DMN from the others, indicating their ability to purify 2,6-DMN form its equilibrium isomeric mixture.

Since the adsorbability of the DMNs seems to depend on the acidic properties of the adsorbent (as illustrated in Fig. 6.4) and the acid strength of the zeolite can be varied by either changing the Si/Al ratio or exchanging part of the exchanged cation (Kulprathipanja and Johnson, 2002; Barthomeuf, 1991; Barthomeuf, 1996), the correlation between the NRVs of each DMN and the strength of the adsorbent acidity (presented in terms of S_{int}) was made as exhibited in Fig. 6.5. It was observed that the NRV magnitude of the DMNs follows the order of 1,5-DMN > 1,6-DMN > 2,6-DMN for almost the employed alkaline and alkaline earth exchanged faujasite zeolites. In general, the adsorption on Y-zeolites seems to have more affinity than that on X-zeolite since the higher NRVs of all DMNs were observed. This result indicates that the variation in the strength of the zeolite acidity due to the change in Si/Al ratio plays an important role on the adsorption of the DMN molecules. The adsorption on the zeolite with the higher acidity strength appears to possess more affinity than that on the lower, except for some X-zeolites, LiX, NaX, CaX.

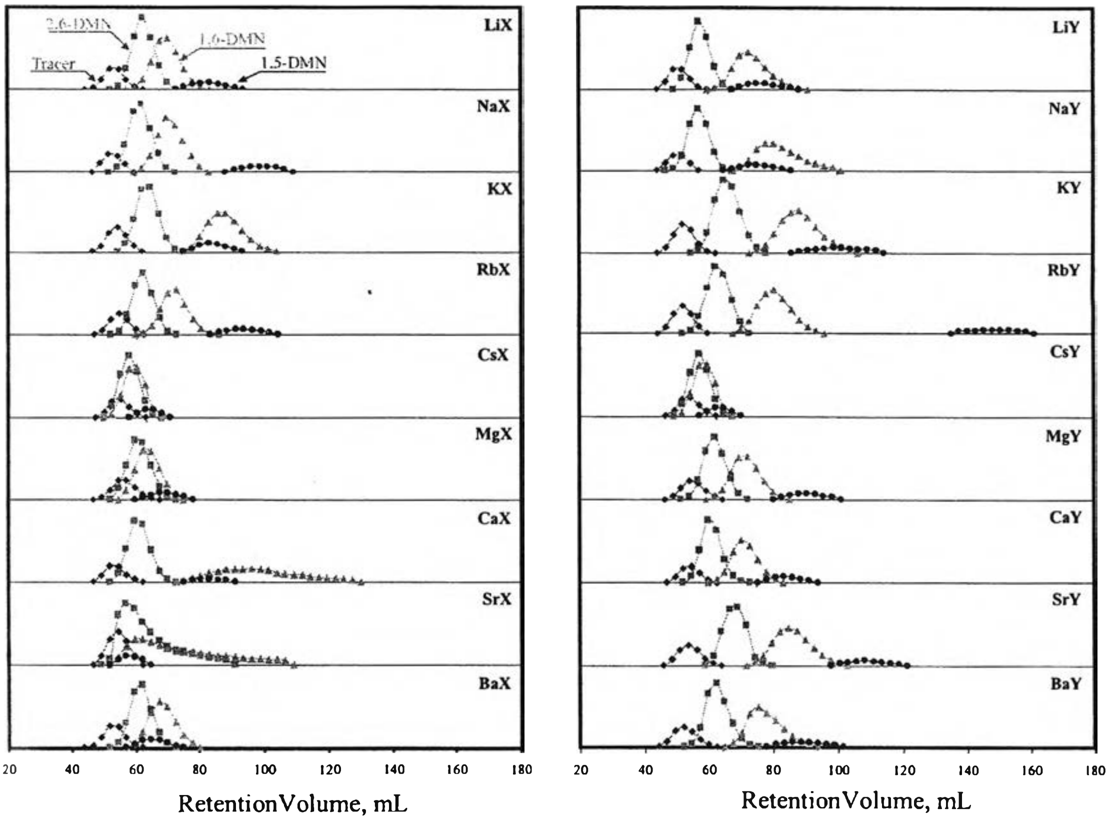


Figure 6.4 Pulse test results of 1,5-, 16,- and 2,6-DMN with a series of alkaline and alkaline earth ion-exchanged faujasite zeolites, 1 h^{-1} LHSV, 180°C.

