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Para-xylene Maximization-Part VI
SHAPE-SELECTIVE PLATINUM-PROMOTED METHYLATION OF TOLUENE.

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ABSTRACT

The need for increasing the production of para-xylene, which is the primary material for producing the polyester fibers, activated this research. Although alkylation reaction are acid catalyzed, we found that a Pt promoter activates this reaction by virtue of the presence of vacant d-orbital in the Pt atom. In this work, a series of catalysts containing 0.1, 0.2 or 0.3%Pt in HZSM-5 zeolite were tested for alkylating toluene with methanol, aiming to produce the xylenes and maximizing para-xylene production during a temperatures range of 300-500^{o}C in presence of hydrogen flow in a continuous-flow fixed-bed reactor. The catalysts were characterized by temperature programmed desorption (TPD) of ammonia for acid sites distribution analysis and platinum dispersion in the catalysts by hydrogen chemisorption. Moreover, the diffusion resistance extent in the current catalysts during the current alkylation reaction has been evaluated via estimation of the Thiele modulus, Φ_L. The selectivity for para-xylene production was found to increase systematically with increasing the Pt content in the catalysts, whereas the unloaded zeolite did not follow this order. The Φ_L values calculated were accordingly found to increase also with increasing the Pt content in the catalysts. Although para-xylene was the highest on the 0.3%Pt/H-ZSM-5 catalyst, the heavy undesired trimethylbenzenes were the lowest to be formed on this catalyst.

KEY WORDS:

Methylation; ZSM-5; Platinum, Methanol; Toluene; Shape-Selective; and Diffusion.

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NOMENCLATURE

Cs	surface concentration, gm mol/cm^3
D_{12eff}	Effective binary diffusion coefficient, cm^2 s^{-1}
D_{eff}	Effective diffusion coefficient, cm^2 s^{-1}
D_{keff}	Effective Knudsen diffusion coefficient, cm^2 s^{-1}
DSC	differential scanning calorimetry
Ea	Apparent activation energy, J mol^{-1}
eu	Entropy unit, cal mol^{-1} K^{-1}
F	carrier gas flow rate (cm^{3}s^{-1} at STP).
h	Plank's constant
k	the true rate constant
K	the adsorption equilibrium constant
k_b	Boltzmann's constant
kK	apparent reaction rate constant
k_v	intrinsic first order reaction rate constant, sec^{-1}
L	the volume of a catalyst /external surface area of particle, cm
m	The order of reaction
R	the gas constant = 8.3144 J/g mol K°
T	absolute reaction temperature, K°
TPD	temperature programmed desorption
w	weight of catalyst, g.
WHSV	Weight hourly space velocity, h^{-1}
x	mole fraction converted
ΔH*	activation enthalpy, J mol^{-1}
ΔH_{des}	enthalpy of NH_3 desorption,Jg^{-1}
ΔS*	entropy of activation
Φ_L	Thiele diffusion modulus for general case, dimensionless

INTRODUCTION

Synthetic zeolites have attracted attention as alkylation catalysts owing to their high acidity, freedom from corrosive substances, potential for regeneration, easy separation from reaction products and elimination of problems associated with disposal of spent catalyst compared to $AlCl_3$ [1,2]. Alkylation of toluene with methanol gives a mixture of xylenes, since the methyl group of toluene is para/ortho directing, and hence, the primary products are supposed to be para- and ortho-xylenes. Nevertheless, since alkylation and isomerization reactions occur simultaneously on acidic catalysts, a mixture of the three xylene isomers is obtained, which may correspond closely to thermodynamic equilibrium. On zeolite catalysts, transformations generally occur within the confines of pore system and catalyzed at cationic sites that are part of the framework structure. The shapes of the various molecules determine whether they are able to diffuse into the pores to a catalytic site, perform the transition state, undergo the reaction then diffuse out [3]. Compared to toluene, methanol is relatively reactive on zeolitic catalysts and forms dimethylether and water at lower temperatures and can be converted to gaseous hydrocarbons at higher temperatures [3,4].

The alkylation of toluene with methanol has been studied by several authors on zeolites as catalysts. Yashima et al. [5,7] used cation exchanged Y-zeolite catalysts. Chen et al. [8] used large crystal and intermediate pore zeolites modified with P and Mg. Bhat [9] used L, ZSM-5 and Y zeolites as catalysts and. Bhat et al. [10] used H-ZSM-8 zeolite. Kaeding et al. [2] and Young et al. [11] used modified ZSM-5 catalysts. Kumar and Ratnasamy [12] used H-ZSM-22 and H-ZSM-23 zeolite catalysts and compared them with H-ZSM-5 zeolite. Mantha et al. [13] used H-ZSM-5 and H-mordenite catalysts. Vayssilov et al. [14] developed a kinetic model using zeolitic catalysts. Kim et al. [15] and Ding et al. [16] tested the alkylation of toluene using various kids of catalysts. Joshi et al. [17] disclosed that the ZSM-12/ ZSM-5 co-crystalline catalyst is a good combination for para-xylene production. Zhu et al. [18,19] and Ghosh and Harvey US patent [20] concluded that the alkylation of toluene with methanol for production of xylene is carried out over acidic zeolites. The acidity and structure of different zeolites are greatly differing, so, the selection of zeolites is the first step to get the suitable catalysts for methylation of toluene. Faramawy [21] found that modification of acidity and structure of ZSM-5 as a common shape-selective zeolite to reduce by-products and improve the selectivity of toluene methylation to maximize p-xylene production.

