

Transformation of C₉ Aromatics on Metal Loaded Mordenite

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금속담지 Mordenite 에 의한 C₉ Aromatics 전환반응

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Abstract : The catalytic activity and selectivity of metal loaded H-mordenite for transalkylation of C₉ aromatics were studied in a continuous flow fixed bed reactor under high pressure. Nickel loaded H-mordenite(T-Ni) catalyst showed high activity and slow decay of activity. Molybdenum and nickel loaded H-mordenite(T-NiMo) catalyst also showed high activity and suppressed coking of hydrocarbons. The selectivity of xylene for T-Ni and T-NiMo catalysts decreased with temperature, but that for T catalyst(commercial grade) monotonically increased with temperature within the experimental range. The performance of T-Ni and T-NiMo catalysts was better than that of T catalyst in terms of initial activity and its decay. The addition of Mo improved slightly stability of T-Ni catalyst.

요 약

C₉ aromatics 의 transalkylation 에 대한 금속담지 H-mordenite 의 촉매활성 및 선택도에 관한 실험이 고압의 연속흐름 고정층 반응기에서 수행되었다. 니켈담지 H-mordenite(T-Ni) 촉매는 높은 활성을 나타내었으며, 이 활성의 감소속도가 느렸다. 몰리브덴 및 니켈이 담지된 H-mordenite(T-NiMo) 촉매도 높은 활성을 나타내었으며, 탄화수소의 탄화를 억제하였다. T-Ni 및 T-NiMo 촉매의 선택도는 실험범위 내에서 반응온도가 증가함에 따라 감소하였지만, 상업적으로 사용되는 T 촉매의 선택도는 반응온도가 증가함에 따라 서서히 증가하였다. 촉매의 초기활성 및 활성감소 측면에서는 T-Ni 및 T-NiMo 촉매의 성능이 T 촉매보다 우수하였으며, 몰리브덴의 첨가는 T-Ni 촉매의 안정성을 다소 개선하였다.

1. INTRODUCTION

Due to the increasing demand of benzene and xy-

lene over toluene in chemical industry, catalyst for toluene disproportionation received a widespread attention during the last several decades. Chronologica-

lly, the types of catalyst developed for this reaction include Friedel-Crafts in 1940s, silica-alumina in 1960s, and zeolite type in 1970s[1].

In general, mordenite among many kinds of zeolites is known to be superior in many respects to amorphous solid catalysts[2, 3]. Aside from being thermally more stable, mordenite has a pore structure that provides it with a shape selectivity for toluene disproportionation reaction[4, 5]. Unfortunately, this pore structure is very sensitive to coking and consequently the activity decay is generally very fast[6].

Recent trend in toluene disproportionation is therefore toward the modification of mordenite to suppress the catalyst deactivation. Efforts that have been made include using aluminum deficient mordenite[1], dry and wet air treatment[5] and metal exchange[1~3, 5~7]. Generally, enhanced catalytic stability has been observed by incorporating metals with mordenite under certain conditions considered.

The transformation of C₉ aromatics into benzene, toluene and xylene(BTX) is also commercially very attractive for the utilization of relatively less valuable C₉ aromatics. Catalysts which have been employed for this reaction mostly follow those for toluene disproportionation, and essentially the same problem has been encountered, namely H-mordenites gave high initial activity and high BTX selectivity. However, a rapid deactivation due presumably to coking imposed a limitation on the use of conventional H-mordenites.

Recently, H-mordenites with various silica-alumina ratios, and with metals such as Pt, Pd, Ni, Cu and As have widely been used to improve the catalytic stability. The reader is referred to references for further details[1, 7~11].

The aim of present work is to prepare metal loaded mordenites using nickel and molybdenum, and to investigate the optimum operating conditions for these catalyst samples. The conditions are as such to cover or to be very close to the actual industrial operations. These include the variation of temperature, pressure, LHSV(liquid hourly space velocity) and the molar ratio of hydrogen to hydrocarbon. Deactivation has been

monitored for over 50 hours on stream. The parent catalyst employed for metal loading is a commercial grade of H-mordenite.

