

EFFECT OF REACTION PRESSURE AND CARRIER GAS ON TOLUENE DISPROPORTIONATION OVER MOLYBDENUM-ZSM-5 CATALYST

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Abstract

A study was conducted to evaluate the effect of reaction pressure on the toluene disproportionation reaction using ZSM-5 zeolite based catalyst impregnated with molybdenum. Results showed that there is a marked difference in toluene conversion and xylenes selectivity using nitrogen and hydrogen carrier gases and the reaction pressure. Toluene conversion under nitrogen pressure was higher than under hydrogen pressure. Toluene conversion was found to increase with increasing in pressure and temperature for both carrier gases. Deactivation of the catalysts was observed faster and greater in nitrogen as compared to hydrogen carrier gas as indicated by higher amount of coke formation.

Keywords: Toluene Disproportionation, ZSM-5, Molybdenum, Nanoporous Catalysts, Reaction Pressure, Temperature, Carrier Gas

1. Introduction

Toluene disproportionation (TDP) is a very useful reaction for converting surplus toluene into the more valuable xylenes as key raw materials for many intermediates of petrochemicals and fine chemicals [1]. Several studies have been conducted to produce better catalysts and employing less severe reaction conditions for this conversion. During this reaction, benzene

and mixed xylenes are produced. Mixed xylenes fraction consists of three isomers namely: para-xylene, ortho-xylene, and meta-xylene. The ortho-xylene and meta-xylene are processed further by isomerization reaction to produce para-xylene, which is used for the production of polyester fibers, resins, and films. Because of the growth in demand for para-xylene, new technologies are needed to convert low value aromatics into mixed xylenes and specifically into para-xylene. Several researchers have investigated different types of catalysts based on different zeolites such as Y, ZSM-5, mordenite, and MCM, and have reported the toluene conversion and xylenes selectivity [2-10]. The effect of crystal size and silicon-to-aluminum ratio of ZSM-5 has been studied along with activation method and pelletization of zeolite [2]. Catalytic activity was enhanced using lower silicon-to-aluminum ratio zeolite. IR spectroscopic measurements using pyridine revealed that during the activation step, a high H⁺ concentration in the cation exchange increases the strength of Bronsted sites, increasing the number of acid sites active in toluene disproportionation. Chaudhari and co-workers [3, 4] have investigated TDP reaction using ZSM-5 as well as Y-zeolite catalysts ion-exchanged with active metals, Ni, Pb and Cr. The reactions were carried out under atmospheric pressure and the effect of type of metal loaded, silica-alumina ratio of the zeolite, type of zeolite, and particle size were also studied. The percent p-xylene yield was found to increase after ion-exchange with active cations and the maximum p-xylene yield of 2.3 percent was obtained with Cr loaded HZSM-5 at 600 °C and 1 atmospheric pressure. Mavrodinova et al [11-14] enhanced p-xylene selectivity during TDP over several zeolite types by replacing the zeolite proton by InO⁺ cations. Tsai [15] reported a novel method using hydrogen to reactivate the active sites on coked mordenite. Recently, several researchers have focused their work on the effect of catalyst acidity on TDP conversion and p-xylene selectivity [16-19]. Al-Khattaf [20] reported that in fluidized bed using Y-zeolite, toluene conversion takes place through disproportionation reaction in trace level when the acidity of the zeolite is low. In case of Y-

zeolite having high acidity, toluene conversion favors the dealkylation and pairing reactions producing more gases.

This paper presents a systematic study using ZSM-5 based catalyst modified with metal that was loaded using impregnation method. Reactions were carried out in nitrogen and hydrogen carrier gases and at different pressure to observe the effect of these variables. The commercial process utilizes 30 bar of hydrogen pressure in the presence of zeolite based catalysts [6].

2. Experimental

2.1. Catalyst Preparation

The catalyst sample used in this study is based on ZSM-5 zeolite and loaded with molybdenum metal by impregnation. ZSM-5 was obtained from CATAL International, UK and has $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30 and a surface area of $400\text{m}^2/\text{g}$. The alumina binder used in the extrudates preparation was Cataloid AP-3 obtained from CCIC, Japan. Cataloid AP-3 contains 75.4 wt% alumina, 3.4 wt% acetic acid and water as a balance. The preparation procedure for the catalyst was as follow: The alumina binder was dispersed in water and stirred for 30 minutes to produce thick slurry. ZSM-5 zeolite was then mixed with the alumina slurry to produce a thick paste. The paste was subjected to an extruder to produce 1 mm thickness extrudates, which were dried at room temperature for 4 hours and then dried at $120\text{ }^\circ\text{C}$ for 2 hours, followed by calcinations at $500\text{ }^\circ\text{C}$ for 2 hours in a temperature programmed furnace. An aqueous solution containing hexaammonium heptamolybdate tetrahydrate was used to impregnate the extrudates with 3% Molybdenum. The metal loaded extrudates were dried at room temperature and in an oven at $120\text{ }^\circ\text{C}$, and finally calcined at $500\text{ }^\circ\text{C}$. The prepared catalyst was designated as Mo/Z.