Aboul-Gheit et al. [22,23] have investigated the promotion of acidic zeolites with a noble metal (Pt) and to stabilize it on the catalyst, activate the formation of carbonium ion necessary for the alkylation reaction.

In the present work, H-ZSM-5 zeolite is loaded with low concentrations of Pt (0.1-0.3 wt%) to be used as catalysts for the alkylation of toluene with methanol in a fixed-bed continuous flow reactor using hydrogen as a carrier and reaction temperatures between 300ºC and 500ºC. Toluene conversion, xylenes and trimethylbenzenes production as well as para-xylene selectivity together with the xylene isomer ratios relative to their thermodynamic equilibrium are correlated with the acid sites density and strength as well as the dispersion of platinum in the zeolite.

EXPERIMENTAL

Catalysts Preparation

The sodium ZSM-5 zeolite, in the form of powder, was transformed to the ammonium form by cation exchange using molar solution of NH_4NO_3 five times; each time for 8 h, using a fresh solution of NH_4NO_3 at 70°C under reflux and stirring. The zeolite was then separated from the solution, washed thoroughly with distilled water and dried overnight at 110°C. The quantity of zeolite thus obtained was calcined at 530°C for 4 h then impregnated with an aqueous solution of H_2PtCl_6 to which was added a small quantity of citric acid to assist Pt penetration into the support (Aboul-Gheit [24,25]. The catalyst was then dried overnight at 110°C, calcined in a muffle furnace at 530°C for 4 h in air, then reduced in a flow of dry hydrogen at 20 cm^3 min^{-1} for 8 h in a quartz tube furnace at 500°C to obtain the Pt/H-ZSM-5 catalysts.

Alkylation Procedure and Apparatus

The catalytic runs were carried out at atmospheric pressure in a fixed-bed down flow reactor. The alkylation runs were carried out at reaction temperatures between 300°C and 500°C, a space velocity of 2.6 h^{-1} and a continuous hydrogen flow of 20 cm^3 min^{-1}. 1 g of the catalyst powder was diluted with inert porcelain particles. A mixture of methanol and toluene (molar ratio 2.5: 1) was fed into the reactor and the product was cooled in a condenser at 3°C then to a receiver. THE liquid and gaseous products were GC analyzed using a column packed with 5% Bentone 34 and 5% diisodecylphthalate on Chromosorb-W.

Surface Area

The BET surface area, and total pore volume were determined by nitrogen adsorption/desorption, using a Quatachrome NovaWin2 apparatus. The data obtained are given in Table 1.

Temperature programmed desorption of ammonia (TPDA)

The procedure of Aboul-Gheit [26, 27] using differential scanning calorimetry (DSC) for detecting and evaluating the desorption of presorbed ammonia from the catalysts via programmed temperature increase in an inert atmosphere was used. Primarily, ammonia was adsorbed on the acid sites of the catalyst after previous heating in air flow at 500°C for 3 h in a silica tube furnace. After cooling to 50°C, ammonia gas flow of 50 cm^3 min^{-1} was applied over the evacuated catalyst. The DSC measurements were then carried out in a DSC-30 unit of the TA-3000 Mettler system, using standard Al crucibles in a flow of 50 cm^3 min^{-1} of oxygen-free nitrogen purge gas. The DSC conditions were: temperature: 50-600oC, heating rate: 5 K min-1, full scale range: 30 mW, plot: 10 cm, sample mass: 10 gm.

The desorption enthalpy obtained corresponds to the acid sites density, whereas the DSC peak temperature was used to compare the acid site strength (Table 2). Two DSC endotherms appear in each thermogram, the higher-temperature-one corresponds to the strong acid sites responsible for catalyzing the reaction under study.

Platinum Dispersion in H-ZSM-5 Zeolite Catalysts (D)

The dispersion of platinum in the support (metal fraction exposed) was determined via hydrogen chemisorption using a pulse technique similar to that used by Freel [28]. A weight of the calcined catalyst was heated in the chemisorption furnace at 500°C for 1 h in a flow of 50 cm^3 min^{-1} of ultra pure hydrogen. The flow was then replaced with oxygen-free nitrogen at 30 cm^3 min^{-1} for 2 h at 500°C (degassing). The furnace was shut-off and the catalyst was cooled to room temperature. Hydrogen was then injected into the nitrogen carrier till saturation (appearance of hydrogen peaks equivalent to complete volume of injected pulses). Hydrogen uptake was calculated as hydrogen atoms adsorbed per total metal atoms on the basis of 1:1 stoichiometry [29]. Table 2 shows the acid sites parameters and metal dispersion.

RESULTS AND DISCUSSION

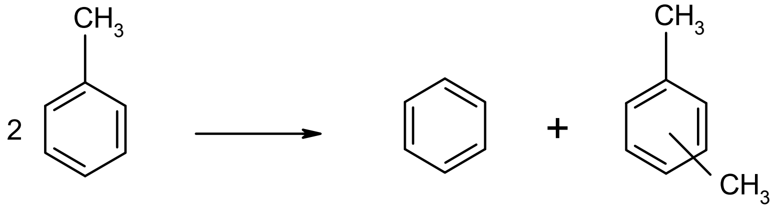
Toluene Conversion

The methylation of toluene with methanol is traditionally accepted as an acid catalyzed reaction. Hence, in the present work, the catalytic acid sites are provided by a solid acidic zeolite, which is capable of carrying out the formation of carbonium ions necessary for this alkylation reaction [30]. This alkylation product includes a mixture of C_8 aromatics (the xylenes plus ethylbenzene) and C_9 aromatics (trimethylbenzenes and ethyltoluene).

