

Enhancement of Conversion and Selectivity by Unsteady-state Operation in Shape-Selective Synthesis of 2,6-Dimethylnaphthalene with ZSM-5

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ABSTRACT

In order to enhance the conversion in shape-selective methylation of 2-methylnaphthalene with HZSM-5 for synthesizing 2,6-dimethylnaphthalene, an important precursor of high performance polyester, a novel reaction method with unsteady-state operation is proposed. From comparison with conventional steady-state reaction method, the unsteady-state reaction method with adsorption at a low temperature and subsequent flush at somewhat elevated temperature was very effective for enhancing the conversion drastically. This new reaction method, named Low Temperature Adsorption and Flush (LTAF) method, made it possible to increase the conversion up to more than 70% without losing shape-selectivity, whereas, by conventional steady-state reaction method, the conversion remained at 10 to 20% level due to restricted diffusion of naphthalene-ring compounds in the HZSM-5 pore. The applicability of the unsteady-state LTAF reaction was shown by methylation of methylbiphenyl with SAPO-11.

1. INTRODUCTION

Shape-selectivity is one of the characteristics of zeolite reaction and utilized for selective synthesis of a particular isomer product beyond the restriction of thermodynamic equilibrium. Synthesis of *p*-xylene by methylation of toluene is a typical example of the shape-selective reaction. 2,6-Dimethylnaphthalene (2,6-DMN), one of ten dimethylnaphthalene isomers, is also expected to be synthesized by the shape-selective methylation of naphthalene or 2-methylnaphthalene with a suitable zeolite.

2,6-DMN is an important precursor of 2,6-naphthalenedicarboxylic acid which is used as a monomer of polyethylenenaphthalate (PEN) or liquid crystal polymer(LCP). PEN is a high-performance polyester which possesses properties, such as tensile

strength, heat resistance, gas barrier property and stability against X-ray, higher than those of polyethyleneterephthalate (PET). PEN has been utilized for many purposes such as photo base-film, high-density digital data storage tape, and heat-resistant thin films for high performance use. Furthermore, PEN is suitable for gas-barrier bottles, especially returnable (reusable) bottles for beer or other carbonic acid containing beverages, which serve for the reduction of hydrocarbon consumption and wastes.

However, 2,6-DMN has been produced from a benzene-ring compound by a synthesis route with many reaction steps. This route includes a reaction step which needs an alkali metal catalyst and a large quantity of organic solvent. In order to establish a "green" synthesis route of 2,6-DMN with less reaction steps and less reaction wastes and consequently to lower the cost of PEN, it is desirable to develop a new process in which naphthalene or 2-methylnaphthalene is directly methylated to 2,6-DMN over a solid catalyst with a high selectivity and a high conversion.

Although many investigations have been conducted for the methylation of naphthalenes, a high selectivity and a high conversion have not been compatible yet. With zeolites such as Y-faujasite or mordenite, which have pore size larger than that of MFI, conversion of the methylation could be high, but selectivity was low (Ebitani et al., 1987). With MFI type zeolites such as ZSM-5, on the other hand, a high 2,6-DMN selectivity was found, but conversion remained at only 10 to 20% (Fraenkel et al., 1986; Komatsu et al., 1994; Weitkamp and Neuber, 1991). This incompatibility has been widely thought inevitable because the size difference between beta, beta-DMN such as 2,6-DMN and other DMN isomers such as 1,6-DMN is so small that the shape-selectivity can be obtained only with an MFI type zeolite whose pore size is almost equal to the size of 2,6-DMN, therefore, molecular diffusion in the pore is extremely restricted. In order to develop the utilization of PEN widely, this incompatibility should be overcome, but a research for enhancing the conversion of the shape-selective reaction is still lacking.

Therefore, the main objective of this study is to investigate how the shape-selective methylation of 2-methylnaphthalene with ZSM-5, an MFI-type zeolite, should be performed for obtaining a high conversion. Firstly, the methylation is conducted in a fixed bed under a steady-state condition as usual, and the effect of reaction parameters on the methylation performance is investigated. Then, in order to overcome the restriction in this reaction, a new, unsteady-state reaction method is applied and the effect and nature of this reaction is investigated.