2. EXPERIMENTAL

2. 1. Catalyst preparation and characterization

H-mordenite with a silica-alumina ratio of 16 was purchased from UOP under commercial name of T catalyst. This catalyst sample was added to aqueous solution of nickel nitrate(Fisher ; $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) for eight hours at room temperature. The slurry was evaporated to paste in a rotary evaporator followed by drying in vacuum oven at 150 °C and 10 torrs for one hour. The catalyst sample thus prepared is called catalyst A hereafter. Catalyst A was washed with distilled water for one hour and dried for six hours at 120 °C followed by calcination in a tube furnace in a dry air stream for two hours at 400 °C, and another two hours at 600 °C. This catalyst sample will be referred as T-Ni catalyst.

A similar procedure was taken to incorporate molybdenum into the catalyst A, to be denoted as T-NiMo catalyst. Catalyst A was dispersed into the aqueous solution of ammonium molybdate(Fisher ; $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) for eight hours at room temperature. Dried sample was subjected to washing, drying and calcination as in the preparation of T-Ni catalyst.

The metal contents of the catalyst samples were determined from ICP(Inductive Coupled Plasma) whereas the surface area and pore size distribution were determined by BET method(Accusorb-2700, Micrometrics) and by mercury porosimeter(Pore sizer-9305, Micrometrics), respectively. The results are summarized in Table 1.

2. 2. Apparatus and experimental procedure

Reaction was carried out in a continuous flow fixed bed reactor, a stainless steel tube of 19mm i.d. and internal volume of 140 cc. Thermocouples were mounted along the tube axis for every 125 mm. Reaction

Table 1. Metal Content, Surface Area and Pore Volume in Each Catalyst

	T	T-Ni	T-NiMo
Ni (wt %)		1.4	1.1
Mo (wt %)			4.9
surface area(m ² /g)	360.0	310.2	298.4
pore area, >60 Å(m ² /g)	137.8	117.3	103.6
pore volume, >60 Å(cc/g)	0.340	0.302	0.281

temperature was controlled by external electric furnace, and the pressure by solenoid valve at the exit of the reactor.

Feed stream was obtained by continuous injection of toluene or C₉ aromatics into hydrogen stream using a micro injection pump and a gas mass flow meter. The purities of hydrogen and toluene in feed stream were respectively over 99.9% and 99.8%. The C₉ aromatics were provided by Yukong, and the composition by liquid volume % is tabulated in Table 2.

Table 2. Composition of C₉ Aromatics

components	liq. vol. %
normal propyl benzene	9.0
m/p-methyl ethyl benzene	32.8
o-methyl ethyl benzene	9.0
1, 3, 5 trimethyl benzene	12.4
1, 2, 4/1, 2, 3 trimethyl benzene	36.8

The outlet stream was separated into gas and liquid and analyzed every one or three hours. Two gas chromatographs were employed to analyze the product stream. For gaseous products, a TCD with 100/200 Carbosieve S-II column, 3 m long and 3 mm i.d., was employed. The analysis of liquid products was performed by a FID with methyl silicon capillary column, 50 m long and 0.2 mm i.d. The details of experimental set-up is schematically shown in Fig. 1.

Transalkylation of C₉ aromatics was investigated under the following conditions : LHSV=1-2.5, T=380-460 °C, P=25 bars, H₂/hydrocarbon=2.0-5.4 (molar ratio). The deactivation of catalyst samples was monitored for over 50 hours on stream at a specified

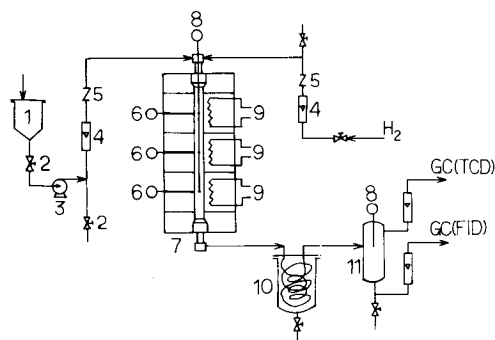


Fig. 1. Schematic diagram of experimental apparatus.

