ELSEVIER

Catalysis Today 29 (1996) 235-240

CATALYSIS TODAY

Hydrocracking of polycyclic aromatic compounds using zeolite catalysts: Explanation of product distribution based on a computer aided molecular design study on the interaction of zeolite and substrates

Masakatsu Nomura [a,*], Kenji Akagi [a], Satoru Murata [a], Hisaji Matsui [b]

[a] *Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565, Japan*
[b] *Research and Development Center, Osaka Gas Co. Ltd., 19-9, 6-Chome, Torishima, Konohana-ku, Osaka 554, Japan*

Abstract

Hydrocracking of phenanthrene was conducted in a batch autoclave system using ZSM-5 (5.5 Å), mordenite (7 Å) and Y-type zeolite (8 Å) as catalysts. The number in brackets is the size of the pore of each zeolite. Close examination of product distribution derived from hydrocracking of phenanthrene indicated that it is strongly affected by the pore size of the zeolite used. Based on the computer aided molecular design studies of each zeolite, the way of aromatic compounds accessing towards the entrance of the pore of zeolite was visualized, herewith being able to explain the characteristic distribution of the products.

Keywords: ZSM-5; Mordenite; Y-type zeolite; Computer aided molecular design

---

1. Introduction

The source of aromatic compounds like naphthalene, phenanthrene, anthracene and pyrene is still, in Japan, coal tar derived from coal carbonization. In general, naphthalene is now widely used as a starting material of phthalic anhydride, dyestuff, medicine and pesticide. On the other hand, phenanthrene (anthracene) and pyrene are used, to lesser degrees, compared with naphthalene. Therefore, there is a constant demand for converting tricyclic or tetracyclic aromatic compounds into benzene and naphthalene derivatives.

Hydrocracking of polycyclic aromatic compounds is believed to proceed via initial hydrogenation of their peripheral ring into a naphthenic ring which cleaves to aliphatic substituents and isomerizes to a branched naphthenic ring and, finally, dealkylation. So, dual functional catalysts are needed for conversion of polycyclic aromatic compounds into monocyclic- or bicyclic aromatic compounds with hydrogenating and cracking abilities. [1,2] In this study, Y-type zeolite, mordenite and ZSM-5 zeolite are applied for the hydrocracking because these three catalysts have different pore

---

[*] Corresponding author.

SSDI 0920-5861(95)00277-4

sizes, 8, 7 and 5.5 Å, respectively. This pore size is expected to affect the distribution of cracked products because these pore sizes have the right size to control the entering of aromatic compounds into channels of zeolite. We also conducted a computer aided molecular design study on the diffusion phenomena of polycyclic aromatic hydrocarbons in the channel of these zeolites to obtain insight into the reaction mechanisms [3–13].

2. Experimental

2.1. Preparation of nickel loaded zeolite catalyst

Three NH_4-substituted zeolites (50 g) were stirred in 1000 ml of aqueous solution of $Ni(NO_3)_2$ (0.25 M) at 90°C for 96 h, then they were filtered and dried at 110°C to obtain nickel cation substituted zeolites. These catalysts were calcined in an air stream at 500°C for 4 h, then being submitted to reduction with H_2 atmosphere at 450°C for 1 h. The content of nickel in each zeolite was determined by using a Rigaku Denki System 3270 type fluorescence X-ray analyzer. The distribution of acid sites in each catalyst is evaluated by measuring temperature programmed NH_3 desorption: the catalyst was first dried at 600°C and then treated in NH_3 stream at 110°C in order to adsorb NH_3 on a catalyst. This treated catalyst was cooled down to 50°C, then heated to 610°C with a rate of 4°C/min in He atmosphere. The amount of NH_3 desorbed was analyzed quantitatively by gas chromatography.

2.2. General procedure for hydrocracking reaction of aromatic hydrocarbons

Polycyclic aromatic hydrocarbon (1 g) and nickel-supported zeolite catalyst (0.5 g) were placed in a 70 ml SUS 316 autoclave, then being pressurized to 70 kg/cm^2 with hydrogen. This was followed by heating to 350°C with a rate of 8°C/min. During the reaction, the temperature was kept at 350°C. After the reaction, the gas produced was collected, an aliquot of which was submitted to GC analysis with a Shimadzu GC-3BT (an active carbon column, 2 m) and a Shimadzu GC-8AIT (a silica gel column, 60–80 mesh, 3 m). Liquid product was recovered by washing the inside of the autoclave with CH_2Cl_2. According to analysis by a JEOL JMS-DX-303HF type GC–MS, the liquid products were assigned. The quantitative analysis was conducted by a Shimadzu GC-14APFSC (CBP-1 capillary column, id 0.5 mm, 25 m). Deposited carbon was defined as the carbonaceous materials remained on the surface or inside the pore of the catalyst after the reaction, the yield of which was calculated based on a microanalysis of the recovered catalyst.