2.2. Catalyst Characterization

The Mo/Z catalyst was characterized for surface area, porosity characteristics and acidity using Quantachrome Autosorb-1C Chemisorption- Physisorption Analyzer equipped with thermal conductivity detector. The BET surface area, pore volume, and pore size distribution were obtained from nitrogen adsorption-desorption isotherms measured at 77K. The Autosorb-1C system is equipped with high sensitivity, thermal conductivity detector and precise vacuum volumetric method for analysis of BET surface area, mesopore and micropore size distribution. The sample was outgassed and evacuated for 2 hours at 100 °C temperature and then under nitrogen flow at 350 °C for 1hour. Then, the nitrogen gas was adsorbed and desorption process was completed. At the end of the run, the system performed the necessary calculations and correlations and the complete results were produced. Acidity of the Mo/Z catalyst was carried out by temperature-programmed adsorption and desorption of ammonia in the temperature range 100 to 800 °C. The equipment was the same Autosorb-1C used for surface area measurement. A certain amount of the sample (0.19 g) was heated from room temperature to 500 °C at the rate of 20 °C/min and evacuated for 2 hours under helium flow. Then, the sample was cooled to 100 °C under helium and the flow was switched to ammonia and the adsorption of ammonia was started at this temperature that lasted for 10 minutes. Then the ammonia flow was stopped, and desorption of ammonia was carried out under helium and the sample was heated up to 800 °C at the rate of 10 °C/min. The response of the TCD was recorded as a function of desorption temperature acidity was calculated. Coke deposited on the spent catalysts was determined by the CHNS elemental analyzer Model Vario EL from Elementar, Germany. The method is based on combustion of the coke to produce carbon dioxide which is then quantified. The surface area, porosity and ammonia-based acidity characteristics of the catalyst are given in **Table 1**.

2.3. Catalyst Evaluation

The Mo/Z catalyst was evaluated in a fixed-bed reaction system at 1.5 LHSV, at nitrogen and hydrogen carrier gas pressure of 1, 5, 10, 30 and 50 bars using pure toluene as the feed. The reactions were also carried out at 30 bar pressure at three different reaction temperature 375, 400 and 425 °C to observe the effect of reaction temperature. Details of the reaction conditions used and the catalyst evaluation runs made in this study are given in **Table 2**. The procedure of catalysts testing and products analyses was as follows: Fifteen (15) ml of the catalyst was charged in the middle part of the reactor provided with inert in the upper and lower portion of the reactor. The total volume of the reactor is 50 ml. The catalyst was calcined and activated in-situ in the presence of nitrogen prior to the reaction. At 300 °C, the feed toluene was started and the temperature was raised to the desired reaction temperature. The reaction product was separated in a gas-liquid separator. Both gas and liquid samples were collected after 6 hours on stream, the time at which the reaction conditions were stabilized and the products collected were representative. Each batch of catalysts was run at a particular temperature and pressure and the run was stopped. The spent catalyst was removed and the reactor was charged with a fresh amount of catalysts and the next run was conducted at different reaction condition. A total of 14 runs were carried out to observe the effect of pressure, type of carrier gas and the reaction temperature on the activity and selectivity of the Mo/Z catalyst.

The liquid reaction products were analyzed using PIONA Analyzer based on Shimadzu gas chromatograph GC-2010 and Shimadzu auto-injector AOC-20i. The PIONA Analyzer is equipped with FID detector and autosampler. The hydrocarbon separation was carried out on 50 meter long and 0.15 mm diameter BP1PONA-M50-050 column under temperature programmed conditions. The components were separated according to their boiling points.

The components were identified using a calibration that was accomplished using a standard hydrocarbon mixture sample having the components of known composition. The composition of the gaseous product was analyzed by a Shimadzu gas chromatograph model 14B, equipped with a flame ionization detector and thermal conductivity detector. The hydrocarbons C₁ to C₅, nitrogen and hydrogen were separated on alumina PLOT, 50 meter capillary column. In gaseous samples collected, no appreciable amount of hydrocarbons were detected and thus the results are not reported.

3. Results and Discussion

3.1. Toluene Conversion

The conversion of toluene at 400 °C is plotted as a function of nitrogen and hydrogen pressure of 1, 5, 10, 30 and 50 bars and is shown in **Fig. 1a**. The plot shows the conversion of toluene increased with increase in reaction pressure for both nitrogen and hydrogen. In the presence of nitrogen, higher toluene conversion was found as compared to hydrogen. Increasing the pressure from 1 to 30 bars provides more adsorption of toluene on the catalyst active sites and thus leads to higher conversion. By increasing the reaction pressure from 30 to 50 bar, the increase in toluene conversion is minimal perhaps due to the occupation of all the active sites with the reactant. Conversion of toluene at 30 bar nitrogen and hydrogen pressure is plotted as a function of reaction temperature and is shown in **Fig. 1b**. Conversion of toluene increased with rise in temperature as expected for equilibrium-limited endothermic reactions. At 375 °C, higher toluene conversion was observed in nitrogen compared to hydrogen carrier gas. This difference of toluene conversion between the carrier gases was reduced as the temperature increased. At 425 °C, the conversion of toluene for both nitrogen and hydrogen pressure are approaching to similar values. Under the hydrogen pressure with rise in temperature, the increase in toluene conversion was found higher as

compared to nitrogen pressure because of slowed deactivation of the active sites.