1. liquid feed tank
2. needle valve
3. Milton Roy micro pump
4. flowmeter
5. check valve
6. temperature controller
7. reactor
8. thermocouple
9. electric heater
10. ice cooled condenser
11. separator

condition : T=380 °C, P=25 bars, LHSV=1, H₂/hydrocarbon=2.0-5.4.

3. RESULTS AND DISCUSSION

Toluene disproportionation over zeolite catalysts gives benzene, xylene and a small amount of trimethylbenzene from xylene disproportionation. Light gases are formed via hydrodealkylation of toluene and aromatic ring cracking.

The product distribution from transalkylation/disproportionation of C₉ aromatics over zeolite catalysts may depend on the feed composition. BTX is the desired product, however light gases as well as C₁₀ aromatics are also formed as by-products.

Presently obtained experimental results on the catalyst performance are presented in terms of conversion, yield and selectivity. To avoid any possible ambiguity, these terms are defined as :

$$\% \text{ conversion} = \frac{\text{moles of toluene or C}_9 \text{ converted}}{\text{moles of toluene or C}_9 \text{ fed}} \times 100 \%$$

$$\% \text{ yield of } i = \frac{\text{moles of component } i \text{ formed}}{\text{moles of toluene or } C_9 \text{ fed}} \times 100 \%$$

$$\% \text{ selectivity of } i = \frac{\text{moles of component } i \text{ formed}}{\text{moles of toluene or } C_9 \text{ converted}} \times 100 \%$$

The effect of temperature on total conversion and BTX yield from C₉ aromatics are shown in Fig. 2. The total conversions for T-Ni and T-NiMo catalysts are higher by approximately 10% throughout the te-

mperature range compared to that of T catalyst. The BTX yield for T catalyst is increased with temperature, whereas ones for T-Ni and T-NiMo catalysts are decreased as the temperature goes up. Apparently, the reversed tendency is mainly due to the yield of xylene. The yield of xylene is decreasing for T-Ni and T-NiMo catalysts.

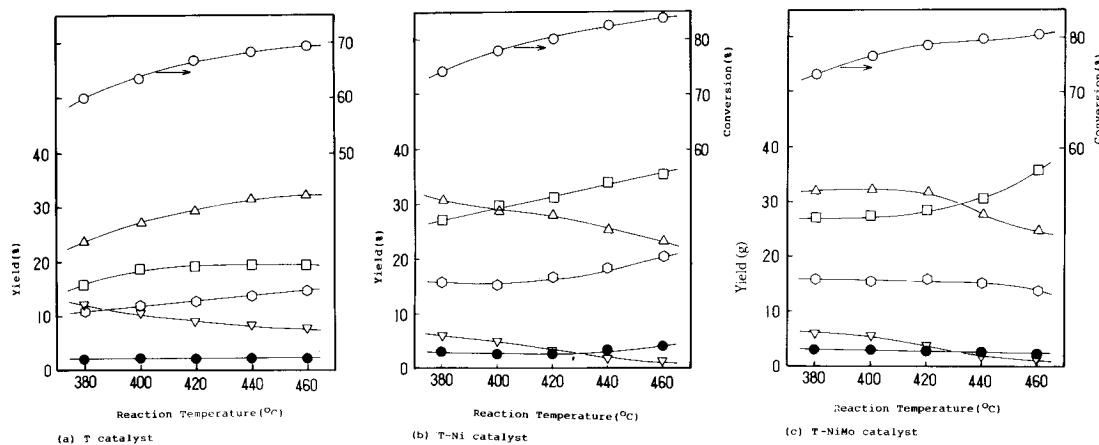


Fig. 2. Effect of reaction temperature on conversion and yield. (p=25 bar, H₂/HC mol ratio=5.4, LHSV=1.0/hr). ●; benzene, ◇; toluene, △; xylene, □; light gas, ▽; C₁₀ aromatics

The hydrodealkylation activity of T catalyst seems lower than that of T-Ni or T-NiMo catalyst. This may be seen from the data obtained at low temperature. At high temperature, BTX formed from hydrodealkylation and aromatic ring disproportionation of C₉ aromatics is subjected to aromatic ring cracking to give light gases. The aromatic ring cracking seems serious for T-Ni or T-NiMo catalyst as in the toluene disproportionation. The yield of C₁₀ aromatics was higher by 5% for T catalyst compared to those of T-Ni and T-NiMo catalysts. This is mainly due to the disproportionation of C₉ aromatics.

