

Selective separation of aromatic compounds using organic-inorganic layered nanohybrids

Kosuke Tsutsumi, Hideyuki Tagaya*

Department of chemistry and chemical engineering, Yamagata University, Yonezawa, Yamagata 992-8510, Japan.

Fax: 81-238-26-3413, e-mail: tagaya@yz.yamagata-u.ac.jp

Nonporous inorganic compounds had no selectivity for the adsorption of the *o*-, *m*-, *p*-xylene mixtures. On the other hand, organic-inorganic nanohybrids were considered as the adsorption medium, and some of them have the selectivity on the adsorption of xylene mixtures. The size of xylene isomers and pore size of the organic-inorganic nanohybrids are primary factor for the selectivity. In this study, the nanohybrids that contained an organic compound between the inorganic layers were prepared, and the possibility as the selective adsorption medium was examined. Various organic-inorganic nanohybrids were modified chemically and their adsorption abilities were evaluated. Preferential adsorption was observed.

Key words: organic-inorganic nanohybrids, adsorption, micropore, xylene

1. INTRODUCTION

Microporous materials such as silica gel, activated carbon and zeolite have high surface areas and are used as adsorbents of various molecules including organic compounds. However, their structures are not flexible. For example, the zeolite frame is rigid and the chemical modification of the frame is limited although zeolite has the advantage to adsorb certain compounds because of its steady porosity frame. On the other hand, an organic polymer is not suitable for obtaining a uniform vacancy although the chemical modification of the surface of them is easy. Recently, the example which used an organic-inorganic nanohybrid as adsorbent was reported [1,2]. New porous materials with high surface area, flexibility and steady frame are expected for organic-inorganic nanohybrids.

p-Xylene is the source of polyesters which are widely used as fibers, plastics and films. The rationalizing energy in a *p*-xylene production process affects the market and earth environment and a low cost process is expected in many fields. In the *p*-xylene production, *p*-xylene is separated from the mixture of xylene isomers that is distilled from petroleum oil and the isomerization process to *p*-xylene of the residual *o*- and *m*-isomers is carried out after the separation. In this separation, *p*-xylene is separated by the difference of physical properties such as the freezing point and selective absorption into the zeolite pores are also carried out.

In this study, organic - inorganic nanohybrids [3-12] were used as adsorbents. It was considered that the pores of the nanohybrids could selectively adsorb *p*-xylene molecule by recognizing the difference of the size of xylene isomers.

2. EXPERIMENTAL

2.1 Preparation of Zn(OH)₂

All reactions were carried out by using commercial reagents without further purification. Zn(OH)₂ was prepared as follows. 15.52 g (5.22×10⁻² mol) of Zn(NO₃)₂·6H₂O (99.0%) was dissolved in 300 ml of

degassed distilled water. Upon adding 300 ml of a degassed 0.23 mol NaOH solution to the Zn(NO₃)₂ solution at 0°C, a white precipitate was obtained. The pH was finally adjusted to *ca.* 7 and continually stirred for 30 min at 0°C. The precipitate was washed three times with distilled water and then dried under reduced pressure for 24 hours at room temperature.

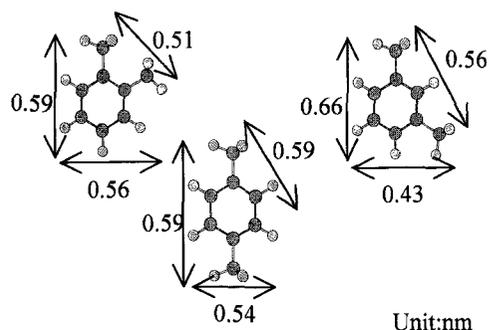


Figure 1 The size of xylene isomers.

2.2 Preparation of Hydroxy Double Salt [13]

15.52g (5.22×10⁻² mol) of Zn(NO₃)₂·6H₂O (99.0%) was dissolved in 80 ml of degassed distilled water. Upon adding 80 ml of degassed 0.86 mol NaOH solution to the Zn(NO₃)₂ solution with continued stirring for 30 min at 0°C, a white precipitate was obtained. The precipitate was washed three times with distilled water and then dried under reduced pressure for 24 hours at room temperature. Preparation of Hydroxy Double Salt (HDS) was confirmed by XRD patterns.

2.3 Preparation of organic-inorganic nanohybrid

All organo derivatization reactions of Zn(OH)₂ were carried out in a CO₂H/OH ratio of 0.5. The organo derivatization reactions of HDS were carried out using 3.2×10⁻⁴ mol of carboxylate and 1.6×10⁻⁴ mol of Zn-HDS in a 5 ml of mixed solvent, such as acetonitrile,

and 15 ml of distilled water, for 6 h under stirring at 60°C. After the reaction, the reaction products were filtered, washed to remove any unreacted carboxylic acid and impurities, and dried under reduced pressure at room temperature.