2. EXPERIMENTAL

2.1. Catalyst and feed materials

As the catalyst of MFI-type zeolite for the shape-selective methylation of 2-methylnaphthalene, HZSM-5 with Si/Al atomic ratio 25 was used. The HZSM-5

crystal size was about 50nm judging from FE-SEM observation and the width of X-ray diffraction main peaks. The HZSM-5 was in the form of pellet with 1.6mm diameter and 3 to 5 mm length. The content of HZSM-5 and alumina binder in the pellet catalyst were 80 and 20 wt%, respectively.

As the feed materials, pure grade 2-methylnaphthalene (2-MN), 1,3,5-trimethylbenzene (mesitylene) as solvent and methanol as the methylation reagent produced by Wako Chemicals (Tokyo) were used. They were mixed and the mixture liquid was fed to the reactor with a syringe pump.

2.2. Reaction equipment

As a fixed bed reactor, a stainless steel tube of 14mm in diameter and 360mm in length was used and installed in an infrared ray furnace. The temperature of the reactor was controlled by a programmable controller so that rapid temperature increase in the catalyst bed was possible. 1 to 9g of the catalyst pellet was packed in the central part of the reactor tube. The upper part of the tube was pre-heating zone which consisted of quartz wool. Nitrogen as carrier gas and feed liquid were separately introduced into the entrance of the pre-heating zone, and the feed liquid was vaporized and mixed with the nitrogen. To the lower end of the reactor tube, a glass receiver was connected. This receiver was cooled by ice/water for recovering the methylation liquid products. Gas was collected with a gas bag.

2.3. Reaction procedure

Two kinds of reaction manner, i.e. the steady-state and the unsteady-state reaction methods, were used. The steady-state reaction was performed as usual fixed bed reaction at a constant reactor temperature with the continuous feed of reactants during all the time period of experiments.

On the other hand, the unsteady-state reaction was performed as follows. In the first step, a certain amount of liquid feed material was introduced to the reactor at a temperature which was much lower than 623 to 723K, usual alkylation temperature range, but sufficient for the vaporization of 2-MN. As this feed temperature, 473 to 503K was chosen in this study. After the liquid feed was finished, as the second step, the reactor temperature was immediately raised to a stripping temperature. The stripping temperature was 573 to 723K in this study. The time for raising temperature was 4 to 25 minutes. After reaching the stripping temperature, the reactor temperature was kept constant for 5 to 60 minutes. In this second step, no reactant or methylation reagent was introduced, and only nitrogen was continuously introduced as the carrier gas.

This two-step unsteady-state reaction method is quite different from the conventional steady-state fixed bed reaction. In the first step, 2-methylnaphthalene and methanol are adsorbed in the ZSM-5 pore at a low temperature. In the second step, the molecules flush out of the ZSM-5 pores due to the temperature rise. If the molecules are

methylation products, the reaction should have been performed in the pore at a temperature between adsorption and flush. This two-step operation may be called Low Temperature Adsorption and Flush (LTAF) method and can be conducted repeatedly. Therefore, the LTAF reaction is an unsteady-state reaction method with temperature-swing.

3. RESULTS AND DISCUSSION

3.1. Effect of reaction parameters on the steady-state methylation of 2-MN

In a usual catalytic reactor, conversion is increased with reaction parameters such as reaction temperature or vapor-catalyst contact time. Therefore, the effect of these parameters on the reaction rate or conversion in the 2-MN methylation with HZSM-5 was investigated in the fixed bed reactor by steady-state operation.

Fig.1 shows the effect of the reaction temperature on the reaction rate constant. In a low temperature range, the reaction rate constant was increased with the temperature, but there was a limit to the increase in the rate constant when the temperature reached about 600K. At higher temperatures, the reaction rate constant was not increased. This result is in good agreement with that by Fraenkel et al. (1986).

Fig.2 shows the effect of contact time, i.e. residence time of the reactant vapor in the fixed bed of HZSM-5, on the conversion. In this study, the conversion is defined as methylnaphthalene conversion, and, therefore, isomerization of 2-MN to 1-MN is not included in the conversion. It is seen in the figure that the conversion was not increased much with the increase in the contact time.