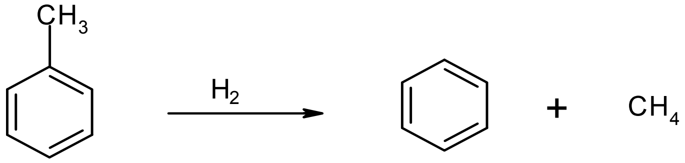
The privilege of using H-ZSM-5 zeolite over other acidic solids is its channel dimension (~5Å) which admits preferentially the formation and diffusion of para-xylene in order to minimize the other xylenes (meta and ortho-xylenes) which possess larger molecular size. Such materials are classified as shape-selective catalysts. However, trimethylbenzenes have also been formed at different concentrations in the product.

Benzene production during the current reaction is a very slow reaction under the current operating conditions. Benzene comprises 0.1-0.3%. Two secondary reactions can produce benzene as follows:

Via toluene hydro-dealkylation



Via toluene disproportionation:



However, the very low production level of benzene indicates that these reactions may be thermodynamically favored.

Although H-ZSM-5 is considered as a typical toluene methylation acidic solid catalyst, Aboul-Gheit et al. [23] have tested promoting H-ZSM-5 and H-MOR zeolites with low platinum content in order to catalyze the stabilization of the carbonium ion via extending its life-time on the catalytic sites. Hence, in the present work, we have changed the platinum content in the catalyst to be between 0.1 and 0.3 wt%.

Fig.1 shows that the total conversion of toluene on unloaded H-ZSM-5 as a catalyst increases with reaction temperature from 24.2% at 300°C up to 48.4% at 400°C, beyond which it decreases with a further increase of temperature to reach 34.5% at 500°C. Evidently, promotion of H-ZSM-5 with 0.1wt%Pt increases toluene conversion during the whole reaction temperature region up to 450°C, beyond which the conversion of toluene slightly decreases, but however, still significantly exceeding that obtained using the unloaded H-ZSM-5 zeolite catalyst.. A further increase of platinum in H-ZSM-5 to 0.2wt% gives some little increase of toluene conversion. However, increasing the Pt further to 0.3wt% in the zeolite results in a significant drop of its activity at all reaction temperatures, compared to the catalysts containing lower Pt contents. Furthermore, the activity of the 0.3wt% Pt/H-ZSM-5 catalyst has dropped to be even lower than that of the unloaded H-ZSM-5 zeolite during the lower reaction temperatures (350–400°C). This can be attributed to some decrease of the catalyst surface area and pore volume (Table 1) and to more significant extent the decrease of acid site number and strength as well as Pt dispersion with increasing the Pt concentration (Table 2). Evidently, the obtained data indicate that a Pt content of 0.3wt% should have exceed the allowable Pt concentration.

Total Xylenes in Products

Fig. 2 shows that the production of total xylenes increases as a function of reaction temperature in different ways. Excluding the overlaps of the curves of the 0.1 and 0.2wt%Pt/H-ZSM-5 catalysts, total xylenes production overlaps; can be generally arranged in the order: 0.1 % Pt > 0.2 % Pt > 0.3% Pt /H-ZSM-5. Even though, the xylenes are generally lower on the unloaded catalyst than on the Pt loaded H-ZSM-5 zeolite catalysts.

However at higher temperatures, the order of activities for total xylenes production is in the order 0.2% Pt > 0.1% Pt > 0.3% Pt / H-ZSM-5.
Hence, the 0.2 wt %Pt /H-ZSM-5 catalyst can be considered as the catalyst of choice for total xylenes production. At low temperatures, the higher activity of the 0.1wt%Pt catalyst can be attributed to the larger space in the channels and cavities of this catalyst than in the two other catalysts, allowing more xylenes production. In contradistinction to what occurs on the Pt loaded catalysts, the decreasing activity of xylenes production at higher temperatures (beyond 400°C) on the unloaded H-ZSM-5 catalyst is evidently attributed to the absence of the noble metal sites which are necessary for carbonium ion stabilization.

Para-Xylene

Para-xylene selectivity

The para-xylene selectivity is of industrial importance because the para xylene isomer is an important starting material for the producting of polyester fibers, adhesives, etc. The para-xylene selectivity increases as the Pt content in the catalyst increases (Fig. 3), due to the effect of platinum on narrowing the channel diameter. Along these channels, the major proportion of xylenes is formed. Fig. 3 shows that the position of the selectivity curve for para-xylene is not as expected, in comparison with the Pt-promoted curves. Its higher position above the curve obtained for the 0.1 and 0.2wt%Pt catalysts and its position below the 0.3wt%Pt catalyst curve can be attributed to the preferential formation and stronger adsorption of para-xylene on the external surface of the H-ZSM-5 zeolite.

Para-xylene production

Para xylenes production is depicted in Fig. 4. The activities of the catalysts under investigation for para-xylene production can be compared practically at reaction temperature of 450°C. At this temperature, the net para-xylene in product comprises 9.4, 10.0 and 12.1% using the 0.1, 0.2 and 0.3wt%Pt/H-ZSM-5 catalysts, respectively (Fig.4). However, at 500°C, para-xylene production has achieved significant enhancements on the 0.1 and 0.2wt%Pt/H-ZSM-5 catalysts producing 11.7 and 11.8 % para-xylene, respectively, whereas on the 0.3wt%Pt catalyst, para-xylene has accomplished insignificant improvement (12.2%). So, it can be said that using the 0.1 or the 0.2wt%Pt/H-ZSM-5 catalysts, a temperature of 500°C is almost optimum for para-xylene maximization, whereas using the 0.3wt%Pt catalyst, a temperature of

450°C can be considered as optimum, depending on the economics of the process. On the other hand, the activity of the unloaded zeolite as a catalyst is comparatively low, producing 8.3% and 8.1% para-xylene at 450°C and 500°C, respectively (Fig. 4).