The change in acidic properties of the zeolite due to the exchange of cation also controls the adsorption of the DMNs. For example, the NRVs of 2,6- and 1,6-DMN over the alkaline exchanged X and Y zeolites slightly increase as the strength of the zeolite acidity increases due to the exchange from Cs to Rb and K, respectively. This result substantiates the previous hypothesis that the adsorption would preferentially take place on an adsorbent with the higher strength acidity than the lower. However, the NRVs of 2,6- and 1,6-DMN slightly decrease for Na-FAU and Li-FAU even they have a higher acid strength and contain a smaller cation size. As the result, it can be concluded that the adsorption on Na-FAU and Li-FAU is not only governed by the adsorbent acid strength, there might also be other parameters affecting the adsorption of the DMNs on those adsorbents, for instance, the DMNs-cation interaction as observed in the cases of benzene and xylene adsorption (Barthomeuf, 1996; Mellot *et al.*, 1994). The adsorption of 1,5-DMN on the alkaline

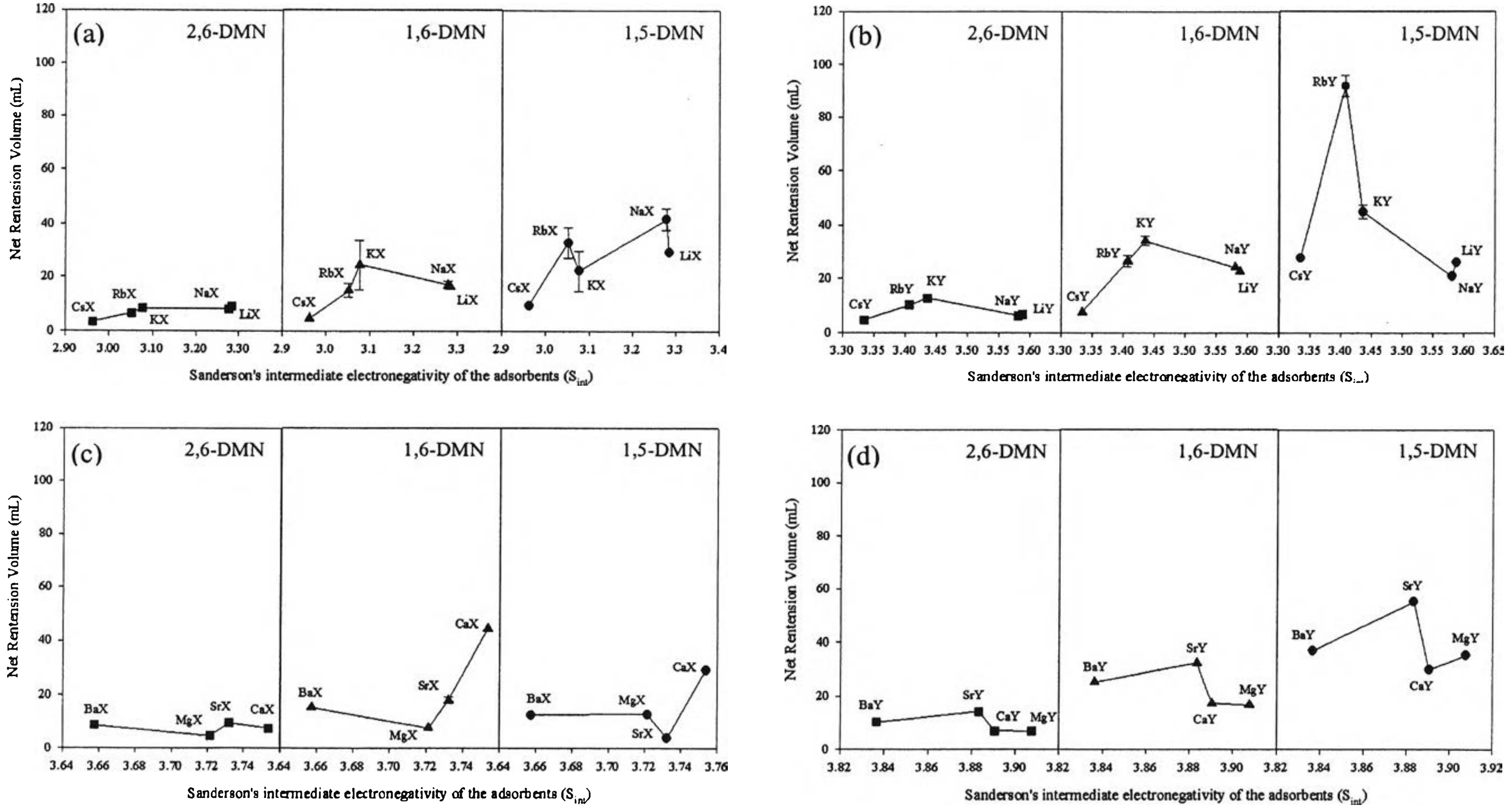


Figure 6.5 Net retention volume as a function of the strength of the adsorbent acidity, S_{int}, of (■) 2,6-DMN, (▲) 1,6-DMN and (●) 1,5-DMN on (a) alkaline-X, (b) alkaline-Y, (c) alkaline earth-X and (d) alkaline earth-Y at 1 h^{-1} LHSV and 180°C.

exchanged Y zeolites seems to be controlled by the hereinbefore discussed mechanisms, except for RbY that the adsorption strangely possesses the most. Nevertheless, no real correlation can be made for the case of 1,5-DMN adsorption.