The effect of temperature on selectivity is shown in Fig. 3. The selectivity of xylene for T catalyst is also increased with temperature, whereas ones for T-Ni and T-NiMo catalysts are decreased as the temperature goes up. The selectivity of light gas for T catalyst stays with temperature within the experimen-

tal range. The ones for T-Ni and T-NiMo catalysts are drastically increased with temperature, and this may be due to high aromatic ring cracking and hydrodealkylation activity of these catalysts.

The yields of ethylbenzene for each catalyst were only below 3 percent(results not shown), in spite of about 42 percent methylethylbenzene(ethyltoluene) in feed. This is due to the relatively faster rates of hydrodealkylation of the ethyl groups as compared with the transalkylation of methyl groups, and consequently feeds high in ethyl groups will provide a yield distribution richer in light gas(that would result from equivalent dimethyl substituents). Thus, while trimethylbenzenes will contribute to the distribution of methyl-aromatics as a feed component with a methyl-to-phenyl ratio of three, methylethylbenzenes will a methyl-to-phenyl ratio of one. Higher yields of benzene will therefore result from methylethylbenzenes

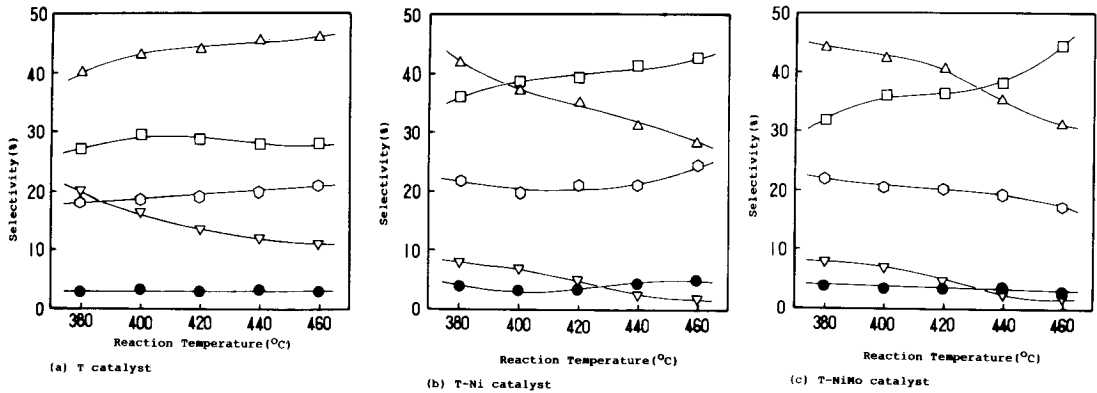


Fig. 3. Effect of reaction temperature on selectivity. ($p=25$ bar, H_2/HC mole ratio=5.4, LHSV=1.0/hr).

● : benzene, ◇ : toluene, □ : xylene, △ : light gas, ▽ : C₁₀ aromatics

than from trimethylbenzenes. Besides n-propyl benzene amount to about 9 percent in feed are hydrodealkylated almost completely for each catalyst, yielding benzene and propane from thermodynamic equilibrium[13]. The yields of benzene however stays around 4 percent throughout. Therefore, it is concluded that the benzene formed has been reacted to xylene or C₉ aromatics.