Excessive Alkylation of Toluene

Trimethylbenzenes (TMBs) are formed as byproducts during the current reaction of toluene methylation both on the unloaded and Pt loaded H-ZSM-5 catalysts. Using the unloaded H-ZSM-5 catalyst, trimethylbenzenes are 4.1% at 300°C and increase to 16.7% at 400°C then drop to 6.7% at 500°C (Fig.5). However, using the 0.1, 0.2 and 0.3%Pt/H-ZSM-5 catalysts, TMBs are around 4.1, 4.6 and 4.3%, respectively at 300°C and increase to a maximum of 15.3, 16.1 and 11.7% at 450°C then decline to 12.1, 14.7 and 10.8% at 500°C. These TMBs are relatively somewhat lower on the 0.3wt%Pt catalyst. This decreasing of TMBs production using the 0.3wt%Pt catalyst, may be due to the lower surface area and acidity of this catalyst than the other used catalysts.

Hydrocracking Products

These products include C_1 up to C_5 hydrocarbons that increase continually with reaction temperature (Fig. 6). On the unloaded zeolite, they range between 5.0 and 6.6% at 300-500°C, respectively, whereas on the Pt/H-ZSM-5 catalysts they are somewhat higher; i.e., ranging between 5.6 and 7.4% at 300°C up to 8.2 and 10.1 at 500°C, with some increase as Pt content increases due to some enhanced hydrogenolysis reactions.

Kinetics of Toluene Alkylation with Methanol Using the Pt/H-ZSM-5 Catalysts:

Reaction rate constant

From the reaction data of total xylene in Fig. 3, the apparent reaction rate constant, Kk has been calculated according to the simple batch equation:

$$kK = \frac{F}{W} \cdot \ln\left(\frac{1}{1-x}\right)$$

$$= \frac{WHSV}{3600} \cdot \ln\left(\frac{1}{1-x}\right) \qquad (1)$$

Thermodynamic Parameters

The activation energy (Ea) for the alkylation reaction using the current catalysts has been calculated using the traditionally accepted Arrhenius equation and kK values obtained before. According to the absolute reaction rate theory, the reaction rate constant is correlated to activation enthalpy ΔH* and activation entropy ΔS*

$$kK = K_v = \frac{k_b T}{h} \cdot e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R} \qquad (2)$$

The apparent activation energy values obtained for the reaction of toluene conversion during its alkylation with methanol are almost indifferent or at least exhibit slightly different values. All Ea values in Table 3 are relatively low showing that diffusion restrictions may play a significant role during this reaction on all current catalysts. Moreover, the ΔS* values are all the same on the four catalysts. These values are relatively highly negative indicating significant molecular restrictions on the catalytic surfaces. Thermodynamically, the way via which activation of these catalysts takes place may be said to follow similar behaviors during diffusion and adsorption in the zeolitic channels and cavities. Fig. 7 shows Arrhenius plot.

Diffusion Effects Resulting via Platinum Inclusion in the Catalysts:

To correlate quantitatively the difference in diffusion resistance in a series of catalysts, the dimensionless parameter Thiele modulus (Φ_L) can be considered the most appropriate approach. This modulus is calculated by iteration on the reaction rate constant k_v applying equations 3 and 4.

$$\Phi_L = L\sqrt{\frac{k_v C^{m-1}}{D_{eff}}} \qquad (3)$$

Detailed calculation of the Thiele modulus is given by Satterfield and Sherwood [31]. The effective binary diffusivity (D_{12}) for methanol and toluene, the Knudsen diffusivity (D_k) and the effective diffusivity (D_{eff}) are correlated together according to:

$$\frac{1}{D_{eff}} = \frac{1}{D_{12eff}} + \frac{1}{D_{keff}} \qquad (4)$$

Hence, the Thiele modulus for the current reaction using Pt/H-ZSM-5 catalysts containing 0.1, 0.2 and 0.3wt%Pt has been calculated. Weisz [32] has indicated that the concentration gradient due to diffusion limitation is negligible when Φ_L is less than unity for first order reactions. Accordingly, the data depicted in Fig. 8 for the current unloaded and Pt loaded catalysts show that all of these catalysts encounter significant diffusion limitation since at all current reaction temperatures, the Φ_L values are higher than 6. Fig. 8 which assumes that the H-ZSM-5 zeolite by itself encounters the lowest diffusion restriction (lowest Φ_L values) at all reaction temperatures, whereas the Pt containing catalysts encounters more significant diffusion restriction. This restriction increases as a function of increasing the Pt content in the catalyst. The Φ_L values calculated for the unloaded H-ZSM-5 catalyst is 6.64-7.91, at temperatures of 300-450ºC respectively, whereas for the catalysts containing 0.1, 0.2 and 0.3wt%Pt, the Φ_L values are 7.61-10.31, 9.23-12.59 and 9.69-13.44, respectively at the same temperatures range. This indicates that H_2PtCl_6 in its solution has penetrated the zeolitic pores during the impregnation process, and deposited in the zeolitic channels causing more restriction of diffusion of the reaction hydrocarbon mixture. Naturally, the penetrating platinum increases as the Pt concentration in the solution increases. Accordingly, we observe that the diffusion resistance increases more significantly via loading with 0.1%Pt in the pore zeolite than through increasing the Pt loading to 0.2%Pt, etc.