These usual ways for enhancing the conversion were not effective in this shape-selective methylation. Moreover, as shown in Fig.3, it was found that most of methanol fed to the reactor was converted to hydrocarbons such as ethylene, propyl-

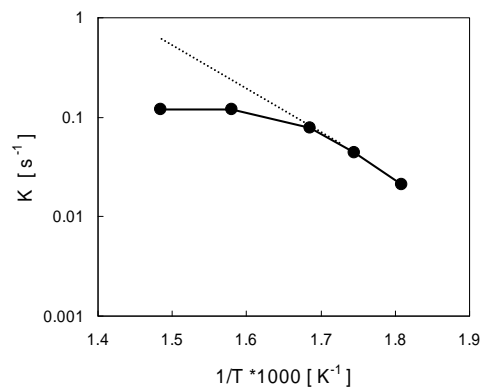


Fig.1 Effect of reaction temperature on the reaction rate constant in the steady-state methylation at 673K

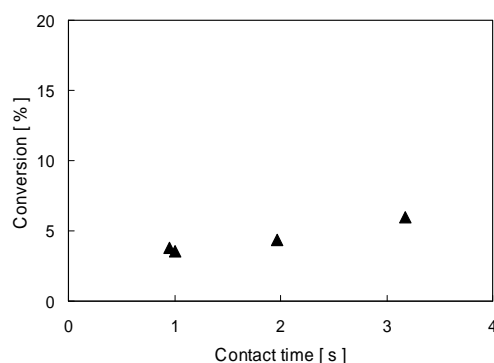


Fig.2 Effect of contact time in the fixed bed on the conversion in the steady-state methylation at 673K

ene and propane, C_4^+ -hydrocarbons and aromatic compounds and very small amount of unreacted methanol or dimethylether(DME) remained at the outlet of the reactor. Under this condition, longer contact time resulted in lowering the 2,6-DMN selectivity and promoting side reaction of methylating reagent (Tsutsui, 2000). This side reaction of methanol to light hydrocarbons is known as methanol conversion over solid acid catalyst (Chang and Silvestri, 1977; Ono and Mori, 1981). It is understood that the methanol conversion proceeded much faster than the methylation of 2-MN which is restricted by diffusion in the ZSM-5 pores. Therefore, it would be necessary to eliminate the methanol conversion for increasing the methylation conversion.

3.2. Methanol conversion and 2-MN methylation at a low temperature with HZSM-5

To investigate the effect of temperature on the methanol conversion over HZSM-5, experiments of methanol conversion were carried out in the steady-state manner. As shown in Fig.4, C_1 - C_4 hydrocarbon gas and aromatic compounds such as toluene, xylene, trimethylbenzene were major products at the temperature higher than 540K. At 500-530K, the yield of hydrocarbon gas and aromatic compounds was very low, and the major product was DME. Since

DME has the same methylation activity over HZSM-5 as methanol (Tsutsui, 2000), it was thought a temperature lower than 540K might be an adequate condition for methylation of 2-MN without causing extreme loss of methanol due to the methanol

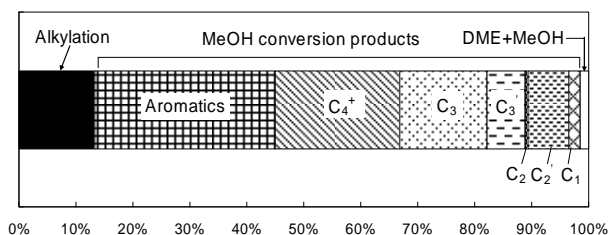


Fig.3 Distribution of methanol carbon in the product at the outlet of fixed bed reactor by the steady-state methylation at 673K