3.2. *Xylenes Selectivity*

Xylene selectivity at 400 °C is plotted as a function of nitrogen and hydrogen pressure of 1, 5, 10, 30 and 50 bar and is shown in **Fig. 2**. The plot shows the xylenes selectivity has increased from 1 to 5 bars, and then decreased with increasing the pressure up to 50 bar for both nitrogen and hydrogen carrier gases. The xylenes selectivity under nitrogen pressure is found to be higher than hydrogen from 1 to 10 bars, but at 30 bar pressure, the results shows that the xylene selectivity for nitrogen pressure decreased and is slightly lower than the xylene selectivity at hydrogen pressure. This trend is similarly exhibited at 50 bar pressure as well. The xylene selectivity using hydrogen pressure is increased from 1 to 30 bars, and then remains almost unchanged up to 50 bar pressure. In the presence of both nitrogen and hydrogen, secondary and tertiary reaction occurs once the xylenes are formed. Some of the xylenes molecules react with toluene molecules and produced trimethylbenzenes and benzene. This results in the increase of benzene concentration and decrease in the toluene concentration. These trimethylbenzene further reacts with toluene to produce higher aromatics that leads to coke formation. Coke has been observed higher on spent catalysts under nitrogen carrier gas as compared to hydrogen. Trimethylbenzene were not detected in the reaction products since these converted into coke and deposited on the catalysts. At 50 bar pressure, the coke on the catalysts decreased the reactivity and thus lower toluene conversion was found.

On the other hand in the presence of hydrogen, hydrogen provides a saturated environment in which the molecules are stabilized after the primary reactions. The presence of reactive hydrogen reduces the tendency of secondary and tertiary reactions thus prevent and reduce

the coke formation. Some amounts of trimethylbenzene are formed and detected in the reaction product and some of them produce coke on the catalyst as a result of further reactions.

Xylenes selectivity obtained at 30 bar nitrogen and hydrogen pressure were plotted as a function of reaction temperature and shown in **Fig. 3**. Xylenes selectivity at 400 °C was found higher under hydrogen presence as compared to nitrogen presence. When the temperature was raised to 425 °C, the difference of xylene selectivity between nitrogen and hydrogen carrier gases was reduced and reached the almost similar level. Among the xylenes isomers, thermodynamic equilibrium was found to be maintained for all reaction temperatures and pressures. On the other hand, ethylbenzene was detected in trace amount in some of the reaction products and was found in hydrogen carrier gas at 30 and 50 bars pressure, but was not found in the range 1-10 bar both under nitrogen and hydrogen pressure.

3.3. *Benzene Selectivity*

Benzene selectivity at 1, 5, 10, 30 and 50 bar nitrogen and hydrogen pressure was plotted as a function of reaction pressure and is shown in **Fig. 4a**. The plot shows the benzene selectivity decreased from 1 to 5 bars, and then increased with increase in pressure for both nitrogen and hydrogen carrier gases. The benzene selectivity from 5 to 50 bars in nitrogen carrier gas was found increasing as compared to benzene selectivity in hydrogen carrier gas. This shows that with increase in pressure, higher amount of benzene was produced as a result of increased secondary and tertiary reaction leading to coke formation. In the presence of hydrogen carrier gas, the benzene selectivity remains almost same from 10 to 50 bars pressure and thus shows that the presence of hydrogen prevents undesirable secondary and tertiary reaction.

Benzene selectivity obtained at 30 bar nitrogen and hydrogen pressure and reaction temperature of 375, 400 and 425 °C is plotted and compared in **Fig. 4b**. In case of nitrogen, benzene selectivity was increased from 375 to 400 °C, and then decreased with increase in reaction temperature from 400 to 425 °C. On the contrary, in the presence of hydrogen, benzene produced was increased with rise in temperature from 375 to 425 °C. This is indicative of the fast and higher catalyst deactivation under nitrogen as compared to hydrogen carrier gas.

Benzene to xylenes molar ratio (B/TX) obtained at 1, 5, 10, 30 and 50 bars nitrogen and hydrogen pressure is plotted and is shown in **Fig. 5a**. The pattern of the plot is quite similar to the one obtained for benzene selectivity. From 1 bar to 5 bars, the B/TX molar ratio decreased and then increased at 10 bars. As the pressure increased from 10 to 30 bar and then 50 bar, the B/TX ratio for nitrogen pressure increased, while for hydrogen carrier gas, it remains same. This result shows that at higher pressure in nitrogen carrier gas, the reaction rate of xylene consumption through transalkylation of toluene and xylenes competes with the reaction rate of xylenes formation through disproportionation of toluene. This is due to the unavailability of reactive hydrogen in the reaction mixture.