CONCLUSION

Although toluene alkylation in an acid catalyzed reaction, the inclusion of platinum in the acidic shape-selective zeolite H-ZSM-5 is found highly beneficial by virtue of enhancing the shape selectivity via increasing the Φ_L values at all reaction temperatures. Platinum activates and stabilizes the carbonium ion necessary for the methylation reaction under study. The platinum content variation in the current catalysts is of prime importance for tracing the activity and selectivity behaviors of the current catalysts used for alkylation ones.

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TABLES

Table 1. Effect of Pt concentration on surface area and pore volume of H-ZSM-5 zeolite.

Catalyst	**BET Surface Area (m^2/g)**	**Total Pore volume (ml/g)**
Untreated H-ZSM-5	345.4	0.220
0.1%Pt/H-ZSM-5	341.5	0.199
0.2%Pt/H-ZSM-5	336.0	0.173
0.3%Pt/H-ZSM-5	292.4	0.153

Table 2. Pt dispersion and acid site strength distribution in the current Pt/H-ZSM-5 catalysts.

Pt content, wt%	**Strong acid sites**		**Pt dispersion, %**
	$\Delta H_{des.}$, Jg^{-1}	**Peak Temp., °C**	
0.0	105.1	380.0	-
0.1	80.8	372.0	0.70
0.2	78.2	368.0	0.68
0.3	61.0	349.0	0.56

Table 3 Activation parameters for the alkylation of toluene with methanol reaction using the current catalysts.

Catalyst	**Activation Energy E_a, ($x10^3 Jmol^{-1}$)**	**Entropy of Activation, ΔS^*eu**
H-ZSM-5	11.0	-74.7
0.1%Pt/ H-ZSM-5	16.8	-72.0
0.2%Pt/ H-ZSM-5	17.1	-72.0
0.3%Pt/ H-ZSM-5	18.8	-71.6

FIGURES

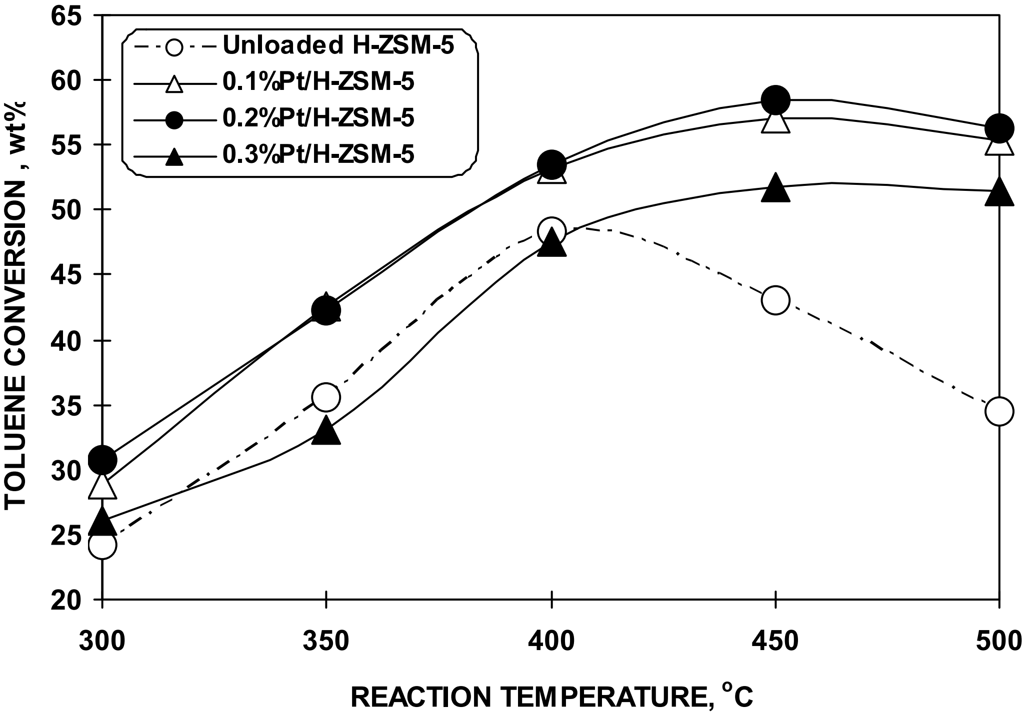

Fig. 1. Toluene conversion during its alkylation with methanol as a function of reaction temperature using catalysts containing various Pt contents supported on **H-ZSM-5** zeolite.