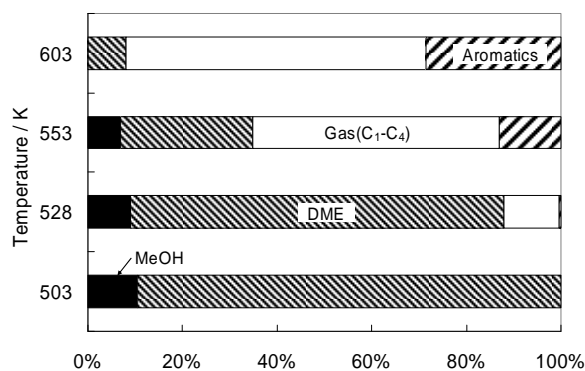


Fig.4 Effect of temperature on the yields in methanol conversion over HZSM-5

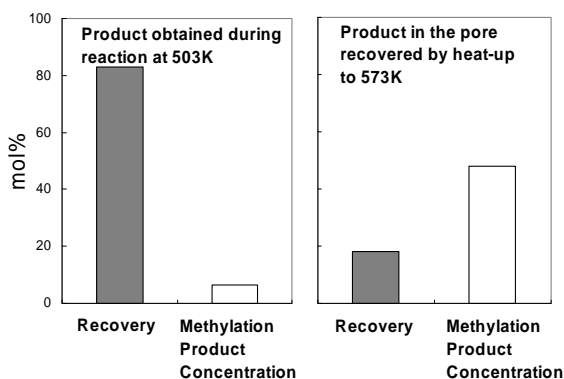


Fig.5 Methylation product recovery rate and concentration of methylated product in the naphthalene compounds obtained during the steady-state reaction at 503K and during stripping by heating-up to 573K

conversion.

Therefore, the steady-state methylation of 2-MN was performed at 503K, at which the methanol conversion to hydrocarbons would be suppressed. As shown in the left figure of Fig.5, the percentage of methylated product to total naphthalene compounds were found only 6-7 mol% in the product oil obtained during the reaction. It was also found that about 80 mol% of the naphthalene compounds fed to the reactor were recovered in this oil and about 20 mol% was missing. Then, the temperature of the HZSM-5 catalyst in the reactor was raised to 573K keeping the nitrogen flow rate as during the reaction to strip the possibly existing compounds in the pore. As shown in the right figure in Fig.5, the missing 20 mol% could be recovered, and, surprisingly, it was found that nearly 50 mol% of naphthalene compounds was methylated products in this stripped oil. This finding led to a new concept of unsteady-state reaction method, i.e. LTAF reaction.

3.3. Effect of LTAF (Low Temperature Adsorption and Flush) method on the shape-selective methylation of 2-MN with HZSM-5

(1) Effect of LTAF method compared with steady-state method

In order to investigate the effect of unsteady-state LTAF method, four experiments were carried out. As shown in Fig.6, run A and D were steady-state methylation for 3h with continuous feed at constant temperature of 573K and 503K, respectively. Feed rate of 2-MN and MeOH were 0.47 and 0.30g/h, respectively, and the amount of HZSM-5 catalyst was 3.0g. Run C was a LTAF methylation in which the feed and adsorption temperature was 503K and the flush temperature 573K. The ratio of the feed 2-MN and methanol to the pore volume of ZSM-5 (F/PV) was about 0.5 g/cm³, and time length for the feed and the temperature rise were 30s and 25min., respectively. Run B was a steady state reaction at 573K with the same feed condition as that in the LTAF method; i.e. the same feed amount (F/PV) and the same feed time length as

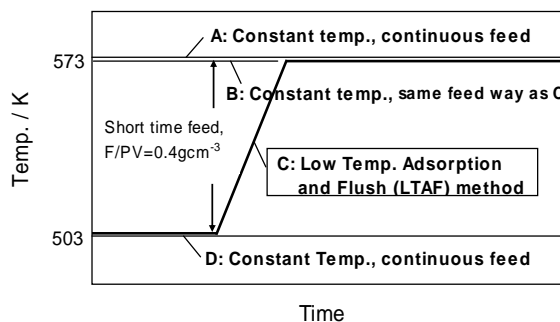


Fig.6 Operation diagram of 2-methylnaphthalene methylation by LTAF and steady-state reaction methods