2.4 Adsorption on nanohybrids

0.05g of organic-inorganic nanohybrid was reacted with 3 ml of xylene mixtures (*o*-: *m*-: *p*-=1:1:1) for a few hours at room temperature. The adsorption media was dissolved in 1mol HCl, and the xylene isomers were extracted using cyclohexane.

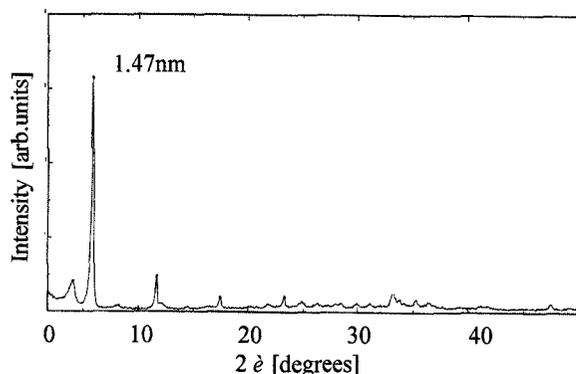


Figure 2 XRD pattern of reaction product of zinc hydroxide with crotonic acid.

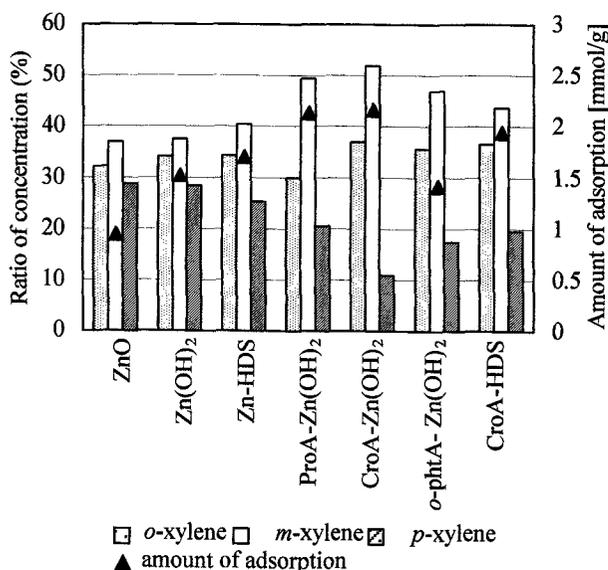


Figure 3 Selectivity on adsorbed xylene isomers and the amounts of the adsorption at room temperature for 4 h

3. RESULTS AND DISCUSSION

The XRD pattern of the reaction product of zinc hydroxide with crotonic acid was shown in Fig.2. The layered structure having a *d*-value of 1.47 nm was

confirmed. Moreover, Table 1 shows that the *d*-spacing and surface properties of these reaction products. These compounds are expected as the adsorbent because they have high surface areas.

Organic-inorganic nanohybrids are good adsorption medium because the amounts of adsorption are about 1.5-2.5 times larger than those of inorganic nonporous compounds. The layered compound is considered to be a porous material with a high surface area. In addition, for an adsorption medium intercalating organic carboxylic acid, layer expansion was attained and it is expected that the adsorption amounts increase due to the expansion of the pore structures. When nonporous inorganic compounds were used as the adsorption medium, there was no selectivity on the adsorption of the *o*-, *m*-, *p*-xylene mixtures. In the case of organic-inorganic nanohybrids, the amount of adsorption of *m*-xylene increased, and that of *p*-xylene decreased. The selectivity of the adsorbed xylene was confirmed as *o*-37%, *m*-52%, *p*-11% for the nanohybrid obtained by the reaction of zinc hydroxide with crotonic acid. It is considered that the affinity of the xylene molecule to the organic compounds between layers and large pore size of the nanohybrids are important.

It is considered that the micropore of organic-inorganic nanohybrids have the ability to attain selective adsorption. In the case of nanohybrids which intercalated different size organic molecule, it is distinct difference on the adsorption ability. Xylene molecules are trapped on the internal micropore due to sterically bulky structures compared to benzene. On the other hand, benzene is possible to go in and out from the internal space of micropore. Therefore, benzene could not be adsorbed so much. In consequence, xylene molecules were adsorbed more than benzene.

The influence of time on the adsorption of the xylene mixtures was examined for an organic-inorganic nanohybrid obtained by the reaction of zinc hydroxide with crotonic acid. The *p*-xylene isomer was adsorbed less than the other isomers. It is considered that *p*-xylene escaped easily from the micropores and then was adsorbed on the surface of the layered compound.