The effects of LHSV on total conversion and BTX yield were examined at a specified condition(Fig. 4). The total conversion was monotonously decreased

with LHSV for T and T-Ni catalyst, whereas it was almost constant for T-NiMo catalysts. The addition of molybdenum therefore improved stability of T-Ni catalyst on LHSV. The yield of xylene was higher by 5-10% for T-Ni and T-NiMo catalysts compared to that of T catalyst. The LHSV is an indication of the severity of the operation. The smaller the LHSV, the greater the amount of catalyst per unit feed and (other things being equal) the greater the severity. Lower space velocities increase the degree of conversion so that, for a given conversion level, lower space

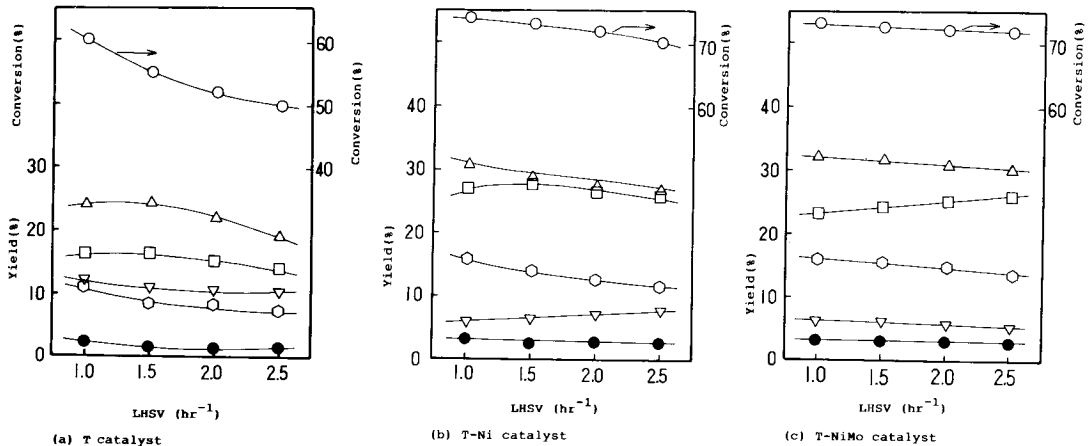
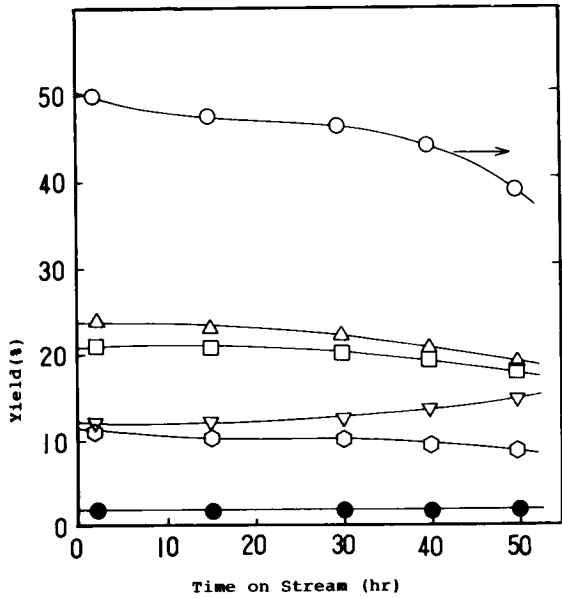


Fig. 4. Effect of space velocity on conversion and yield. ($T=380$ °C, $p=25$ bar, H_2/HC mole ratio=5.4).

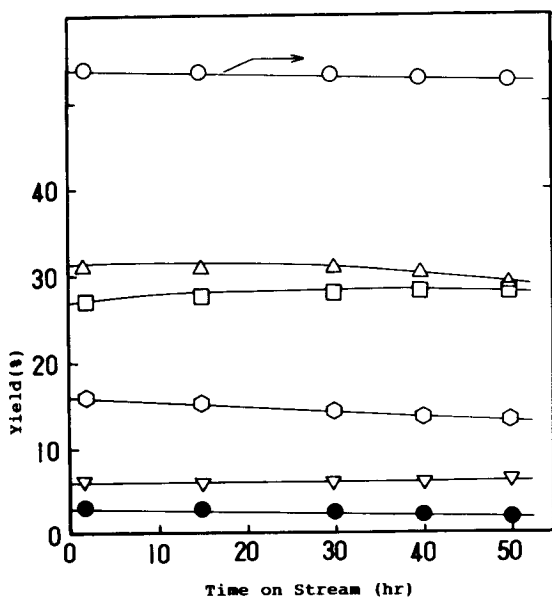
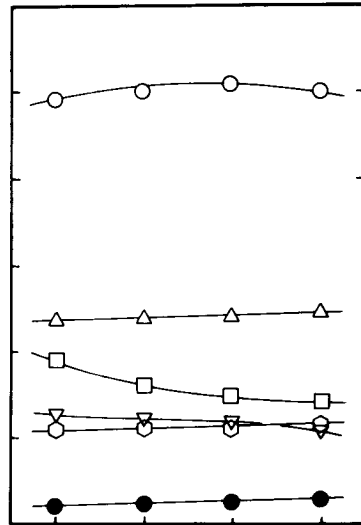
● : benzene, ◇ : toluene, △ : xylene, □ : light gas, ▽ : C₁₀ aromatics