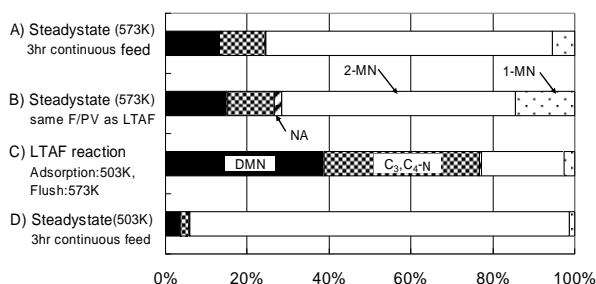


Fig.7 Comparison of product yields in methylation of 2-methylnaphthalene with HZSM-5 by LTAF and steady-state reaction methods

those in run C.

Fig.7 represents the results of these runs. The summation of DMN, C₃-, C₄-N (trimethyl-, ethylmethyl-, and tetramethyl- naphthalene), and NA (naphthalene) yields correspond to MN conversion. LTAF reaction (run C) showed the highest conversion of about 78 mol%. In steady-state reaction at 573K (run A, B), MN conversion was about 25mol%, even with the same feed quantity and method as in LTAF (run B). Steady-state reaction at 503K (run D) gave only 6mol% conversion. From this comparison, effect of adsorption at a low temperature is clear. Especially, the difference between run C and B verifies that only low F/PV value does not cause an enhanced conversion but the adsorption at a low temperature in the pore is essential for LTAF. The possible question that the high conversion in LTAF reaction could be only the result of reaction after the temperature reached the stripping temperature is clearly denied.

(2) Effect of F/PV

In order to clarify the effect of adsorption in the ZSM-5 pore on the LTAF reaction, experiments were carried out with various ratios of the 2-MN and methanol feed quantity to the pore volume (F/PV). In these experiments, the feed temperature and

As shown in Fig.8, the MN conversion was increased with decrease in F/PV. For F/PV less than 1g/cm³, the conversion was at a high level, but when F/PV was larger than 1g/cm³, the conversion was decreased towards the level by steady-state reaction. This means that only the reactant molecules adsorbed in the ZSM-5 pore can react at up to 70 to 80 mol% MN conversion by acid sites in the pore during the time before flushing out by increased temperature, and, on the other hand, excess molecules which

stripping temperature were 503K and 573K, respectively.

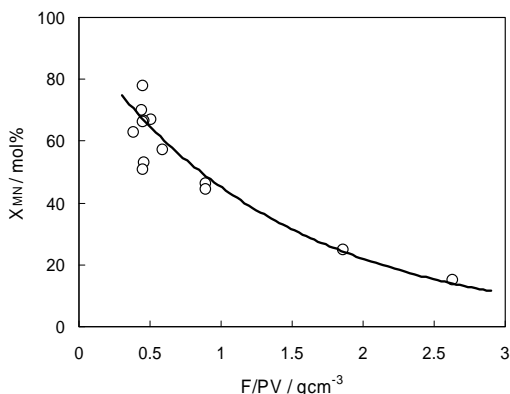


Fig.8 Effect of the feed material quantity per HZSM-5 pore volume, F/PV, on methylnaphthalene conversion, X_{MN}, in methylation of 2-methylnaphthalene by LTAF reaction method

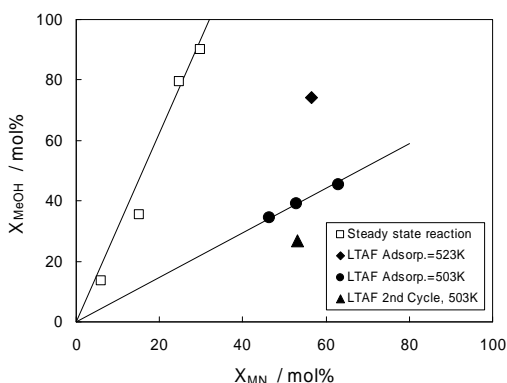


Fig.9 Relationship between methanol conversion, X_{MeOH}, and methylnaphthalene conversion, X_{MN}, in methylation of 2-methylnaphthalene with HZSM-5 by LTAF and steady-state reaction methods

stayed outside the pore are desorbed quickly by increased temperature without reacting sufficiently.