B/TX obtained at 30 bar nitrogen and hydrogen pressure is plotted as a function of reaction temperature and is shown in **Fig. 5b**. In case of nitrogen, B/TX ratio increased from 375 to 400 °C and then decreased with increase in reaction temperature from 400 to 425 °C. On the contrary, in the presence of hydrogen, B/TX ratio increased with increase in reaction temperature from 375 to 425 °C. This is indicative of the faster deactivation of the catalyst under nitrogen as compared to hydrogen.

3.4. *C₉+ Aromatics Produced*

The amount of C₉+ aromatics produced at 1, 5, 10, 30 and 50 bar nitrogen and hydrogen pressure is plotted and is shown in **Fig. 6a**. In case of nitrogen carrier gas, C₉+ aromatics were found increasing with pressure in the range 1 to 10 bars, and then remains unchanged up from 10 to 50 bars. More C₉+ aromatics were detected in hydrogen carrier gas as compared to nitrogen. Among the C₉ produced, higher concentration was observed for 1,2,4-trimethylbenzene compared to other C₉ isomers. Other C₉ compounds produced were 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, 1-methyl-3-ethylbenzene, 1-methyl-4-ethylbenzene, and 1-methyl-2-ethylbenzene. At the 30 bars reaction pressure under both nitrogen and hydrogen carrier gases, more C₉+ aromatics were produced when the temperature was increased from 375 to 425 °C (**Fig. 6b**). More C₉+ aromatics were detected in hydrogen carrier gas compared to nitrogen. This is because in the presence of reactive hydrogen, further reactions leading to coke formation were reduced as compared to the reactions in the presence of inert nitrogen.

3.5. *Effect of Carrier Gas Type and Pressure*

Conversion of toluene under nitrogen carrier gas was found higher than hydrogen. Such phenomenon has been reported in the literature [21] and results of toluene disproportionation under nitrogen were found in agreement with our study. The dependence of toluene conversion on the type of carrier gas can be explained based on the atomic and molecular sizes of the carrier gas, and its behavior during the reaction network. Nitrogen is a bigger molecule compared to hydrogen and it is relatively inert, whereas hydrogen is the smallest molecule and it participates in the reaction network responsible for production of BTX and higher aromatics. In the presence of nitrogen, mainly toluene adsorption, diffusion and

reaction occur on the active sites of the catalyst and this leads to higher toluene conversion. Some physical adsorption of nitrogen may occur on the active sites, but due to its inertness, nitrogen does not proceed to the reactivity stage. When hydrogen is used instead of nitrogen, both hydrogen and toluenes are adsorbed, diffused and took part in the reaction. Because of smaller size, diffusion of hydrogen is faster than toluene. Thus, there are competing reactions where hydrogen occupies some of the active sites and converts into atomic hydrogen which are involved in the reactions. This competing adsorption, diffusion and activation of hydrogen molecule on the active sites may lower the toluene conversion. This phenomenon can also be explained based on Bronsted and Lewis acidity. Presence of hydrogen may lead to decrease in Bronsted acidity and thus decrease in the concentration of intermediates benzylic carbocations, leading to lower toluene conversion [22,23].

Conversion of toluene was found increasing in the presence of nitrogen and hydrogen carrier gases in the range 1 to 30 bar pressure. From 30 to 50 bar, the toluene conversion remains similar. Conversion of toluene at 30 and 50 bars is quite similar and it was found that increasing the reaction pressure above 30 bars, has no significant effect on toluene conversion. This shows the limits of adsorption, diffusion and reactivity as a function of reaction pressure. Singer et al [24] have reported a very recent study on the pressure effect on the alkylation of toluene with ethane. They have shown that the toluene conversion during toluene alkylation reaction has increased from 17 to 28% at 350 °C by increasing the reaction pressure from 30 to 50 bars. This is probably due to the reason that the catalyst deactivation has reduced at higher pressure because of stronger adsorption and reaction of ethane molecules on the catalysts at higher pressures. This is also due to the increase in adsorption, diffusion and reactivity of ethane molecule on the catalyst at higher pressure because of its relatively smaller size compared to the bigger molecules such as toluene.

3.6. *Coke on Spent Catalysts*

The coke deposited on all the spent catalysts has been plotted in **Fig. 7**. Coke is basically formed as a result of secondary and further reactions of toluene with xylenes and higher aromatics produced, and the severity of these reactions is determined by the type of carrier gas. The data shows that the spent catalysts obtained under hydrogen carrier gas at pressures in the range 1 to 50 bars, possess lower coke contents as compared to the spent catalysts obtained under nitrogen carrier gas. This could be because of contribution from several factors. One of the factors could be that since hydrogen takes part in these reactions occupying some active sites, reducing the severity of the secondary, tertiary and further reactions which produced multialkyl substituted benzene and polyaromatics that leads to deposits on the catalysts in the form of coke. On the other hand, nitrogen being an inert gas does not take part in the reaction and thus a larger amount of active sites are available for secondary and tertiary reactions that eventually lead to higher coke formation. Another reason may be that in the presence of reactive hydrogen, the coke precursors are desorbed easily from the catalyst surface as compared to inert nitrogen carrier gas. The amount of coke in nitrogen carrier gas decreased from 30 to 50 bar pressure. This effect may be due to extraction and desorption of coke precursors at high pressure [24]. Initial reactions steps involved in toluene disproportionation reaction, C₉ and coke formation are shown in **Fig. 8**.