2.3. A method for the simulation of the diffusion phenomena of aromatic hydrocarbons in the pore of the zeolites

Simulation of diffusion phenomena of aromatic substrates in the pore of the zeolite was carried out by using a Titan 750V graphic workstation (Kubota Pacific Computer, Inc.) and a commercial CAMD software, Polygraf (Ver. 3.1, Simulation Technology, Inc.). For the simulation, impulse dynamics methods were used, where the substrate, having some initial rate, was forced to move toward the target molecule (e.g., zeolite). The following parameters were employed in this study; an initial velocity of the model molecules: 2000 K (corresponding to the 0.02 Å/fs), time for simulation: 3000 steps (3.0 ps) and the temperature of simulation: 300 K.

3. Results and discussion

3.1. Characterization of three different nickel-loaded zeolites

The contents of nickel in Y-type zeolite, mordenite and ZSM-5 type zeolite were deter-

Table 1
Characterization of three different nickel-loaded zeolites

	ZSM-5	Mordenite	Y-type
Nickel concentration (wt.-%)	1.22	1.77	3.11
NH_3 desorption (μmol/g)			
H-zeolite	549	1660	1566
Ni-zeolite	644	1745	2272

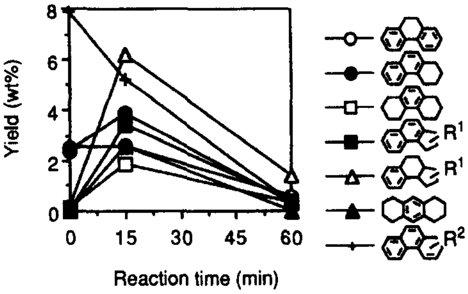

Fig. 1. Time profile of the yield of hydrogenated and isomerized phenanthrenes from the hydrocracking of phenanthrene over nickel-loaded Y-type zeolite (R^1 = H or Me, R^2 = Me or Et).

mined to be 3.11, 1.77 and 1.22 wt.-% (Table 1), respectively, based on measurements by X-ray fluorescence. The results suggest that the larger the size of the pore is, the higher is the concentration of nickel on the catalysts when similar preparative methods are applied. The amounts of NH_3-desorption are also shown in Table 1. From this table, the order of the amount of acid sites in these zeolites obeyed to the following sequence: ZSM-5 < Y-type ⩽ mordenite. As to nickel-loaded catalysts, the amount of acid sites was found to increase compared with those of the corresponding protonated zeolites.

3.2. Hydrocracking of polycyclic aromatic hydrocarbons by using nickel-loaded zeolites

Hydrocracking of phenanthrene over the nickel-supported Y-type zeolite was conducted at 350°C [14]. By changing the duration of the reaction from 0, 15 to 60 min we found that the recovery of phenanthrene decreased from 79.6%, 15.9% to 0.7%, respectively (Table 2). The gaseous products increased in the following order, 5.0 (0 min), 15.2 (15 min) and 67.5% (60 min). The plots of product yields against reaction time (Fig. 1) indicate that in the case of the reaction time being 0 min, 9,10-dihydro- and 1,2,3,4-tetrahydrophenanthrene are produced at first, then these are isomerized to a five membered saturate ring and skeletally isomerized to *sym*-octahydroanthracene along with the formation of *sym*-octahydrophenanthrene. Amounts of these compounds were decreasing at 60 min of reaction time due to their cracking. When the reaction time was 60 min, propane, n-butane and isobutane became the main gaseous products, this indicates that dealkylation reaction occurred, to some extent, from 15 min reaction to 60 min reaction. Mono- and diaromatic compounds produced are benzene, cyclohexane, tetralin and indan, along with their alkylated derivatives.

Table 2
Hydrocracking of phenanthrene over the nickel-loaded zeolites

Catalyst	Y-type	Y-type	Y-type	Mordenite	ZSM-5
Reaction time (min)	0	15	60	60	60
Product distribution (wt.-%)					
Gas	5.0	15.2	67.5	53.8	10.4
Liquid	15.6	49.2	31.3	26.4	20.6
Deposited carbon	8.2	10.4	10.7	3.3	1.2
Recovery of phenanthrene	79.6	15.9	0.7	22.3	71.1
Total	108.4	90.7	110.2	105.8	103.3

The results for the hydrocracking reaction of phenanthrene using nickel-supported ZSM-5, mordenite and Y-type zeolites were summarized in Table 2 and Fig. 2. Table 2 shows that the catalytic activity of these zeolites increases according to the following order; ZSM-5 (28.9%) < mordenite (77.7%) < Y-type (99.3%), where the numbers in parenthesis indicate the conversion of phenanthrene in the hydrocracking using these catalysts. This order agrees well with the increasing order of the pore size. Since the size of phenanthrene is reported to be 7.9 Å, the molecules is thought not to be able to enter the

