

TOLUENE DISPROPORTIONATION OVER METAL LOADED MORDENITES CATALYTIC ACTIVITY, SELECTIVITY AND AGING

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Abstract—The catalytic activity and selectivity of metal loaded H-mordenite for toluene disproportionation was 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 T-Ni and T-NiMo catalysts were lower than that of T catalyst (commercial grade). The performances of T-Ni and T-NiMo catalysts were better than T catalyst in terms of initial activity and its decay. The addition of Mo improved slightly stability of T-Ni catalyst.

INTRODUCTION

Due to the increasing demand of benzene and xylene over toluene in chemical industry, catalyst for toluene disproportionation received a widespread attention during the last several decades. Chronologically, 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, and its pore structure provides it with a shape selectivity for toluene disproportionation reaction [4,5]. Unfortunately, this pore structure is however 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] etc.. 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 is 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. Conditions were 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 toluene. Deactivation has been monitored for over 50 hours on stream. The parent catalyst employed for metal loading was a commercial grade of H-mordenite.

EXPERIMENTAL

1. Catalyst preparation and characterization

H-mordenite with a silica-alumina ratio of 16 was

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 |

purchased from UOP under commercial name of T catalyst. This catalyst sample was added to aqueous solution of nickel nitrate [Fisher; Ni(NO₃)₂·6H₂O] for eight hours at room temperature. The slurry was evaporated to paste in a rotatory 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 here. 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 referred to T-Ni catalyst.

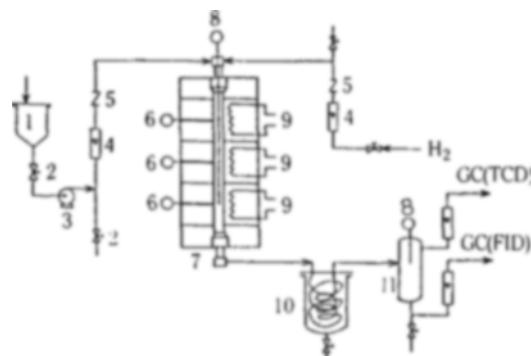
A similar procedure was taken incorporate molybdenum into the catalyst A for the preparation of T-NiMo catalyst. Catalyst A was dispersed into the aqueous solution of ammonium molybdate [Fisher; (NH₄)₆Mo₇O₂₄·4H₂O] for eight hours at room temperature. Dried sample was subjected to washing, drying and 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. Apparatus and experimental procedure

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

**Fig. 1. Schematic diagram of experimental apparatus.**

| | |
|-------------------------|---------------------------|
| 1. Liquid feed tank | 2. Needle valve |
| 3. Milton Roy micropump | 4. Flowmeter |
| 5. Check valve | 6. Temperature controller |
| 7. Reactor | 8. Thermocouple |
| 9. Electric heater | 10. Ice cooled condenser |
| 11. Separator | |

The outlet stream 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 were 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.

Toluene disproportionation was investigated under the following conditions: LHSV = 1–2.5, T = 380–460°C P = 5–35 bars, H₂/toluene = 2.0–4.2 (molar ratio). The deactivation of catalyst samples was monitored for over 50 hours on stream at a specified condition: T = 380°C, P = 25 bars, LHSV = 1, H₂/toluene = 4.2.

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.