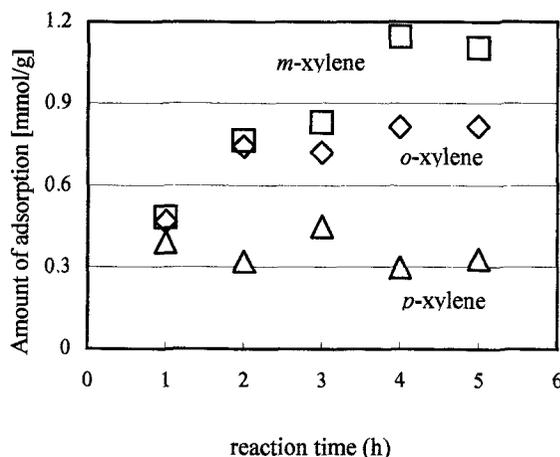


Figure 4 The effect of time on the adsorption of the xylene isomers at room temperature for 1-5 hours.

The influence of temperature on the adsorption of the xylene mixture was examined. The amount of adsorption decreased with an increase in adsorption temperature. The selectivity of the adsorbed xylene was disappeared with an increase in adsorption temperature., and theoretical results were obtained.

As the next step, information on the physical characteristics of the reaction products of zinc hydroxide with crotonic acid was obtained by measuring pore size distribution. It is confirmed from pore distribution that the nano hybrid has pore of 0.6 nm and 0.9 nm. It seems that the pore of 0.9 nm corresponded to distance between layers. The pore of 0.6 nm equivalent to the size of xylene. It is considered that the pore of 0.6 nm becomes the main factor when the xylene molecules were separated according to the size of xylene molecules.

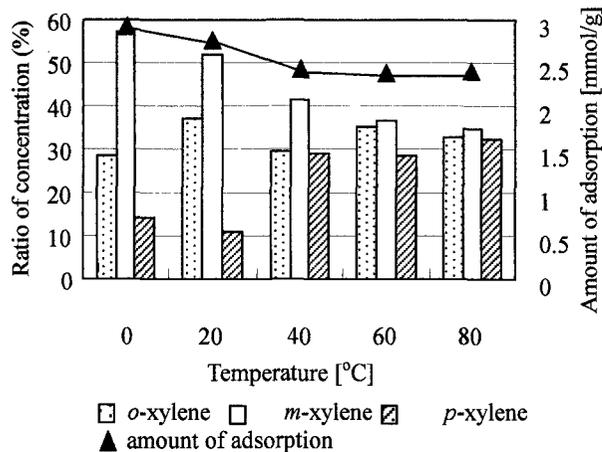


Figure 5 The influence of temperature of zinc hydroxide-crotonic acid on the adsorption of the xylene isomer and amount of adsorption at 0-80°C for 4 hours.

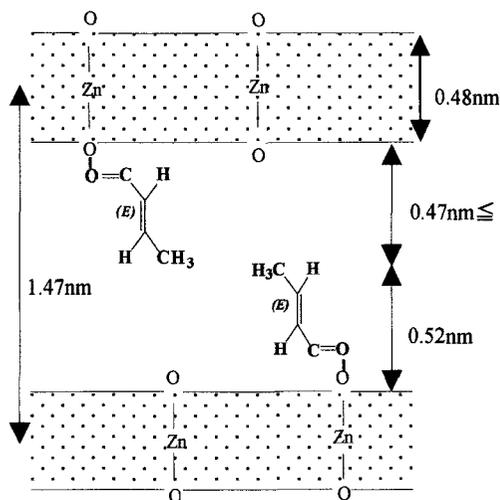


Figure 6 The image figure that interlayer spacing of zinc hydroxide-crotonic acid nano hybrid.

Furthermore, the reaction product of zinc hydroxide with propionic acid was used because the nano hybrid has the pore of around 0.6 nm. The pore size was considered from the size of organic compound and the interlayer spacing measured by XRD pattern. However, pore size distribution suggested no proof of the presence of pore of around 0.6 nm. This result suggests that it is difficult to predict and control the size of pore in the organic-inorganic nano hybrids with different interlayer spacing and size of an organic molecule. It was also confirmed that HDS-maronic acid nano hybrid had the pore of around 0.6 nm. Therefore, it is expected that HDS-maronic acid nano hybrid could adsorb xylene molecules selectively. The amount of adsorption on HDS-maronic acid nano hybrid is larger than those of other nano hybrids. It might be due to a large surface area. It was considered that the nano hybrid could have ability to adsorb *m*-xylene at 0°C, although the selective adsorption and the amounts of adsorption decrease with an increase in adsorption temperature as shown in Figure 7. The tendency is also observed for typical adsorbent.

