

Kinetics and Mechanism of Toluene Hydrodealkylation on Nickel / Alumina Catalyst

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ABSTRACT. The use of 6% Ni/Al₂O₃ catalyst for the hydrodealkylation of toluene (THD) using the pulse technique at differential reactor conditions has been investigated. The hydrodealkylation selectivity (or the selectivity to benzene production) was optimum at 593 K showing some hydrogenation of the aromatic ring at lower temperatures and favoring hydrocracking at higher temperatures. Activation energy was found to be 97.9 kJ.mol⁻¹. Reaction rates at low conversion runs were interpreted both by empirical power equation of the type $r = K P_T^m P_H^n$ and by Langmuir-Hinshelwood type equations, determining the corresponding parameters. A good fit to the experimental results was obtained with the empirical equation ($m = 0.65$; $n = 0.16$) and the L-H equation of the form:

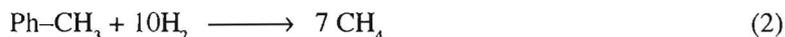
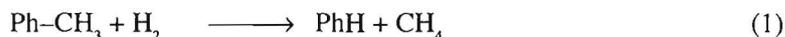
$$r = 4.104 P_T P_H^{1/2} / (1 + 0.037 P_T + 0.086 P_H^{1/2})^2$$

A reaction sequence is presented for the rate determining surface reaction suggesting sequential reactant absorption at a common catalytic site for toluene and atomic hydrogen.

The catalytic hydrodealkylation of alkyl aromatics is an alternative route in the production of benzene and naphthalene which are used as semi-finished products in a number of fundamental organic synthesis. It has the advantage of selectively promoting dealkylation without producing polynuclear hydrocarbons as a result of dehydrogenation, ring rupturing and condensation reactions associated with other dealkylation process. This type of reaction is well represented by the simplest of the

series, toluene hydrodealkylation (THD), using a wide variety of metal catalysts such as Co, Mo, CoMo supported metal catalysts and the Cr_2O_3 , Ce_2O_3 , Al_2O_3 , SiO_2 , Fe_2O_3 oxide catalysts (Gardos *et al.* 1986, Haber and Zienkiewics 1984).

The reaction proceeds under normal hydrodealkylation conditions via two competitive pathways as shown below:



Reaction (1) is the desirable hydrodealkylation reaction while reaction (2) represents the complete hydrogenolysis of toluene to methane.

A wide range of other catalysts have been investigated with the aim to obtain higher benzene yield, lower catalyst cost, and greater catalyst resistance to deactivation. Studies conducted by several workers (Dini *et al.* 1977, Dydykina *et al.* 1969, Grenoble 1979a) have shown that among group VIII and group VIIB metals supported on alumina, Rh appeared to be the most active metal for the toluene hydrodealkylation reaction. Although not extensively evaluated in the reported studies, Ni was cited by Grenoble to give the highest relative specific activity with a value of 1000 as compared to 329 for Rh. In terms of selectivity Ni had a relative value of 0.94 which was comparable to that of Rh at 1.0. Based on this initial encouraging observation, nickel may likewise be classified among promising catalysts for THD. Kinetic parameters for the THD reaction for the different noble metals observed at the specified reaction conditions lead Grenoble (1979b) to suggest a general power rate law expression in the form

$$r = kP_T^n P_H^{1-n(a+1)}$$

where r is the rate of reaction, k is the rate constant, P_T is the pressure of toluene, n is the reaction order with respect to pressure of toluene, P_H is the pressure of hydrogen and a is hydrogen coefficient representing the degree of dehydrogenation of the toluene methyl group. It was derived from an assumed reaction sequence where product desorption was taken as the rate determining step.

A more specific kinetic investigation on nickel over alumina catalyst alone and derivation of the plausible rate equation is presented by this study

Experimental

Chemicals

Toluene of more than 99% purity was obtained from Merck, Germany. Benzene was supplied by BDH and was of more than 99% purity. Further gas chromatographic test indicated no detectable contaminants. The gases including hydrogen, nitrogen, and oxygen of purity greater than 99.5% were obtained from the Saudi Industrial Gas Company and were allowed to pass through molecular sieve driers prior to being used in the system.