The strength of the adsorbent acidity appears to govern the adsorption of the DMNs on the alkaline earth exchanged faujasite zeolites similar to those on the alkaline exchanged faujasites. The adsorption of 2,6-DMN tends to increase from BaY to SrY due to the increase in the zeolite acid strength and decrease for CaY and MgY, respectively. It is noted that the dissimilarity in the 2,6-DMN adsorption tendency over the alkaline earth exchanged X zeolites would be due to the lower S_{int} of MgX than that it should be resulting from the lower in the degree of Mg exchange. This result suggests that the effect of interaction between DMN and a cation would be more pronounced than that of the adsorbent acid strength since the trend of the DMNs' NRV will be identical to those of Y-zeolites if the S_{int} is ordered regarding to the calculation from 100% degree of exchange (Ba>Sr>Ca>Mg). Interestingly, it was observed that the adsorption of 2,6- and 1,6-DMN on the alkaline and alkaline earth exchanged faujasites decreases when the exchanged cation size is lower than 1.02 A°, such as Li-FAU, Na-FAU, Mg-FAU and Ca-FAU. However, the hypothesis is not valid for the case of 1,6-DMN adsorption on CaX and most cases of 1,5-DMN adsorption, except for that on the alkaline earth exchanged Y zeolites.

Fig. 6.6 shows the adsorption selectivity of 1,6- and 1,5-DMN respected to 2,6-DMN as a function of the adsorbent acid strength (presented in term of S_{int}). It was found that there is no correlation between the zeolite acid strength and the adsorption selectivity of the DMNs observed as in the case of xylene isomers adsorption (Seko *et al.*, 1979) even some correlations between the NRVs of DMNs and S_{int} have been revealed. This result suggests that the adsorption of the DMNs would not be governed by only the DMN-cation and acid-base interaction. Other parameters that could affect the adsorption must be taken into account for understanding the complex adsorption behavior of the DMNs.