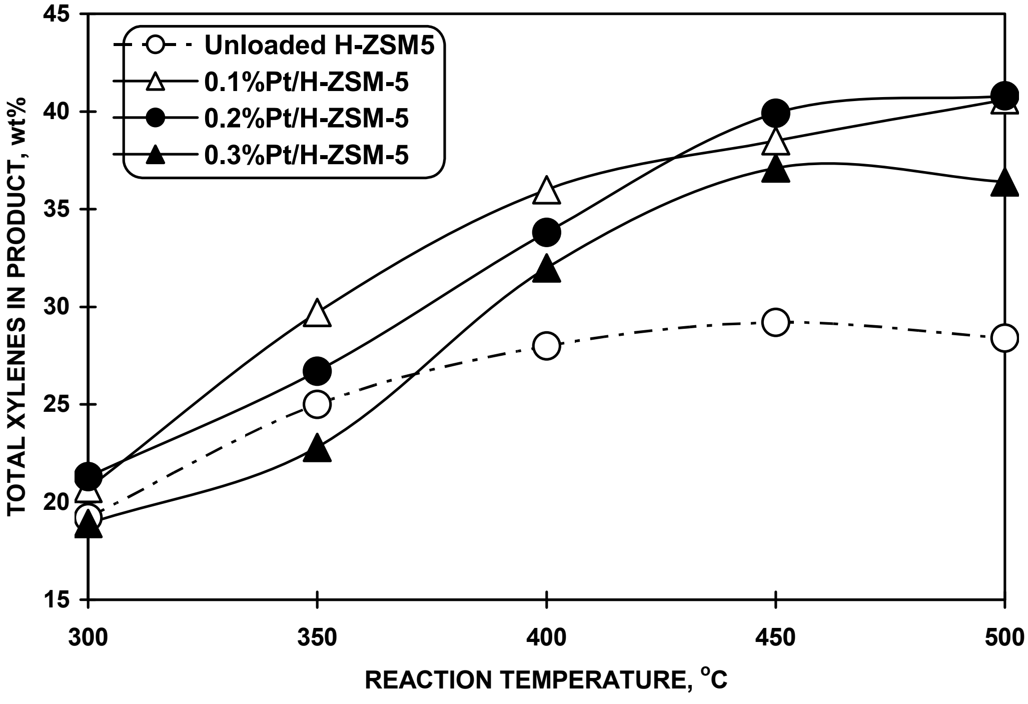

Fig. 2. Total xylenes production during toluene alkylation with methanol as a function of reaction temperature using catalysts conaining various Pt contents supported on **H-ZSM-5** zeolite.

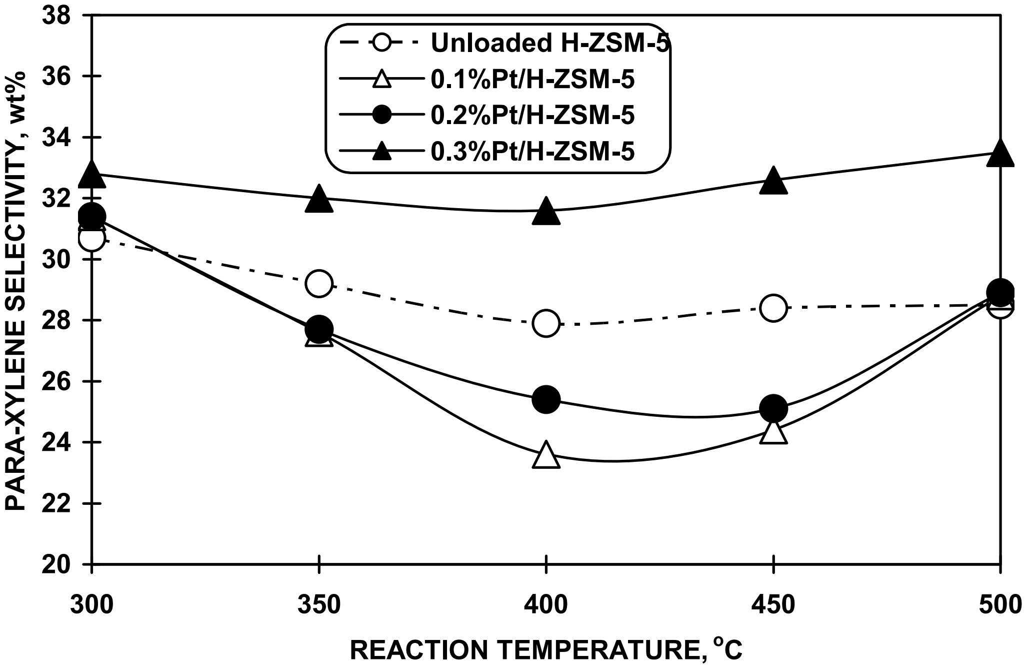

Fig. 3. Para-xylene selectivity during toluene alkylation with methanol as a function of reaction temperature using catalysts conaining various Pt contents supported on **H-ZSM-5** zeolite.

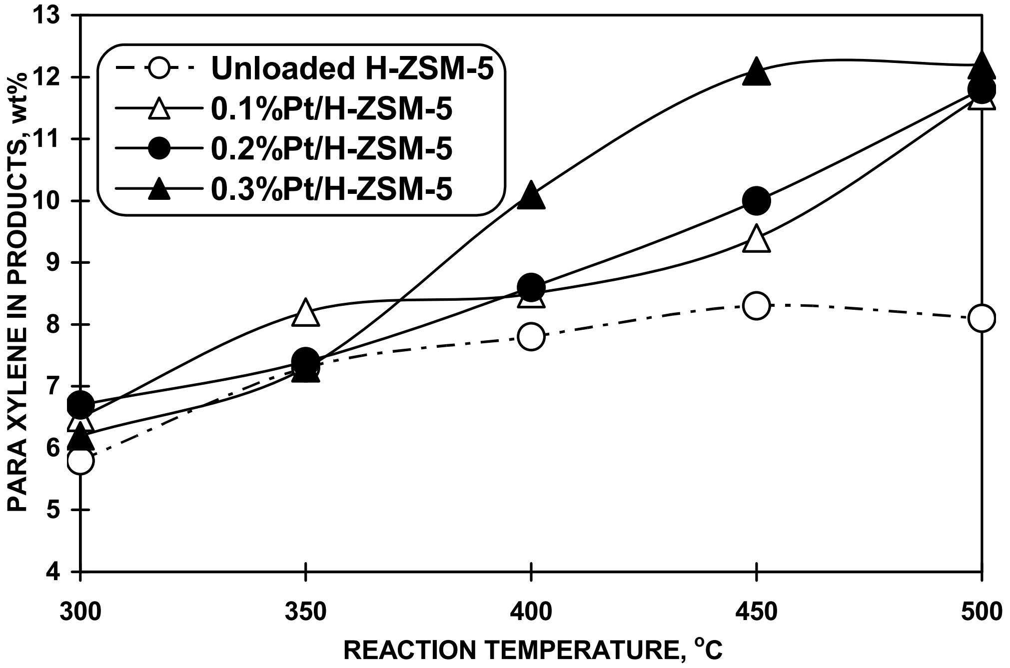

Fig. 4. Para-xylene in products during toluene alkylation with methanol as a function of reaction temperature using catalysts conaining various Pt contents supported on H-ZSM-5 zeolite.