velocities normally will require a lower reaction temperature. These trends for each catalyst were illustrated in Figs. 2 and 4. A gradual selectivity for T catalyst loss is incurred as the operating severity is raised. For T-Ni and T-NiMo catalysts, the selectivity of ben-

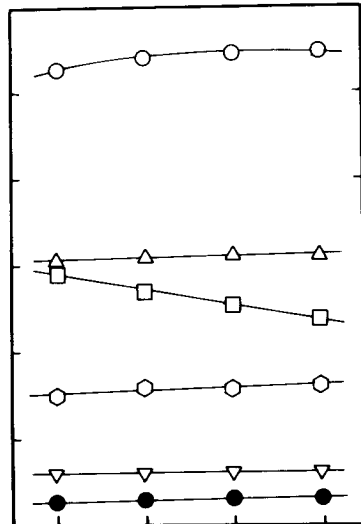
zene and xylene hardly change by operating severity. This is a consequence of the increased undesirable side reaction. The benzene through C₁₀ aromatics ring loss experienced for each catalyst is a good index of catalyst selectivity.



(a) T catalyst



(b) T-Ni catalyst



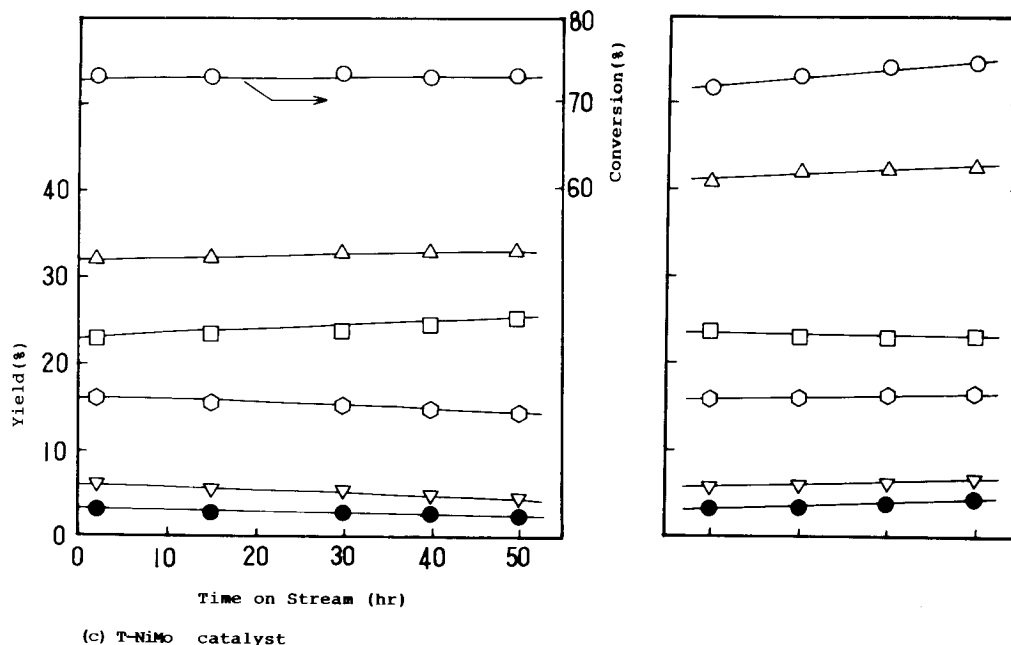


Fig. 5. Effect of activity decay of catalyst on conversion and yield. ($T=380\text{ }^{\circ}\text{C}$, $p=25\text{ bar}$, $\text{LHSV}=1.0$ /hr, H_2/HC mol ratio=5.4). ●; benzene, ◇; toluene, △; xylene, □; light gas, ▽; C_{10} aromatics