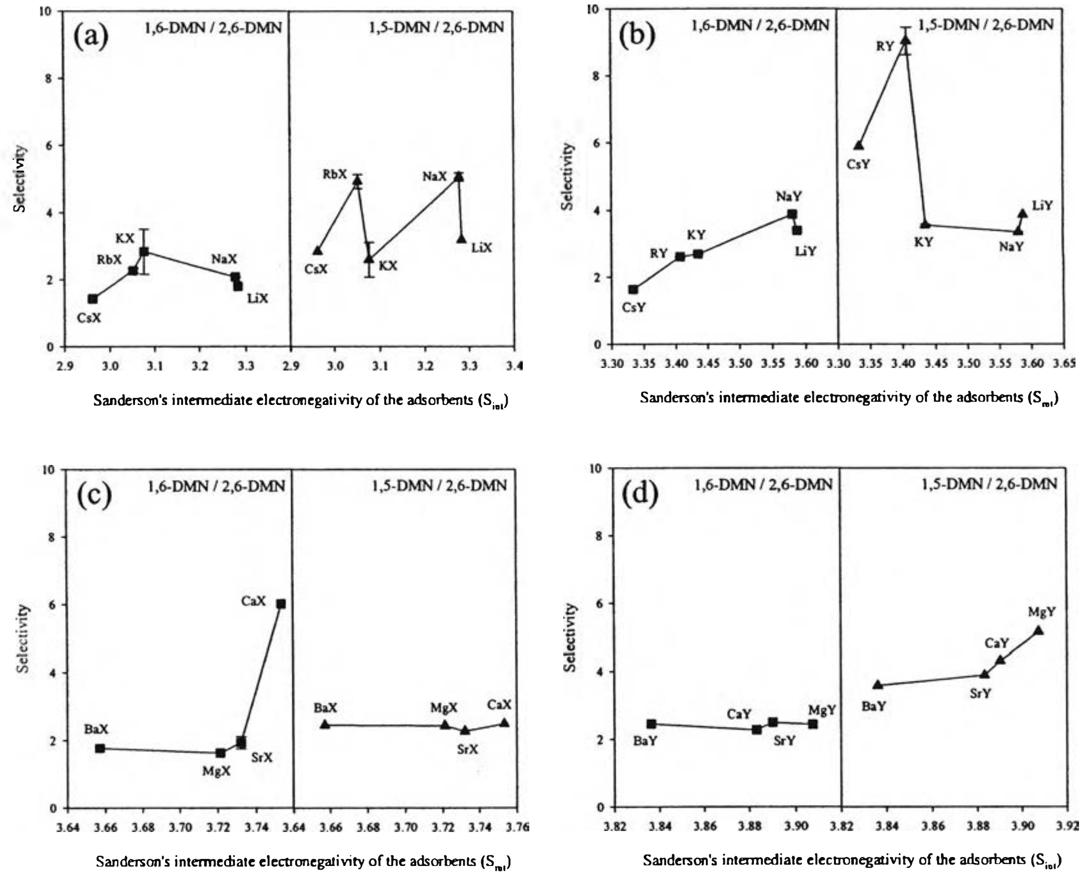


Figure 6.6 Adsorption selectivity as a function of the strength of the adsorbent acidity, S_{int}, of (a) alkaline-X, (b) alkaline-Y, (c) alkaline earth-X and (d) alkaline earth-Y at 1 h^{-1} LHSV and 180°C.

6.4.3 Breakthrough Study

The breakthrough technique was performed for two selected adsorbents, NaY and KX, in order to observe the adsorption behavior of the DMNs under the high concentration circumstance. Since the breakthrough profiles of the DMNs and the tracer over NaY and KX are different only in the breakthrough time of each DMN, only those of NaY at 160 and 180°C were selected to be shown in Fig. 6.7. It was observed that the elution order of the DMNs still agrees well with the pulse test results. The roll up of the concentrated DMN species were also observed before reaching the breakthrough region and desorption region as normally observed for the competitive adsorptions (Heinen *et al.*, 2000; Lillo-Ródenas *et al.*, 2006; Shin *et al.*, 2002). This result is due to the displacement of the less firmly adsorbed DMN on the surface by the others in the adsorption period, and the displacement of the strongly adsorbed species by the desorbent in the desorption period. As a result, molecular displacement should be taken into account as another parameter governing the adsorption of the DMNs on ion-exchanged faujasite adsorbents.