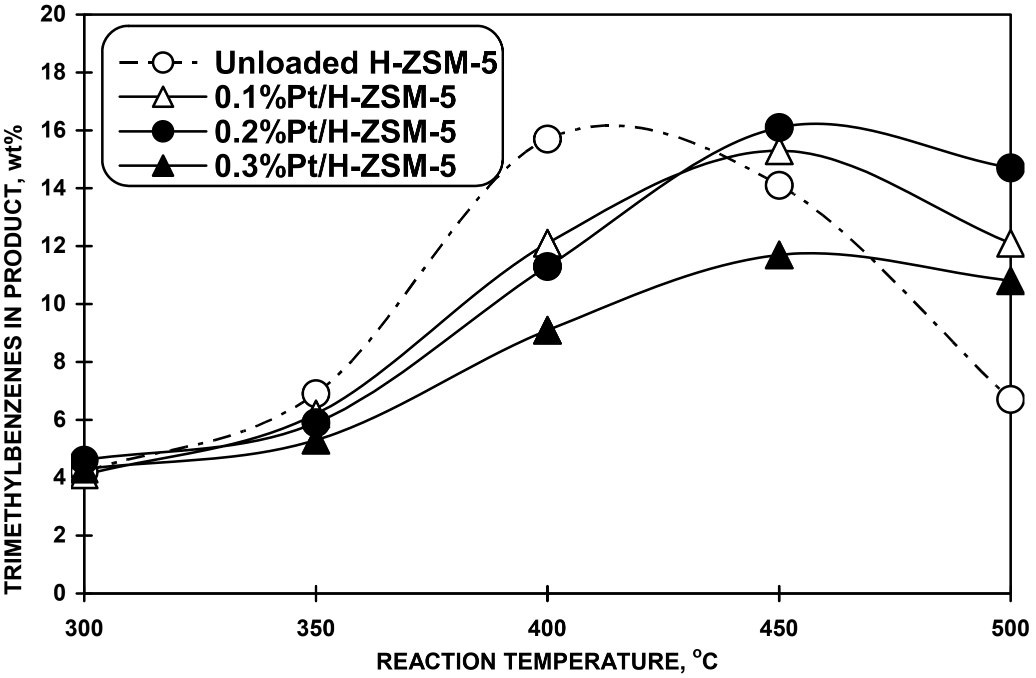

Fig. 5. Formation of trimethylbenzenes during toluene alkylation with methanol as a function of reaction temperature using catalysts containing various Pt contents supported on **H-ZSM-5** zeolite.

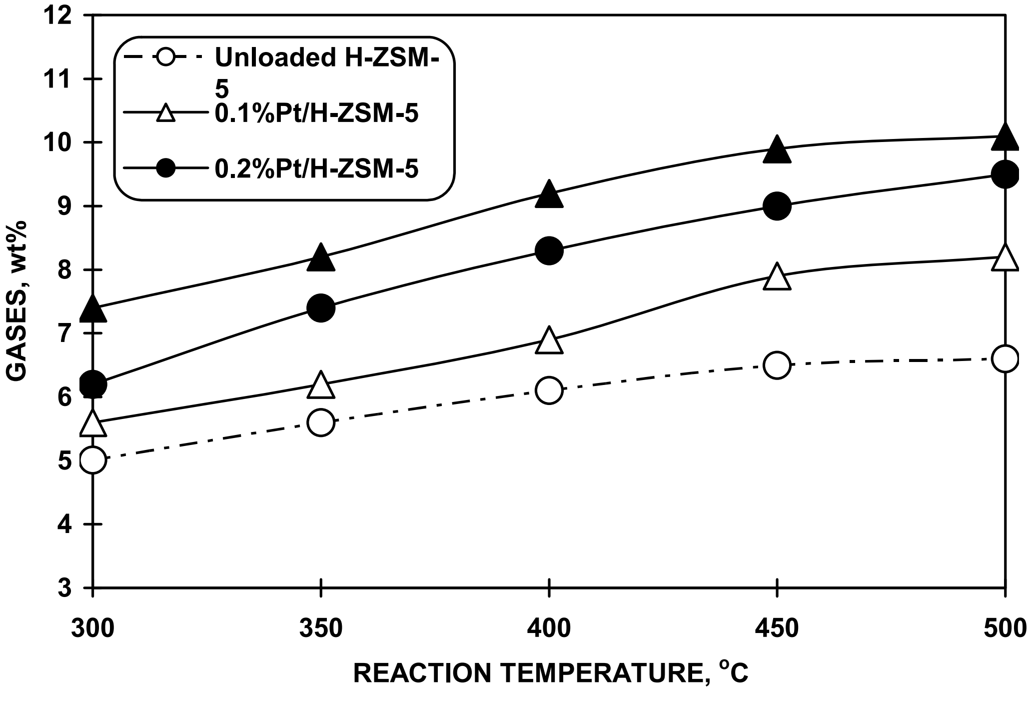

Fig. 6. Total gases produced during toluene alkylation with methanol as a function of reaction temperature using catalysts containing various Pt contents supported on **H-ZSM-**