(3) Methanol conversion and MN conversion by the LTAF reaction

Fig.9 shows the correlation between the MN conversion and the methanol conversion to hydrocarbons. It is clear that the methanol conversion was remarkably reduced and MN conversion was highly enhanced by LTAF reaction compared with steady-state reaction. This means that the selectivity of methanol to methylation is much increased by the LTAF reaction. As unconverted methanol and DME can be used as the methylation reagent by the recycle, the reduction of methanol conversion can also contribute to the process economics.

Fig.10 represents the yield of 2,6-+2,7-DMN and MN conversion by LTAF compared with the reported data by the conventional steady-state reaction. It is shown in this figure that drastic increase in MN conversion and 2,6- +2,7-DMN yield was obtained by LTAF method. The selectivity to 2,6-+2,7-DMN was maintained in this increase in conversion.

As 2,7-DMN can be efficiently separated from DMN isomers by combination of distillation and adsorption technology and can be selectively isomerized to 2,6-DMN with HZSM-5 (Tsutsui, 2000; Tsutsui et al., 2002), 2,6- +2,7-DMN yield has an important industrial meaning. It is understood that very high 2,6- +2,7-DMN yield can be obtained by LTAF reaction from Fig.10. It is also shown in the figure that the 2,6-+2,7-DMN yield and selectivity were further increased when 2,4-dimethylquinoline (2,4-DMQ) was added. It is thought that this increase was due to the deactivating effect of 2,4-DMQ to acid sites on the external surfaces of ZSM-5 crystals as reported for

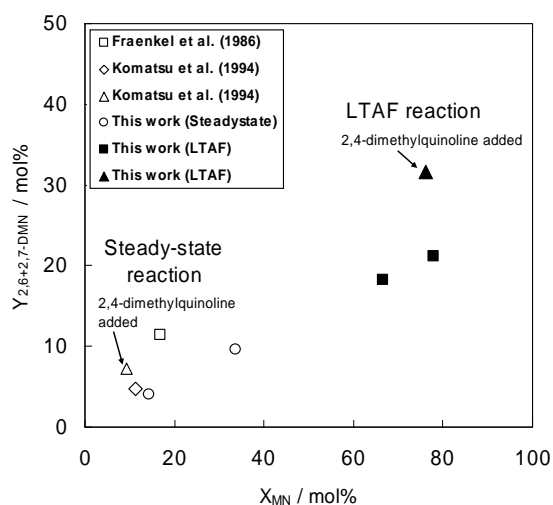


Fig.10 2,6- and 2,7-DMN yield and methylnaphthalen conversion, X_{MN} , in methylation of 2-methylnaphthalene by LTAF and steady-state reaction methods

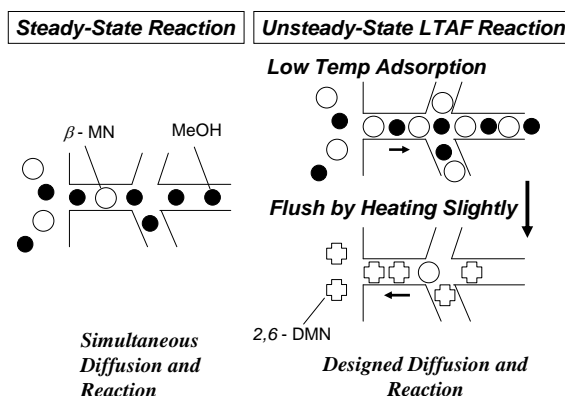


Fig.11 Conceptual scheme of molecular diffusion and reaction in the HZSM-5 pores by unsteady-state LTAF reaction method and steady-state reaction

p-xylene isomerization (Namba et al., 1984).

3.4. Significance of unsteady-state LTAF reaction

The results obtained in this study indicate the general significance of the unsteady-state LTAF reaction to promote a selective reaction in a molecule diffusion restricted reaction field such as zeolite pores. The shape-selective methylation of 2-MN in HZSM-5 pore is a typical case.