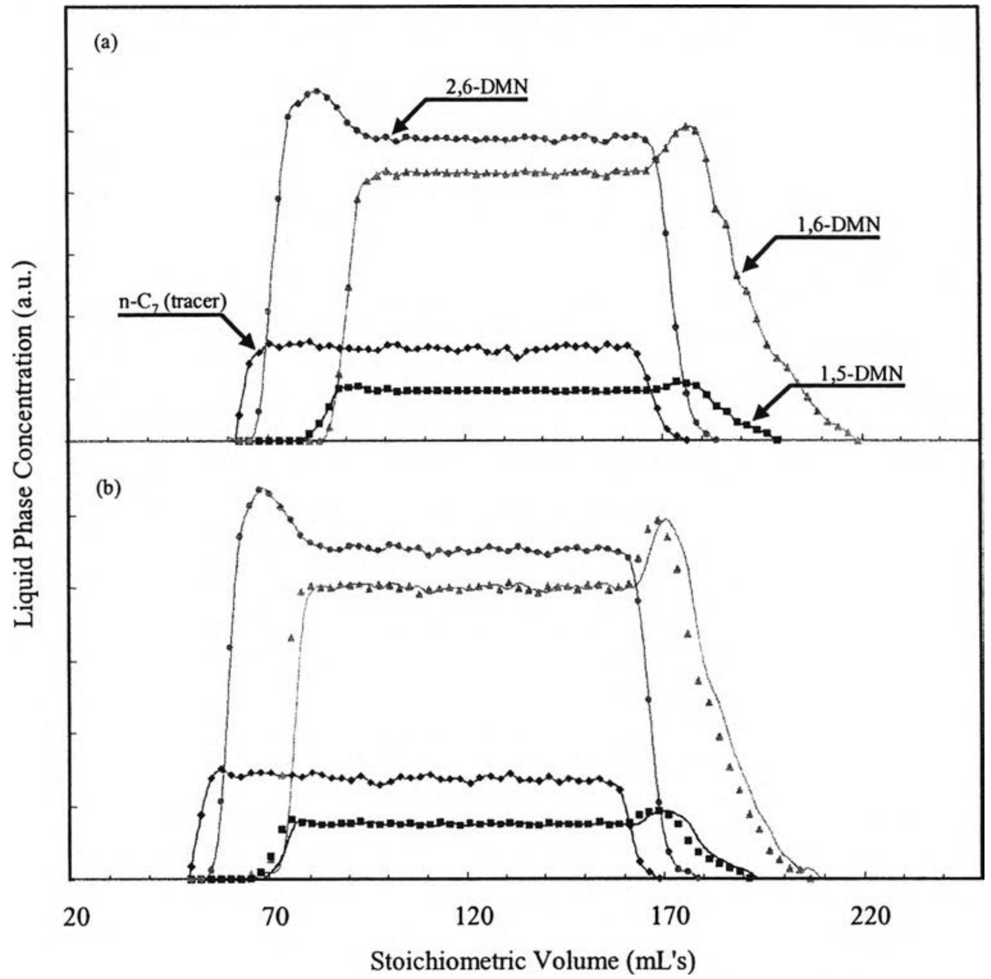


Figure 6.7 Breakthrough curves of 1,5-, 16,- and 2,6-DMN on NaY, 1 h^{-1} LHSV at (a) 160°C and (b) 180°C.