4. Conclusions

Following conclusions can be drawn from this study.

- Toluene conversion under nitrogen carrier gas was higher than under hydrogen. Toluene conversion was found to increase with increasing the pressure from 1 to 30 bars under both nitrogen and hydrogen carrier gases. There was very little or no change observed in

toluene conversion while increasing the reaction pressure from 30 to 50 bars.

- Toluene conversion under hydrogen carrier gas at 375 °C was found quite lower as compared to under nitrogen, but this difference in toluene conversion was reduced as the temperature increased and reached at a similar value at 425 °C for both nitrogen and hydrogen carrier gases.
- Xylene selectivity was found higher and stable under hydrogen carrier gas as compared to nitrogen. At 5 bars pressure, highest xylene selectivity was found under both nitrogen and hydrogen carrier gases. Xylene selectivity was found decreasing with increase in pressure, and the decrease was more pronounced under nitrogen carrier gas.
- Xylene selectivity was found decreasing with increase in reaction temperature and the decrease was sudden and more evident in case of hydrogen carrier gas compared to nitrogen. At 425 °C, the xylene selectivity under nitrogen carrier gas was found similar to under hydrogen.
- Benzene selectivity was found increasing with increase in reaction pressure under both nitrogen and hydrogen. The trend was in fact a reverse reflection of the xylene selectivity data. Under nitrogen, higher benzene selectivity was observed as compared to hydrogen carrier gas.
- Under nitrogen compared to hydrogen at higher pressure, the rate of reaction of xylene consumption through transalkylation of toluene and xylenes competes with the reaction rate of xylenes formation through disproportionation of toluene due to the unavailability of reaction hydrogen. This resulted in higher benzene formation, lower C₉+ formation, and higher coke formation and deposition on the catalyst. This leads to faster deactivation of the catalyst under nitrogen as compared to hydrogen as well as reduced xylene selectivity. This was confirmed by the higher amount of coke measured on the spent catalyst from nitrogen carrier gas runs as compared to hydrogen.

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Table 1. Surface area, porosity and acidity of Mo/Z catalyst.

Table 2. Reaction conditions used and the reaction runs made in this study.

Table 1. Surface area, porosity and acidity of Mo/Z catalyst.

| No. | Property | Value |
|------------|---|--------------|
| 1 | Surface Area, m ² /g | 333.2 |
| 2 | External Surface Area, m ² /g | 110.4 |
| 3 | Micropore Surface Area, m ² /g | 223.3 |
| 4 | Total Pore Volume (cc/g) | 0.391 |
| 5 | Micropore Volume (cc/g) | 0.094 |
| 6 | Average Pore Diameter (Å) | 46.9 |
| 7 | Total Ammonia Acidity, mmol/g | 0.625 |
| 8 | % Weak Acidity (100-380 °C) | 80.6 |
| 9 | % Strong Acidity (380-800 °C) | 19.4 |

Table 2. Reaction conditions used and the reaction runs made in this study.

| Reaction Run No. | Temperature, °C | Liquid hour space velocity (LHSV), hr⁻¹ | Pressure, bar | Carrier Gas |
|-------------------------|------------------------|---|----------------------|--------------------|
| 1 | 400 | 1.5 | 1 | <i>Hydrogen</i> |
| 2 | 400 | 1.5 | 5 | <i>Hydrogen</i> |
| 3 | 400 | 1.5 | 10 | <i>Hydrogen</i> |
| 4 | 400 | 1.5 | 30 | <i>Hydrogen</i> |
| 5 | 400 | 1.5 | 50 | <i>Hydrogen</i> |
| | | | | |
| 6 | 400 | 1.5 | 1 | Nitrogen |
| 7 | 400 | 1.5 | 5 | Nitrogen |
| 8 | 400 | 1.5 | 10 | Nitrogen |
| 9 | 400 | 1.5 | 30 | Nitrogen |
| 10 | 400 | 1.5 | 50 | Nitrogen |
| | | | | |
| 11 | 425 | 1.5 | 30 | <i>Hydrogen</i> |
| 12 | 425 | 1.5 | 30 | Nitrogen |
| | | | | |
| 13 | 375 | 1.5 | 30 | <i>Hydrogen</i> |
| 14 | 375 | 1.5 | 30 | Nitrogen |

FIGURE CAPTIONS

Fig. 1. Conversion of toluene using hydrogen (■) and nitrogen (–) carrier gases as a function of (a). reaction pressure at 400 °C, and (b). reaction temperature at 30 bar.

Fig. 2. Xylenes selectivity using hydrogen (■) and nitrogen (–) carrier gases as a function of reaction pressure at 400 °C.