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

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

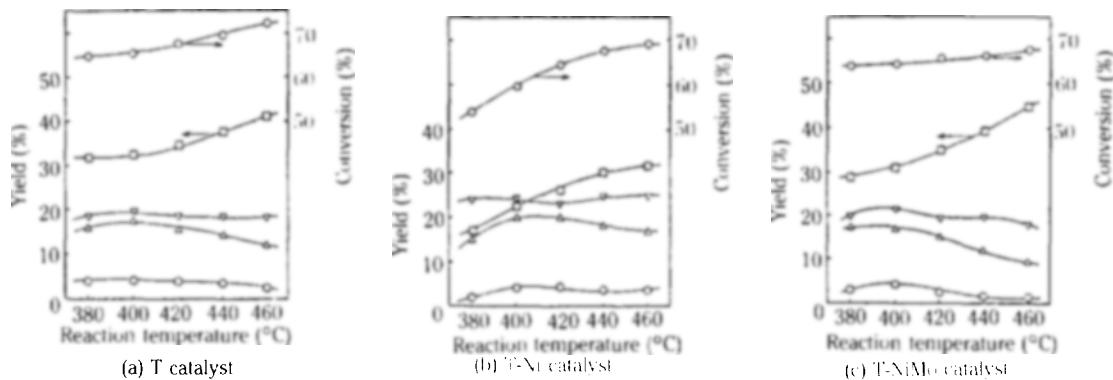


Fig. 2. Effect of reaction temperature on conversion and yield.

($P = 25$ bar, H_2/HC mole ratio = 4.2, LHSV = 1.0/hr). \blacktriangledown : benzene, \blacktriangle : xylene, \square : light gas, \circ : C_9 aromatics

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

$$\% \text{ selectivity of } i =$$

$$\frac{\text{moles of component, } i \text{ formed}}{\text{moles of toluene converted}} \times 100\%$$

The effects of temperature on total conversion and yield for each catalyst are shown in Fig. 2. The experimental conditions are given at the bottom of the figure. For three of the catalyst samples, the conversions increases monotonically with temperature within the experimental range. It is noted that the total conversions for T-Ni and T-NiMo catalysts are significantly higher compared to that of parent T catalyst. Benzene is formed from the hydrodealkylation of toluene as well as from toluene disproportionation. The yield of benzene over xylene is therefore primarily due to the hydrodealkylation which also gives identical moles of methane as well. However, the light gas formation for T-Ni and T-NiMo catalysts is several higher order compared to that of T catalyst, and is favored as the temperature goes up. Obviously, aromatic ring cracking is indicated.

Fig. 3 shows the variation of selectivity with temperature for each catalyst. The selectivities of benzene and xylene for T catalyst are relatively higher order compared to those of T-Ni or T-NiMo catalyst, with exception of that of xylene at 380°C. The selectivity of benzene for each catalyst varies little with temperature within experimental range, but that of xylene for T-Ni and T-NiMo catalysts decrease with temperature.

Aiming at higher yield of benzene and xylene, the effects of LHSV and pressure on the catalyst performance were monitored at 380°C.

The effect of space velocity on catalyst performance is displayed in Fig. 4 for each of the catalyst samples.

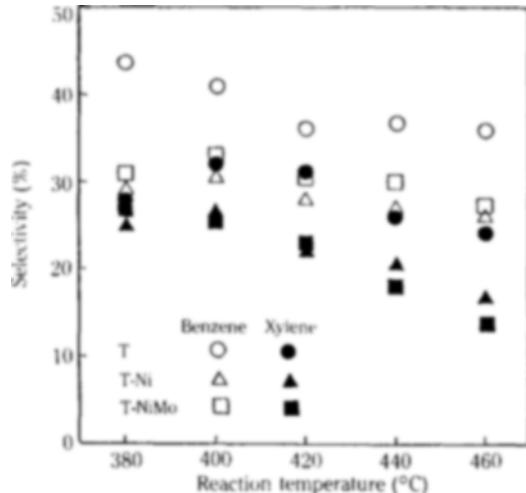


Fig. 3. Effect of reaction temperature on selectivity.

($P = 25$ bar, H_2/HC mole ratio = 4.2, LHSV = 1.0/hr)

The total conversion is notably decreased as the LHSV is increased for T-catalyst, yet no significant decrease is observed for T-Ni or T-NiMo catalyst. However, the selectivity of benzene slightly increased from 29% to 31% as the LHSV is increased for T-Ni catalyst, whereas the ones for T and T-NiMo catalysts decreased about 3% and 2%, respectively as the LHSV is increased. These values are no significant variations with LHSV within experimental range. Therefore, no limitation due to external diffusion is obvious. The yield of benzene and xylene, as expected, is decreased with LHSV, and no significant difference is seen among the catalysts. Light gas reaches a maximum at LHSV slightly above 1.5 for each catalyst.