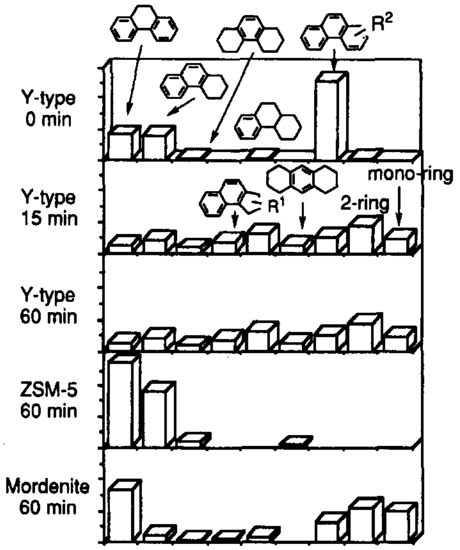

Fig. 2. Product distribution from the reaction of phenanthrene over three nickel-loaded zeolites at 350°C under 70 kg/cm^2 of H_2 (R^1 = H or Me, R^2 = Me or Et).

channel of neither mordenite nor ZSM-5 type zeolite. Therefore, when using these two catalysts, the reaction might proceed at the outer acid sites. On the other hand, the substrate could enter the channel of the Y-type zeolite so that the reaction could proceed effectively to form smaller products such as gaseous products.

When using presulfided nickel-molybdenum catalyst (S/NiMo–Al_2O_3), which is often used in upgrading reaction of heavy oils, conversion of the substrate reached 99.6%, while the major products were hydrogenated phenanthrene, anthracene and benzindan derivatives, especially, yields of *sym*-octahydro- and perhydrophenanthrene being 50.4 and 15%, respectively. This indicates that the catalyst does not have a cracking ability.

Distribution of liquids products (Fig. 2) clearly indicates that with the run using ZSM-5 (the smallest pore size), the main product is 9,10-dihydro-, 1,2,3,4-tetrahydro- and *sym*-octahydrophenanthrene derivatives along with their isomers (5 membered ring compounds). On the other hand, mordenite also shows very interesting product distribution similar to those obtained with ZSM-5 catalysts. 9,10- And 1,2,3,4-positions of phenanthrene can approach near the mouth of channels of each catalyst, being able to take up hydrogen atoms activated on the channel of each catalyst. Isomerization of the naphthenic ring to a 5-membered ring probably takes place near the mouth of these channels, however, they can not enter into these channels due to steric hindrance. On the other hand, dihydro-, tetrahydro- and octahydro-derivatives are not main products in case of the Y-type zeolite. They are converted to benzene and cyclohexane derivatives. These findings clearly suggest that a skeleton of phenanthrene can enter into the channel of the Y-type zeolite which has a 8 Å pore size.

3.3. Computer simulation for diffusion phenomena of phenanthrene in the channel of the zeolites

In order to obtain insight into the diffusion phenomena of the polycyclic aromatic hydrocarbons in the channel of the zeolites, a computer aided molecular design study was conducted [15]. The model compounds showed the following three different kinds of diffusion behavior according to the bulkness of the substrates and the size of the zeolite's channel: (a) in the case that the size of the channels is wider than the size of the model molecules, the molecules can diffuse easily into the channel of the zeolite, that is, they can move easily from outside to the inside (b) with the case that the molecules have a similar size to the pore diameters of the zeolites, the model molecules move from the outside to the entrance of the channel where they remain and (c) in the case that the size of the pore channel is smaller than that of the model molecules, the substrate stays at the entrance of the channel for a short period, then is repelled away from the catalyst. Table 3 and Fig. 3 show the summarized results of the diffusion behavior of the model molecules and the time profile of this simulation, respectively.

With the Y-type zeolite, benzene, naphthalene and phenanthrene showed the type (a) be-

Table 3
Simulation of the diffusion phenomena of aromatic hydrocarbons

Model molecule	Zeolite		
	ZSM-5	Mordenite	Y-type
Benzene	(b)	(a)	(a)
Naphthalene	(b)	(a)	(a)
Phenanthrene	(c)	(a)	(a)

havior, this suggests that its pore diameter allows these molecules to diffuse freely (Fig. 3, bottom). On the other hand, pyrene showed the type (b) behavior. When using mordenite, similar behavior to that of the Y-type zeolite was observed (Fig. 3, middle). On the other hand, as to ZSM-5, all the molecules can not enter and some escape from the channel due to steric repulsion (Fig. 3, top).