Fig. 3. Xylenes selectivity using hydrogen (■) and nitrogen (–) carrier gases as a function of reaction temperature at 30 bar pressure.

Fig. 4. Selectivity of benzene using hydrogen (■) and nitrogen (–) carrier gases as a function of (a). reaction pressure at 400 °C, and (b). reaction temperature at 30 bar.

Fig. 5. Selectivity of benzene using hydrogen (■) and nitrogen (–) carrier gases as a function of (a) reaction pressure at 400 °C, and (b) reaction temperature at 30 bar.

Fig. 6. C₉+ aromatics produced using hydrogen (■) and nitrogen (–) carrier gases as a function of (a) reaction pressure at 400 °C, and (b) reaction temperature at 30 bar.

Fig. 7. Effect of reaction pressure on coke deposited on the spent catalysts at 400 °C in the presence of hydrogen (■) and nitrogen (–) carrier gases.

Fig. 8. Reactions steps involved in toluene disproportionation reaction and coke formation.

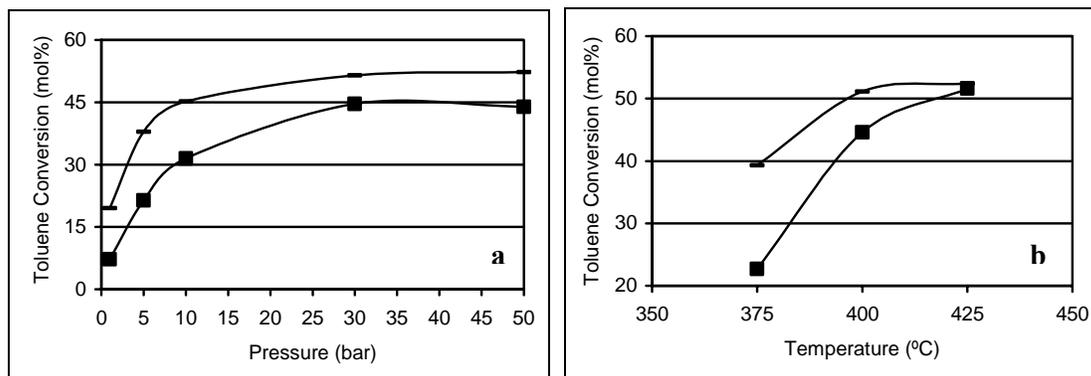


Fig. 1. Conversion of toluene using hydrogen (■) and nitrogen (×) carrier gases as a function of (a). reaction pressure at 400 °C, and (b). reaction temperature at 30 bar.

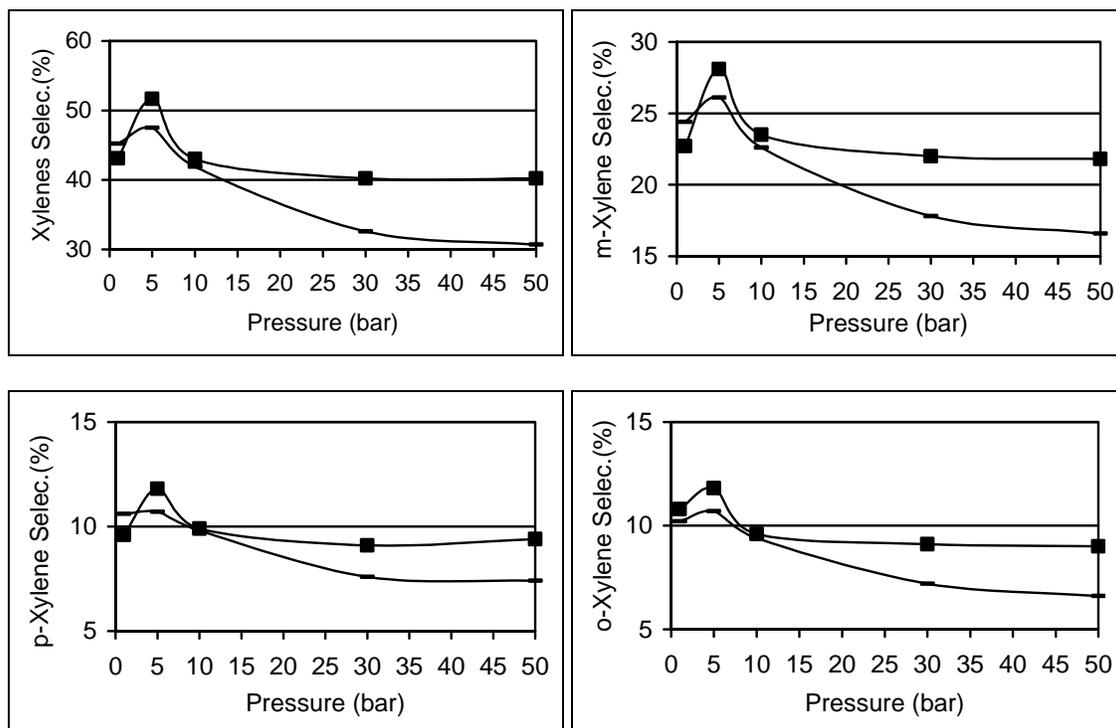


Fig. 2. Xylenes selectivity using hydrogen (■) and nitrogen (-) carrier gases as a function of reaction pressure at 400 °C.