Such a reaction cannot be performed effectively in a usual, steady-state reaction method. In the steady-state reaction, the molecule diffusion rate is much less than the reaction rate at a high temperature enough to perform the reaction. Diffusivity in the zeolite pore is dependent on the molecular size (Fujikata, et al., 1998; Masuda et al, 1998). Consequently, in this case, the effective reaction rate of methylation of 2-MN is low, and side reactions such as methanol conversion proceed. It is because of excess molar ratio of methanol/2-MN in the pore due to the difference of diffusion rate. At a low temperature, not only the reaction rate is low but the molecular exchange rate between inside and outside of the pore is also very low. It means the conversion cannot be increased in the steady-state flow reactor contacting.

In the LTAF reaction, the adsorption of reactants in the designed quantities can be carried out at a low temperature unless the feed amount does not exceed the adsorption capacity. Consequently, a high amount of reactants with proper molar ratio can be introduced in the pore and excessive concentration of methanol can be prevented. When the temperature is raised, the reaction rate of methylation is increased and the partition of the methylated molecules in the pore is decreased due to thermodynamic equilibrium at the temperature. This means the molecules easily react and are desorbed from the pore. In such a case as alkylnaphthalene in HZSM-5 pore, the diffusion in the pore is so restricted that the methylation proceeds to a high conversion before desorbing from the pore. This results in the concentration of the reactants in the pores much higher than that which would be obtained by steady-state method at the increased temperature. Actually, nearly $1\text{g}/\text{cm}^3$ of reactant mixture per pore volume was reacted at a very high conversion in the pore as indicated in Fig.10. It means that very high efficiency of acid site utilization in the pore is possible. This effect of the LTAF reaction is conceptually shown in Fig.11.

Thus, an effective procedure in which a diffusion restricted reaction is promoted and an undesirable side reaction is suppressed is made possible by the unsteady-state LTAF method. This effect cannot be obtained by the conventional steady-state reaction method.

3.5. Application of unsteady-state LTAF reaction

The applicability of the unsteady-state LTAF reaction was tested in methylation of methylbiphenyl with SAPO-11. As shown in Fig,12, conversion was increased drastical-

ly as obtained in the methylation of 2-methylnaphthalene with ZSM-5. From these results, it can be said that the unsteady-state LTAF reaction is a powerful tool for enhancing the reactivity in diffusion-restricted reactions with zeolites.

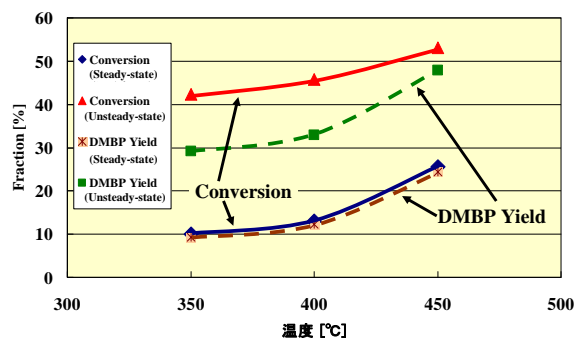


Fig.12 Comparison of conversion in methylation of methylbiphenyl with SAPO-11 by unsteady-state LTAF reaction and steady state reaction

4. CONCLUSION

An effective reaction method for enhancing conversion in shape-selective methylation with MFI-type zeolite was investigated. A remarkable enhancement of conversion was obtained without losing selectivity by a new unsteady-state reaction method with adsorption at low temperature and subsequent flush or stripping at somewhat elevated temperature (LTAF: Low Temperature Adsorption and Flush method) compared to conventional steady-state reaction.

More than 70% conversion was possible by the LTAF method in a lower temperature range than that in the conventional steady-state reaction, in which the conversion was limited at 10 to 20mol% by restricted diffusion in the MFI pores. The selectivity of methanol to methylation was remarkably increased and side reaction such as methanol conversion was reduced by this LTAF method.

The applicability of the unsteady-state LTAF reaction was shown by methylation of methylbiphenyl with SAPO-11. It is thought that the unsteady-state LTAF reaction is a powerful tool for enhancing the reactivity in diffusion-restricted reactions with zeolites.

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