The effect of pressure on catalytic performance is given in Table 2, Fig. 5 and 6. The molar ratio of hydrogen to toluene was 4.2. The kinetic model of

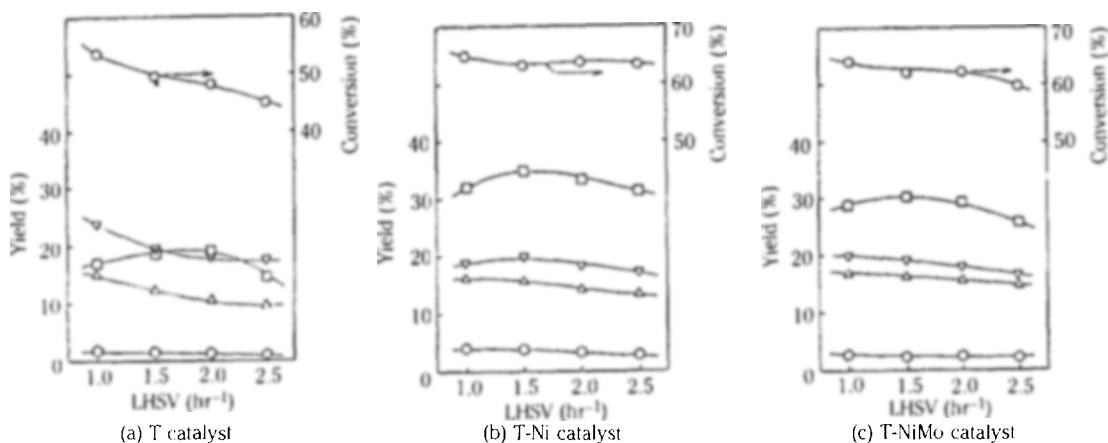


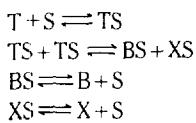
Fig. 4. Effect of space velocity on conversion and yield.

(T = 380°C, P = 25 bar, H₂/HC mole ratio = 4.2), ▽: benzene, △: xylene, □: light gas, ○: C₉ aromatics

Table 2. Effect of low pressure on catalytic activity
(T = 380°C, H₂/HC = 4.2, LHSV = 1.0/hr, 2 hr
on stream)

| Pressure (bar) | 5 | 10 | 15 | 20 | 25 |
|-----------------|------|------|------|------|------|
| Conversion (%) | | | | | |
| T catalyst | 29.0 | 43.5 | 50.5 | 53.0 | 54.0 |
| T-Ni catalyst | 35.0 | 52.0 | 60.0 | 63.5 | 65.0 |
| T-NiMo catalyst | 34.0 | 51.5 | 59.0 | 63.0 | 64.0 |

toluene disproportionation over mordenite proposed by Pukanic and Massoth [12] is as follows.



where S is the active site, T the toluene, B the benzene and X the xylenes. From this kinetic scheme, they derived the equation (1) for a low value of conversion rate (that allows one to neglect the reverse reaction and the adsorption of products) as the reaction of two adsorbed toluene molecules on adjacent site is the rate determining step.

$$r = k \left(\frac{k_T P_T}{1 + k_T P_T} \right)^2 \quad (1)$$

$$k_T = \frac{\theta_T}{P_T (1 - \theta_T)} \quad (2)$$

where r is the disproportionation rate, P_T the toluene pressure, k = k_sC_m with k_s the rate constant of superficial reaction and C_m the total concentration in active sites; k_T is equilibrium constant for toluene adsorption. The equilibrium constant k_T is a function of P_T and of

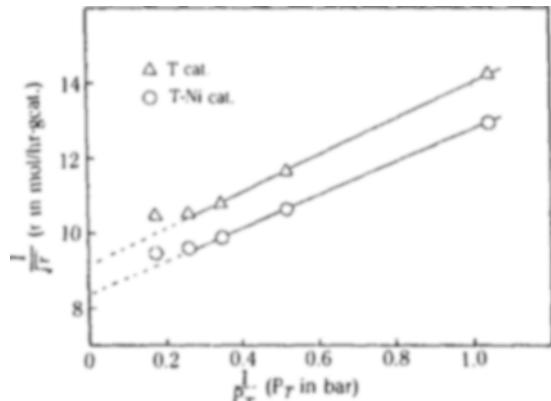


Fig. 5. Variation of the toluene disproportionation rate(r) with toluene pressure (P_T). Verification of the kinetic model proposed by Pukanic and Massoth [12].