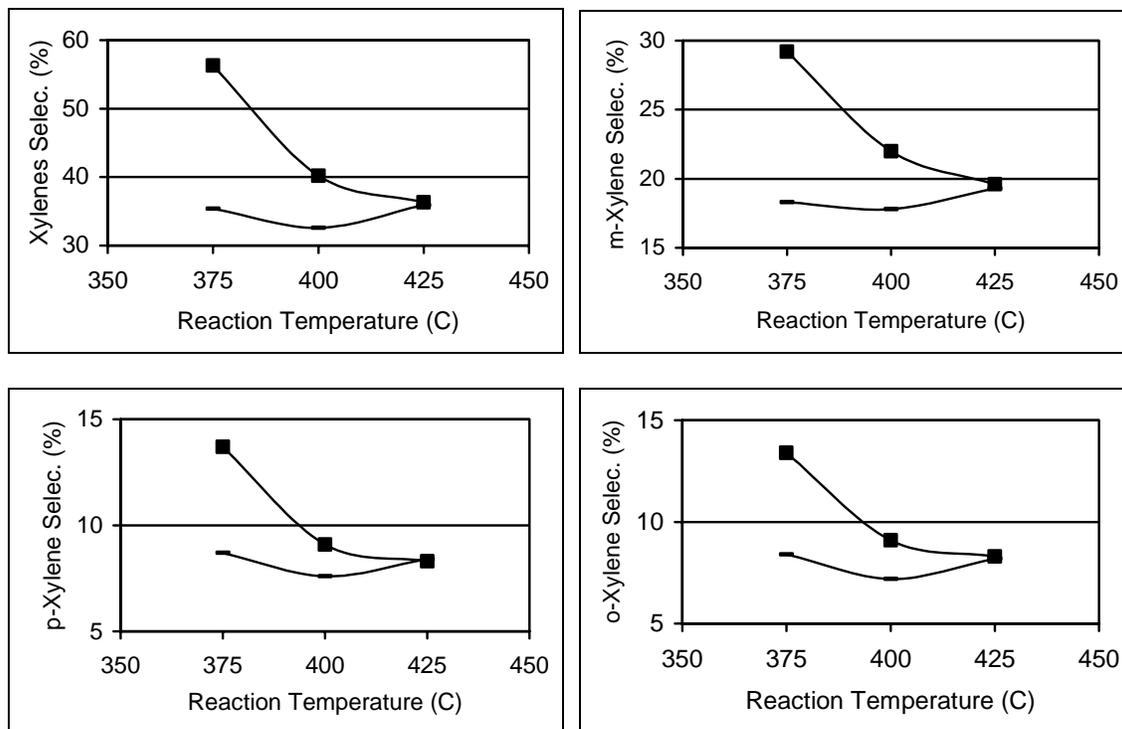


Fig. 3. Xylenes selectivity using hydrogen (■) and nitrogen (—) carrier gases as a function of reaction temperature at 30 bar pressure.

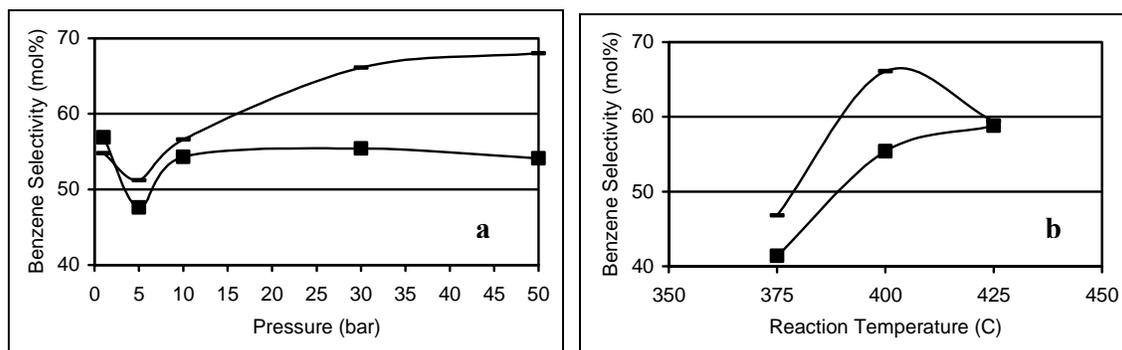


Fig. 4. Selectivity of benzene using hydrogen (■) and nitrogen (□) carrier gases as a function of (a). reaction pressure at 400 °C, and (b). reaction temperature at 30 bar.