The catalyst deactivation and the yield of products were monitored for over 50 hours on stream at a specified condition: $T=380\text{ }^{\circ}\text{C}$, $P=25\text{ bars}$, $\text{H}_2/\text{C}_9=5.4$ and $\text{LHSV}=1.0$. The results are shown in Figure 5. From the figure, it is obvious that the initial activity as well as the stability of the parent T catalyst has significantly been improved by metal loading. The initial activity of T-Ni and T-NiMo catalysts is higher by approximately 13% than to that of T catalyst. In about 40 hours on stream, the activity of T catalyst shows a rapid drop, whereas the activity of T-Ni and T-NiMo catalysts stays over 95% of their initial values up to 50 hours on stream. The initial yield of xylene is approximately 24% and monotonously decreased to about 19% in 50 hours on stream for T catalyst. For T-Ni and T-NiMo catalysts, the yield of xylene hardly changes by time on stream, and the value for T-NiMo catalyst generally is higher by approximately 1–3% compared to that of T-Ni catalyst.

From Fig. 6, the catalytic activity for each catalyst

is decreased smoothly with time on stream as the mole ratio of H_2/C_9 aromatics is increased. Hydrogen decreases the deactivation of mordenites by reducing the rate of coke formation and its toxicity[5]. The positive apparent order in hydrogen found with all the mordenites can be explained by the regeneration of the active sites due to the removal of the coke deposited on the catalysts[5, 12]. The deactivation of the catalyst probably comes from coke fouling. As this is generally admitted for mordenites, coke acts by blocking the pores and not by simply covering the active sites. Indeed the deposit of a very small quantity of coke(1 wt. %) eliminates more than 95% of the activity[5]. However, the aging effect of coke strongly depends on the operating conditions: under high hydrogen pressure the aging effect is very small.

In the present experiment this was tested. The amount of coke formed on catalyst after 50 hours of streaming was measured by the weight loss after regeneration at $600\text{ }^{\circ}\text{C}$ for four hours, and the results

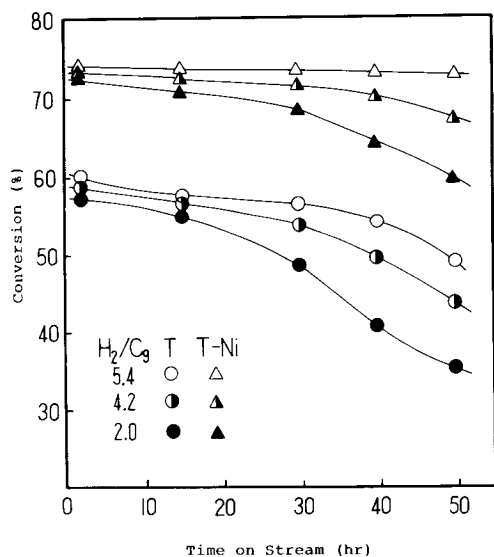


Fig. 6. Effect of hydrogen on catalytic activity. (T= 380 °C, LHSV=1.0/hr, p=25bar)

are tabulated in Table 3. The data show that the carbon content was much less in T-Ni and T-NiMo catalysts compared to that of T catalyst confirming that metal loading improves the stability by suppressing coke formation.

The effect of metal loading on mordenite may come

Table 3. Amount of Coke Formed on Catalyst after 50 hrs. Streaming

catalyst	T	T-Ni	T-NiMo
wt%	15.3	8.9	8.6

from the dual function of metal zeolites, i.e., the hydrogenation activity of metal component and disproportionation activity of acid zeolite[6, 7]. It is generally accepted that the incorporation of nickel into the mordenite is to enhance the catalytic activity via the increased surface acidity, and decrease the selectivity due to the side reaction such as hydrodealkylation and aromatic ring cracking[1].