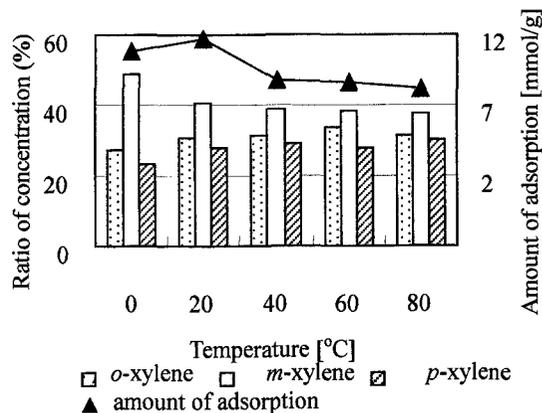


Figure 7 The influence of temperature of HDS-maronic acid nano hybrid on the adsorption of the xylene isomer and amount of adsorption at 0-80°C for 4 hours.

4. CONCLUSION

When nonporous inorganic compounds were used as the adsorption medium, there was no selectivity for the adsorption of the *o*-, *m*-, *p*-xylene mixtures.

The selectivity on the xylene molecules was confirmed as *o*-37%, *m*-52%, *p*-11% for the reaction product of zinc hydroxide with crotonic acid.

The influence of the reaction time on the adsorption of the xylene mixtures was confirmed for a complex of zinc hydroxide-crotonic acid nano hybrid. The *p*-xylene isomer was adsorbed less than the other isomers. It is considered that *p*-xylene easily escaped from the pores and then was adsorbed on the surface of the layered compound.

The zinc hydroxide-crotonic acid nano hybrid has small pores of 0.6 nm which was confirmed by the pore distribution measurement.

Organic-inorganic layered nano hybrids have a high surface area as porous materials. It was confirmed that the adsorption amount on the nano hybrids was high

compared to the inorganic nonporous compound. The selective adsorption of the *o*-, *m*-xylene isomers on the hybrids was improved for the zinc hydroxide-crotonic acid nanohybrid.

REFERENCES

- [1] Y. You, H. Zhao G. F. Vance, *J. Mater. Chem.*, 12, 907 (2002)
- [2] J. W. Johnson, A. J. Jacobson et al., *J. Am. Chem. Soc.*, 111, 381 (1989)
- [3] M. Ogawa, K. Kuroda, *Chem. Rev.*, 95, 399 (1995)
- [4] M. Inoue, H. Kominami, Y. Kondo and T. Inui, *Chem. Mater.*, 9, 1614, (1997)
- [5] A. C. Recoura, R. Hebd, *Seances Acad. Sci.*, 132, 1414, (1901)
- [6] W. Feitknect, K. Maget, *Helv. Chem. Acta.*, 32, 1653 (1949)
- [7] W. Stählin, H. R. Oswald, *J. Solid State Chem.*, 2, 252 (1971)
- [8] M. Meyn, K. Beneke G. Lagaly, *Inorg. Chem.*, 32, 1209 (1993)
- [9] H. Morioka, H. Tagaya, M. Karasu, J. Kadokawa, K. Chiba, *J. Solid State Chem.*, 117, 337 (1995)
- [10] H. Tagaya, H. Morioka, M. Karasu, J. Kadokawa, K. Chiba, *Supramolecular Science*, 2, 33 (1995)
- [11] H. Morioka, H. Tagaya, M. Karasu, J. Kadokawa, K. Chiba, *J. Solid State Chem.*, 117, 337, (1995)
- [12] H. Tagaya, H. Morioka, M. Karasu, J. Kadokawa, K. Chiba, *Supramolecular Science*, 2, 33 (1995)
- [13] M. Meyn, K. Beneke, G. Lagaly, *Inorg. Chem.*, 32, 1209 (1993)

(Received December 10, 2005; Accepted March 13, 2006)

Table 1 The interlayer spacing and surface properties of various organic-inorganic monohybrids.

Host	Guest	interlayer spacing (nm)	$d_{average}$ (nm)	$S_{Langmuir}$ (m ² /g)	V_p (cc/g)
Zn(OH) ₂	propionic acid	1.40	0.97	101.0	0.0451
	crotonic acid	1.47	0.90	83.4	0.0375
	<i>o</i> -phthalic acid	1.53	0.89	27.2	0.0126
Zn-HDS	maronic acid	0.96	0.90	318.4	0.0292
	crotonic acid	1.48	1.14	68.8	0.0327

$d_{average}$: SF Method Pore Diameter

$S_{Langmuir}$: Langmuir Surface Area

V_p : SF Method Pore Volume