Table 6.3 lists the adsorption selectivity and capacity of NaY and KX that were calculated using the ratio between the NRV of the interested species and a numerical integration of the breakthrough curves for the DMNs, respectively. The adsorption selectivity under the high concentration circumstance (breakthrough test) of both NaY and KX are greater than those of the low concentration testing (pulse test). However, the temperature dependence of the adsorption selectivity is present in the same tendency as that of the pulse test. These results indicate that the feed concentration also plays a role on the adsorption of DMNs on the faujasite adsorbents regarding the difference in the displacement behaviors, while the temperature controls the molecular diffusion. For the adsorption capacity, the suppression with the temperature increment substantiates our previous discussion on the limitation of the molecular diffusion.

Table 6.3 Total adsorption capacity and adsorption selectivity of the selected potential adsorbent calculated form breakthrough experiment with 1 h^{-1} LHSV

Adsorbent	Temperature	Total adsorption Capacity^{a}	1,6- / 2,6-DMN Selectivity	1,5- / 2,6-DMN Selectivity
NaY	160	9.95	9.57	6.52
	160^{b}	-	5.61	3.87
	180	13.74	3.28	2.93
	180^{b}	-	3.87	3.35
KX	180	6.83	6.99	6.31
	180^{b}	-	2.83	2.59

^{a} mL / 70 $mL_{adsorbent}$

^{b} From experimental pulse tests.

Even the 2,6-DMN purification can be accomplished only in a rejective system that normally entails the lower purity of the chemical (Barger *et al.*, 1991; Kulprathipanja and Johnson, 2002), more than 99% of 2,6-DMN purity can still be achieved at the early of the breakthrough profile (based on the employed analytical technique). This result would suggest the successful of using ion-exchanged faujasite zeolites for the 2,6-DMN purification, particularly for the NaY adsorbent.

6.5 Conclusions

The equilibrium mixture of 1,5-, 1,6- and 2,6-DMN was investigated for it adsorpability on a series of alkaline and alkaline earth ion-exchanged faujasite zeolites. At least molecular diffusion, acid-base interaction, preferential interaction with cation and molecular displacement were revealed to govern the adsorption of the DMNs on the adsorbents. The results from the pulse test technique and breakthrough technique showed that all ion-exchanged faujasite zeolites can only provide a rejective system for 2,6-DMN, and some of them could be potentially used for the 2,6-DMN separation applications.

6.6 Acknowledgements

The authors would like to thank the Ph.D. Royal Golden Jubilee Program (PHD/0147/2547), Thailand Research Fund; Petrochemical and Environmental Catalysis Research Unit under Ratchadapisek Somphot Endowment, PTT Consortium, The Petroleum and Petrochemical College, Chulalongkorn University; and UOP LLC for the supports on this work. Laboratory assistances from Darryl M. Johnson and the adsorbents from Jim Priegnitz, both from UOP LLC, are appreciated.

6.7 References

Barger, P.T., Barder, T.J., Lin, D.Y. and Hobbs, S.H., "Continuous process for the production of 2,6-dimethylnaphthalene," US Patent 5 004 853 (1991), to UOP LLC.

Barthomeuf, D., "Acidity and Basicity in Zeolites", *Catalysis and Adsorption by Zeolites*," G. Öhlmann *et al.* (Eds.), pp.157-169, Elservier Science Publisher B.V., Amsterdam, 1991.

Barthomeuf, D., "Basic Zeolites: Characterization and Uses in Adsorption and Catalysis," Cat. Rev. - Sci. Eng., 34, 521-612 (1996).

Chem systems, 2,6-Dimethylnaphthalene (2,6-DMN):99/00S7, *Chem Systems Report*, 2000.

De Meyer, K.M.A., Chempath, S., Denayer, J.F.M., Martens, J.A., Snurr, R.Q. and Baron, G.V., "Packing effects in the liquid-phase adsorption of C_5-C_{22} *n*-alkanes on ZSM-5," J. Phys. Chem. B, 107, 10760-10766 (2003).

Dixit, L. and Rao, T.S.R. P., "Polarizability model of acidity of zeolites," Zeolites, 16, 287-293 (1996).