T and T-Ni catalysts have been used to study the effect of feedstocks, which are mixture of C₉ aromatics and toluene, on transalkylation reaction. The results are shown in Table 4. An increase of C₉ aromatics in the feedstock caused a decrease in the relative consumption of toluene for each catalyst. It may be due to the dealkylation of C₉ aromatics or transalkylation of xylene and benzene to toluene.

Increased C₉ aromatics content of the feed results in increased xylene yield and reduced benzene yield as a consequence of the higher methyl/phenyl ratios. For a mixed feedstock of varying C₉ aromatics conce-

Table 4. Effect of Feedstocks on Transalkylation Reaction(380 °C, 25 bar, LHSV=1.0, H₂/HC=5.4)

% C ₉ aromatics	0		10		20		30		50		100	
	2	50	2	50	2	50	2	50	2	50	2	50
T catalyst												
benzene	+24	+19	+21	+17	+18	+15	+15	+12	+11	+9	+2	+2
toluen	-54	-42	-46	-35	-36	-25	-27	-17	-10	-6	+11	+9
xylene	+15	+12	+16	+13	+17	+13	+19	+16	+21	+18	+24	+20
C ₉	+2	+2	-6	-4	-11	-8	-17	-12	-28	-21	-60	-48
coke, wt %		11.2		11.8		13.9		14.5		14.8		15.3
T-Ni catalyst												
benzene	+19	+19	+17	+16	+15	+13	+12	+10	+8	+7	+3	+2
toluen	-65	-61	-55	-51	-44	-42	-32	-29	-17	-14	+16	+14
xylene	+16	+16	+17	+16	+18	+18	+19	+18	+21	+20	+21	+20
C ₉	+4	+3	-7	-6	-13	-11	-20	-18	-36	-34	-73	-72
coke, wt %		7.0		7.0		7.5		8.2		8.5		8.9

* '+' and '-' denote the absolute % change for each component.

ntrations the unit is operated such that the overall conversion of the toluene plus C₉ aromatics is at the desired value. Following literature[13], a higher reaction temperature is necessitated to maintain the same overall conversion (all else being the same) as the feed C₉ aromatics content is raised. Table 4 is illustrative of the effect on equilibrium yields of benzene and xylene as a function of the C₉ aromatics concentration in the fresh feed. The trends are fairly obvious and affords the refiner significant flexibility with respect to benzene and xylene production rates, to the extent that the feed methyl/phenyl ratio can be adjusted.

It was found that the more the C₉ aromatics in the feedstock, the more the coke formed for each catalyst. Considering coke formation, the optimal ratio of C₉ aromatics to toluene in feedstock is probably around 0.1 and 0.2, respectively for T and T-Ni catalysts. It was also found that the more the C₉ aromatics in the feedstock, the more the xylene formed and the less the benzene produced for each catalyst. In this case, the increase of xylene was higher in T catalyst compared to that of T-Ni catalyst. Moreover, the yield of benzene and xylene for T catalyst were higher by 2-4 % throughout the ratios of C₉ to toluene compared to that of T-Ni catalyst on 2 hours stream.

4. CONCLUSIONS

The following major conclusions were drawn from the present work. Nickel loaded H-mordenite(T-Ni) catalyst showed high hydrocracking due to its high activity and slow decay of activity. Molybdenum and nickel loaded H-mordenite(T-NiMo) catalyst also showed high activity and suppressed coking of hydrocarbons. The selectivity of xylene for T catalyst increased with temperature, whereas ones for T-Ni and T-NiMo catalysts decreased with temperature within the experimental range.

The carbon content in T catalyst after 50 hours of streaming was 15.3 wt. % and these values in T-Ni and T-NiMo catalysts were 8.9 wt. % and 8.6 wt. %,

respectively.

Considering coke formation, the optimal ratios of C₉ aromatics to toluene were 0.1 and 0.2 for T and T-Ni catalysts, respectively. The addition of molybdenum improved slightly stability of T-Ni catalyst.

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