In a preceding chapter, we stated that nickel-loaded Y-type zeolite easily hydrocracks phenanthrene to monocyclic- and bicyclic aromatic compounds while in the case of nickel-loaded ZSM-5 zeolite, only the hydrogenation reaction was observed. These results could be clearly explained on the basis of the results of simulation. In case of Y-type zeolite, phenanthrene could move from outside to the inside of the channel, where it is hydrogenated and cracked. On the other hand, in case of ZSM-5 type zeolite, phenanthrene could not enter the pore, consequently, it is hydrogenated at active sites at the surface or the entrance of the pore. Although phenanthrene in both Y-type zeolite and mordenite showed a similar diffusion phenomena, the cracking of this molecule in H_2 atmosphere resulted in a significantly different product distribution. Several factors were thought to be the origin of the difference, such as, concentration of acid sites (concentration of Al in these zeolites), concentration of nickel species on the zeolites and so on. In order to conduct the simulation in a simple way, we employed the silicalites, i.e., Si–O compounds, which do not have any aluminum or nickel atoms, so that we could not consider these factors on the simulation. However, both catalytic activity and simulation of diffusion in ZSM-5 zeolite were very different from those of Y-type zeolite and mordenite so that this kind of simulation seems to predict the reaction pathway or the product distribution.

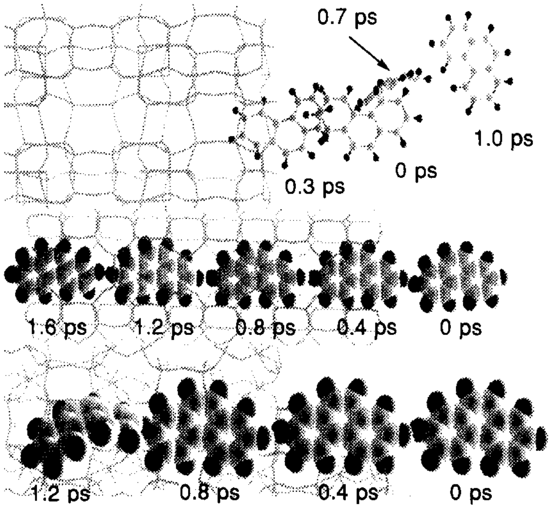

Fig. 3. Time profile of the simulation of diffusion of phenanthrene in the channel of ZSM-5 (top), mordenite (middle) and Y-type zeolite (bottom).

Although the simulation study on interaction between zeolites and substrates was conducted under very limited conditions, the results of simulation seems to be able to account for the results of a hydrocracking reaction of aromatic hydrocarbons with nickel-loaded zeolite catalysts such as ZSM-5, mordenite and Y-type zeolite. We believe that the results obtained in this study can afford a clear understanding about the steric control of zeolites on product distribution.

References

[1] H.W. Hayes Jr., J.F. Parcher and N.E. Halmer, Ind. Eng. Chem. Process Des. Dev., 22 (1983) 401.
[2] A.T. Lapinas, M.T. Klein, B.C. Gates, A. Macris and J.E. Lyons, Ind. Eng. Chem. Res., 26 (1987) 1026.
[3] K. Nakamura, S. Murata and M. Nomura, Energy Fuels, 7 (1993) 347.
[4] S. Murata, M. Nomura, K. Nakamura, H. Kumagai and Y. Sanada, Energy Fuels, 7 (1993) 469.

[5] T. Dong, S. Murata, M. Miura, M. Nomura and K. Nakamura, Energy Fuels, 7 (1993) 1123.

[6] T. Takanohashi, M. Iino and K. Nakamura, Energy Fuels, 8 (1994) 395.

[7] G.A. Carlson, Energy Fuels, 6 (1992) 771.

[8] J.-L. Faulon, G.A. Carlson and P.G. Hatcher, Energy Fuels, 7 (1993) 1062.

[9] J.-L. Faulon, P.G. Hatcher, G.A. Carlson and K.A. Wenzel, Fuel Process. Technol., 34 (1993) 277.

[10] J.-L. Faulon and P.G. Hatcher, Energy Fuels, 8 (1994) 402.

[11] J.-L. Faulon, J.P. Mathews, G.A. Carlson and P.G. Hatcher, Energy Fuels, 8 (1994) 408.

[12] A. Miyamoto and M. Kubo, J. Jpn. Petrol. Inst., 36 (1993) 282.

[13] Y. Oumi, H. Yamano, H. Himei, M. Katagiri, M. Kumo, R. Vetrivel and A. Miyamoto, Shokubai, 73 (1994) 65.

[14] H. Matsui, K. Akagi, S. Murata and M. Nomura, J. Jpn. Petrol. Inst., submitted for publication.

[15] H. Matsui, K. Akagi, S. Murata and M. Nomura, Energy Fuels, 9 (1995) 435.