θ_T the fraction of surface covered by toluene. Equation (1) can be written:

$$\frac{1}{\sqrt{r}} = \frac{1}{k_T \sqrt{k}} \frac{1}{P_T} + \frac{1}{\sqrt{k}} \quad (3)$$

This model predicts a linear at low level of conversion and/or with small amount of benzene and xylene. However, with a significant amount of benzene and xylene at high conversion, the reverse reaction together with adsorption of products also becomes significant. In this case, the rate equation will tend to be independent of toluene pressure and side reaction such as xylene disproportionation and aromatic ring cracking will occur. Fig. 5 obtained from Table 2 shows that equation (1) is verified for low level of conversion rate and/or with low value of pressure

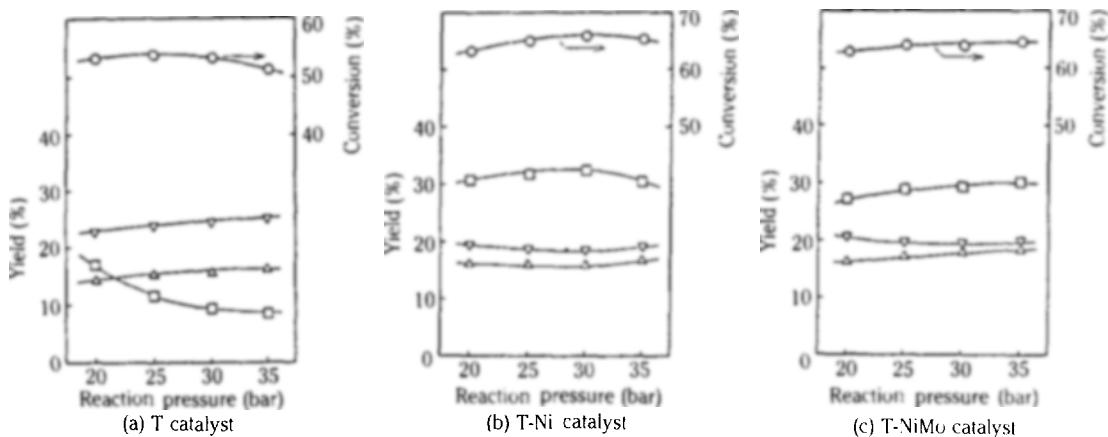


Fig. 6. Effect of reaction pressure on conversion and yield.

($T = 380^\circ\text{C}$, H_2/HC mole ratio = 4.2, LHSV = 1.0/hr), ∇ ; benzene, Δ ; xylene, \square ; light gas

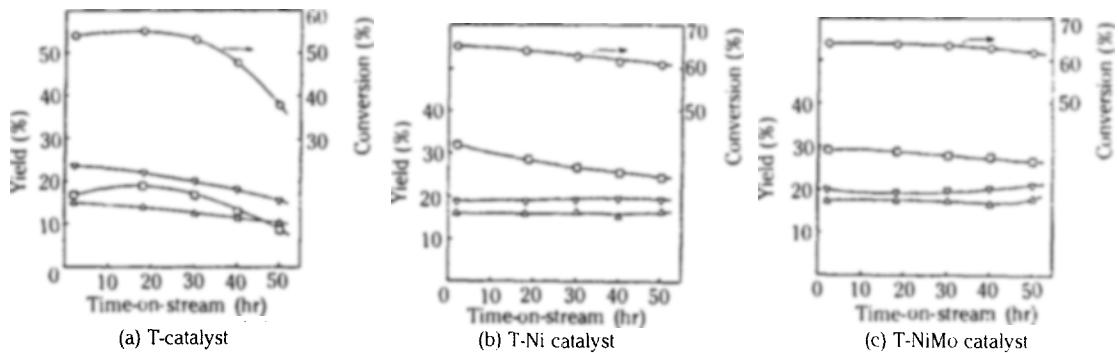


Fig. 7. Effect of activity decay of catalyst on conversion and yield.