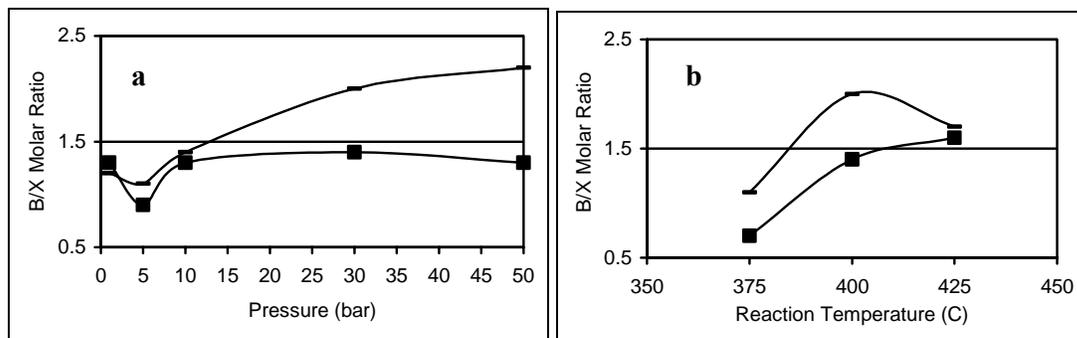


Fig. 5. Selectivity of benzene using hydrogen (■) and nitrogen (□) carrier gases as a function of (a) reaction pressure at 400 °C, and (b) reaction temperature at 30 bar.

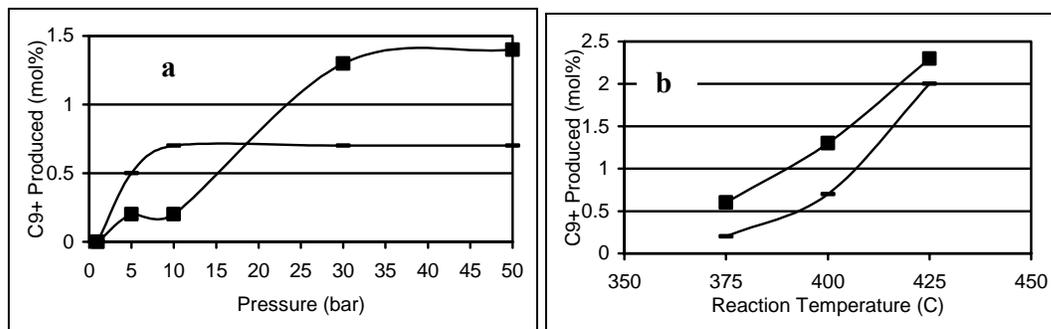


Fig. 6. C₉+ aromatics produced using hydrogen (■) and nitrogen (□) carrier gases as a function of (a) reaction pressure at 400 °C, and (b) reaction temperature at 30 bars.

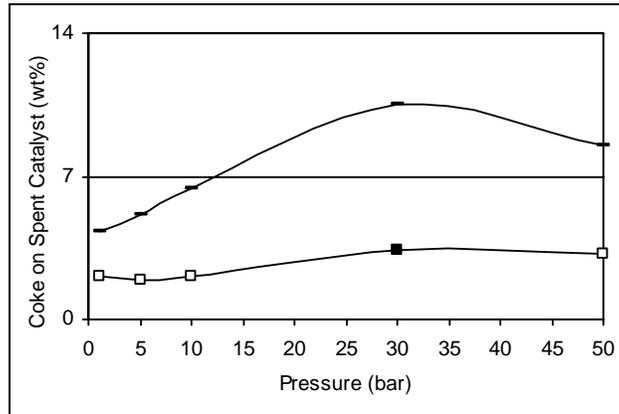


Fig. 7. Effect of reaction pressure on coke deposited on the spent catalysts at 400 °C in the presence of hydrogen (■) and nitrogen (□) carrier gases.

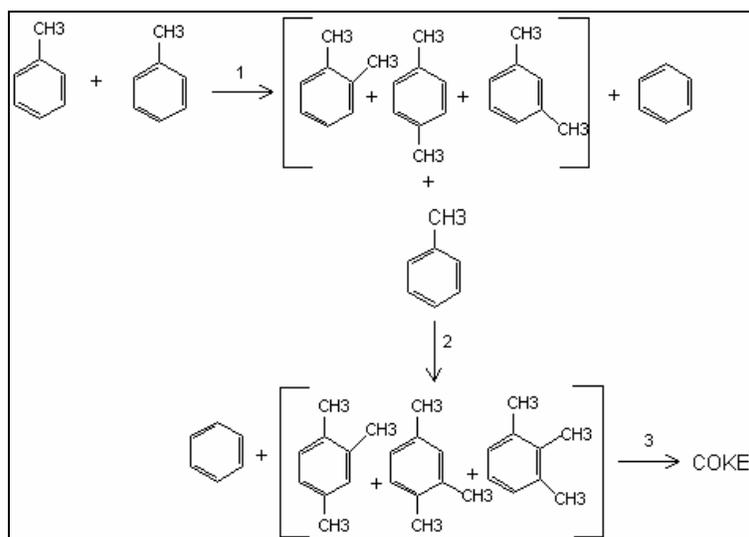


Fig. 8. Reactions steps involved in toluene disproportionation reaction and coke formation.