Gorring, R.L., "Diffusion of normal paraffins in zeolite T occurrence of window effect," J. Catal., 31, 13-26 (1973).

Heinen, A.W., Peters, J.A. and Bekkum, H.V., "Competitive adsorption of water and toluene on modified activated carbon supports," Appl. Catal., A, 194 –195, 193–202 (2000).

Inui, T. and Pu, S.B., "Separation of 2,6-dimethylnaphthalene from a mixture of its isomers using lithium-incorporated zeolite Y synthesized by rapid crystallization method," Sep. Tech., 5, 229-237 (1995).

Kraikul, N., Rangsunvigit, P. and Kulprathipanja, S., "Isomerization of 1,5- to 2,6-Dimethylnaphthalene and Its Thermodynamic Aspects," Chem. Eng. J., 114, 73-79 (2005).

Kraikul, N., Rangsunvigit, P. and Kulprathipanja, S., "Unexpected Roles of Toluene in the Catalytic Isomerization of 1,5- to 2,6-Dimethylnaphthalene", Appl. Catal-A: Gen., In press.

Kulprathipanja, S. and Johnson, J.A., "Liquid Separation," *Handbook of Porous Solids Volume 4.*, F. Schüth, K. Sing and J. Weitkamp (eds.), WILEY-VCH, Weinheim, 2002.

Lillo-Ródenas, M.A., Fletcher, A.J., Thomas, K.M., Cazorla-Amorós, D. and Linares-Solano, A., "Competitive adsorption of a benzene–toluene mixture on activated carbons at low concentration," Carbon, in press (2006).

Maki, T., Yokoyama, T., Nakanishi, A., Shioda, K. and Asatani, H., "Process for separating 2,6-dimethylnaphthalene," US Patent 4 791 235 (1988), to Mitsubishi Chemical Industries Limited.

Mellot, C., Espinat, D., Rebours, B., Baerlocher, Ch. and Fischer, P., "Location of meta-xylene in BaX zeolite and model for the filling of the supercages," Catal. Lett., 27, 159-169 (1994).

Millini, R., Frigerio, F., Bellussi, G., Pazzuconi, G., Perego, C., Pollesel, P. and Romano, U., "A priori selection of shape-selective zeolite catalysts for the synthesis of 2,6-dimethylnaphthalene," J. Catal., 217, 298-309 (2003).

Mortier, W.J., "Zeolite Electronegativity Related to Physicochemical Properties," J. Catal., 55, 138-145 (1978).

Nakao, N., Yamamoto, K., Motoyuki and M., "Method for concentrating 2,6-dimethylnaphthalene," US Patent 6 706 939 (2004), to Kobe Steel Ltd.

Rota, R., Morbidelli, M., Rombi, E., Monaci, R., Ferino, I. and Solinas, V., "Adsorption equilibria of dimethylnaphthalene isomers," Ind. Eng. Chem. Res., 35, 199-206 (1996).

Seko, M., Mlyake, T. and Inada, K., "Economical p-Xylene and Ethylbenzene Separated from Mixed Xylene," Ind. Eng. Chem. Prod. Res. Dev., 18, 263-268 (1979).

Shin, H.C., Park, J.W., Park, K. and Song, H.C., "Removal characteristics of trace compounds of landfill gas by activated carbon adsorption," Environ. Pollut., 119, 227–236 (2002).

Smith, T. G., Weis, J. M. and Viswanath, Y., "Crystallization of 2,6-Dimethylnaphthalene," US Patent 5 977 426 (1999), to BP Amoco Corporation.

Verduijn, J. P., Janssen, M. J. G., De Gruijter, C. B., Koetsier, W. T. and Van Oorschot, C. W. M., "Process for separating dimethylnaphthalene isomers with zeolite L agglomerates," US Patent 5 146 040 (1992), to Exxon Chemical Patents Inc.

Wei, J., "Nonlinear phenomena in zeolite diffusion and reaction," Ind. Eng. Chem. Res., 33, 2467-2472 (1994).