($T = 380^\circ\text{C}$, $P = 25$ bar, LHSV = 1.0/hr, H_2/HC mole ratio = 4.2), ∇ ; benzene, Δ ; xylene, \square ; light gas

(5-20 bar). Presently obtained results generally follow the tendency described above. The results obtained from T catalyst [Fig. 6(a)] show a linearly increasing yield of benzene and xylene, whereas the ones for T-Ni and T-NiMo are almost independent of pressure. It should be noted that the total conversion for T catalyst is significantly lower compared to that for T-Ni or T-NiMo catalyst.

The light gas formation is drastically decreased with pressure for T catalyst as expected. Probably, this is due to the fact that light gas is formed from aromatic ring cracking as well as from hydrodealkylation. However, the ones observed for T-Ni and T-NiMo catalyst are not clear.

The conversion of toluene, and the yield of products as a function of time-on-stream for each catalyst are shown in Fig. 7. The results were obtained at a specified conditions: 380°C , 25 bars, LHSV = 1, and $\text{H}_2/\text{toluene} = 4.2$. 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 is higher by approximately 10% compared to that of T catalyst. In about 30 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 benzene is approximately 24% and monotonically decreased to about 16% in 50 hours on stream for T catalyst. The yields of xylene follows pretty much the same tendency, however, at a lower level. For T-Ni and T-NiMo catalysts, the yields of benzene and xylene hardly change by time-on-stream. The ones for T-NiMo catalyst generally follow the same tendency with T-Ni catalyst, and the values are higher by approximately 1-2% compared to that of T-Ni catalyst respectively.

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 re-

Table 3. Amount of coke formed on catalyst after 50 hrs streaming

| Catalyst | T | T-Ni | T-NiMo |
|----------|------|------|--------|
| wt% | 12.3 | 7.7 | 7.6 |

generation of the active sites due to the removal of the coke deposited on the catalyst [5,13]. The mechanism of toluene disproportionation involves a nucleophilic attack of the benzenium ion formed by the adsorption of a toluene molecule, forming a diphenylmethane-type intermediate. This intermediate is formed by a nucleophilic attack of a benzilic carbocation formed on a Brønsted acid site by a toluene molecule [6]. The inhibiting effect of hydrogen on toluene disproportionation can be explained quite well within the scope of this mechanism, since the formation of benzilic carbocation is produced with the elimination of a hydrogen molecule. Hence, the effect of hydrogen is to displace the equilibrium and thus to decrease the number of adsorbed benzilic carbocations as well as the toluene disproportionation rate.

The effect of metal loading on mordenite may come 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]. Under high hydrogen pressure, obtained results generally follow these tendencies for a long time (up to 50 hours on stream) in contrast with literatures [1,5,6,9] resulted by operating under low hydrogen pressure. The improvement in stability upon nickel loading is due to the assisting effect of metallic nickel for the hydrogenation and elimination of some unsaturated hydrocarbons, which otherwise would polymerize and block the active sites.

The deactivation of the catalyst probably comes from coke posioning. 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 re-

generation at 600°C for four hours, and the results 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.

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 benzene and xylene in T catalyst was higher than those in T-Ni and T-NiMo catalysts, and its yield for benzene also was higher than the latters. However, the former in the yield of xylene was somewhat lower than the latters.

The carbon content in T catalyst after 50 hours of streaming was 12.3 wt%, and these values in T-Ni and T-NiMo catalysts were 7.7 wt% and 7.6 wt%, respectively.

The performance of T-Ni and T-NiMo catalysts were better than T catalyst in terms of initial activity and its decay. The addition of molybdenum improved slightly stability of T-Ni catalyst.

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