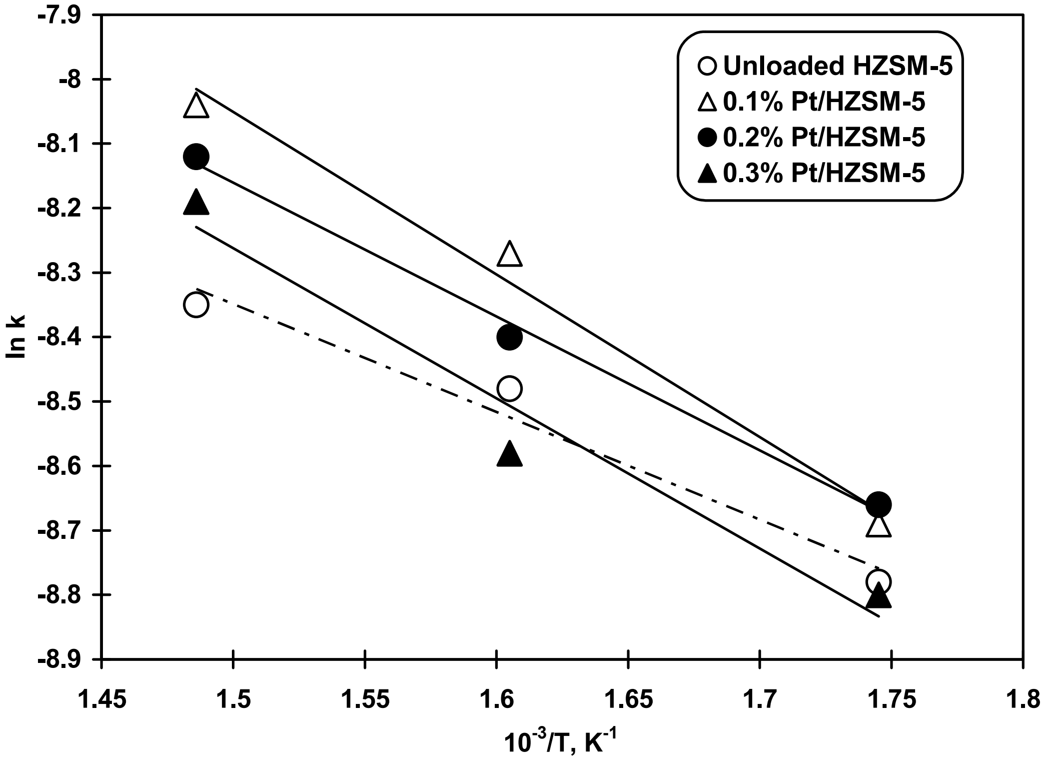

Fig. 7. Arrhenius plot for alkylation of toluene with methanol reaction using the Pt/H-ZSM-5 catalysts.

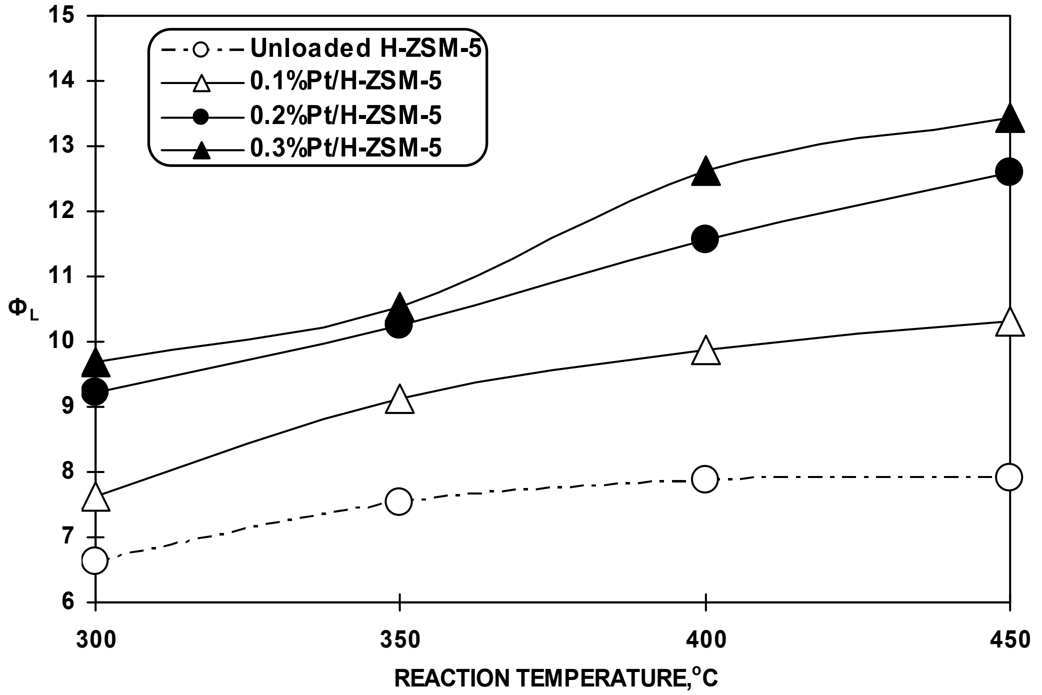

Fig. 8. Thiele modulus (Φ_L) for the methylation of toluene with methanol using unloaded and Pt loaded H-ZSM-5 catalysts at different reaction temperatures.