Catalyst preparation and characterization

The catalyst was prepared by the incipient wetness method using known weights of hydrous nickel nitrate and γ -alumina to give the corresponding weight percentage of Ni over Al_2O_3 . Reduction was carried out initially by gradual heating to 623 K under a stream of hydrogen (40 ml/min) and continued for 24 hrs.

The BET surface area, $s_{(\text{BET})}$, as well as the pore volume, V_p , were calculated from the nitrogen adsorption-desorption isotherm at 78 K. The free metal surface area, $S_{(\text{M})}$, was determined from the hydrogen chemisorption at 298 K.

Hydrodealkylation procedure

Preliminary hydrodealkylation reaction of toluene was observed at the temperature range of 550-640 K using the pulse technique and utilizing a continuous flow reactor system under a flow of hydrogen as illustrated in Fig. 1. Initial selectivity determination was found necessary to get the optimum working temperature. The effect of the reactant partial pressure was then determined in two separate runs; initially with toluene pressure from 15 to 40 Torr at constant hydrogen pressure (710 Torr), and finally with toluene fixed at 25 Torr and hydrogen varied from 84 to 234 Torr. After the weighed amount of catalyst had reached the desired reaction temperature, toluene pulses was introduced to the hydrogen stream allowing pre-mixing in a temperature conditioning zone prior to entry to the reactor. All measurements were performed after temperature and flow steady state conditions had been attained as monitored by a thermal conductivity detector (TCD) connected to the system. Conditions were set so as to ensure conversion values of less than 10%. This parameter limits the reactor response to a differential conversion mode where heat and mass transfer effects are minimized, significant effects due to product inhibition are eliminated, and observations are confined to the initial rates and initial product distributions. Rate of THD was calculated based on the following equation:

$$r = \infty F/w \quad (3)$$

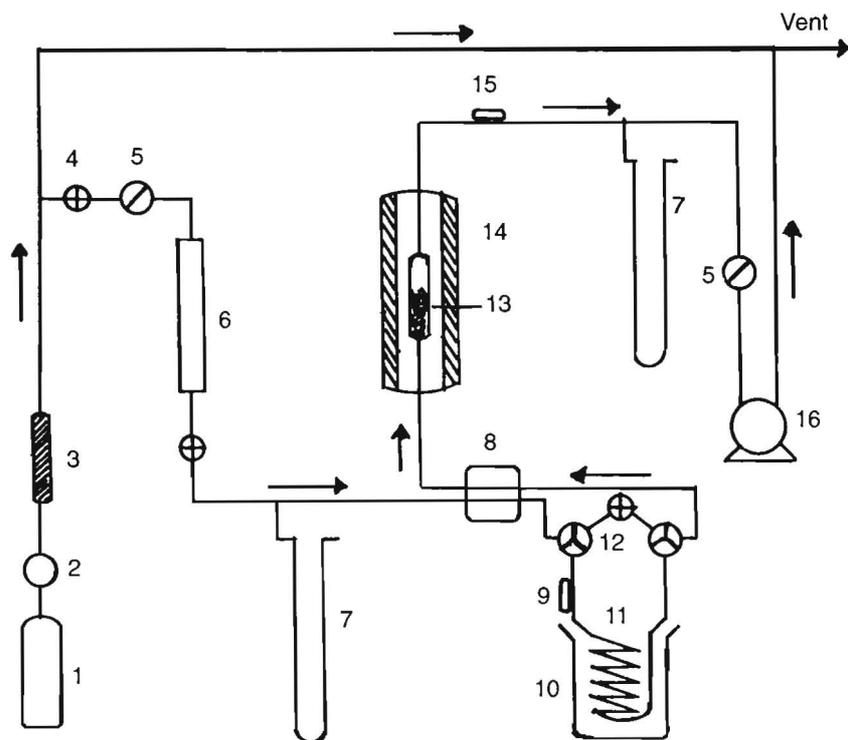


Fig. 1. Schematic diagram of the flow reactor system composed of the following:

- | | |
|-----------------------------------|----------------------------------|
| (1) H ₂ cylinder | (9) reactant introduction port |
| (2) pressure regulator | (10) temperature controlled bath |
| (3) silica gel | (11) glass coil |
| (4) shut-off valve | (12) two-way stopcock |
| (5) metering valve | (13) catalyst holder |
| (6) rotameter | (14) reactor |
| (7) Hg manometer | (15) effluent sampling point |
| (8) Thermal conductivity detector | (16) vacuum pump |

where r is the rate in $\mu\text{mol}\cdot\text{min}^{-1}\cdot\text{gm}^{-1}$ Ni or $\mu\text{l}\cdot\text{min}^{-1}\cdot\text{gm}^{-1}$ Ni, F is the toluene flow rate in $\mu\text{mol}\cdot\text{min}^{-1}$ or $\mu\text{l}\cdot\text{min}^{-1}$, α is the fraction of toluene converted to products and w is the weight of Ni in gm.

Effluents were collected at the sampling point after the reactor when the system was observed to assume the steady state characteristics. Gas chromatographic analysis was made on 20% DC-200 on 60/80 mesh chromosorb P column using an FID detector.

Results and Discussion

Preliminary activity evaluation was carried out on three catalysts containing different Ni loading (2%, 4% and 6% Ni) over $\text{-Al}_2\text{O}_3$. Partial characterization given in Table 1 showed almost insignificant deviation in $S_{(\text{BET})}$ and pore volume values between the catalysts. However, H_2 chemisorption revealed that the metal content gave rise to free metal surface area which ranged from $0.28 \text{ m}^2\text{gm}^{-1}$ for the 2% Ni to $1.06 \text{ m}^2\text{gm}^{-1}$

Table 1. Surface area, pore volume and free metal surface area of the different catalysis

Catalyst	$S_{(\text{BET})}$ ($\text{m}^2 \text{ gm}^{-1}$)	V_p (ml gm^{-1})	$S_{(\text{M})}$ ($\text{m}^2 \text{ gm}^{-1}$)
2% Ni/ Al_2O_3	110.16	0.31	0.28
4% Ni/ Al_2O_3	102.82	0.28	0.62
6% Ni/ Al_2O_3	102.95	0.28	1.06

for the 6% Ni. The greater free metal surface area can be viewed to suggest higher activity for the 6% Ni. This was confirmed by initial catalytic activity run demonstrating a parallel trend and with a practically sixfold increase from $150 \mu\text{mol} \cdot \text{min}^{-1} \cdot \text{gm}^{-1}$ of the 2% of the Ni catalyst to a leveling off of activity at $850 \mu\text{mol} \cdot \text{min}^{-1} \cdot \text{gm}^{-1}$ of the 6% Ni catalyst (Fig. 2). No apparent activity was discernable below the 2% Ni level, an observation similar to that gathered by Hill and Selwood (1949) for the hydrogenation of benzene where it was suggested that a critical nickel content (3% Ni) below which the catalysts were very much less active. Accordingly, subsequent study was carried out using the 6% Ni/ Al_2O_3 catalyst.

Initial gas chromatographic analysis of the effluents taken at different temperatures revealed three reaction products namely benzene, methane, and methylcyclohexane in amounts corresponding to the occurrence of hydrodealkylation, hydrocracking, and hydrogenation processes, respectively. Fig. 3 illustrates that at 549 and 556 K, methylcyclohexane was detected indicating saturation of the aromatic ring by hydrogen as one of the current reaction proceeding at about 9.0-10.4 % selectivity in addition to hydrodealkylation which proceeds at 89.6 to 91.0 % selectivity. Selectivity for hydroalkylation is calculated according to the following relation;

$$\%S_B = (r_B \times 100) / (r_B + r_C + r_H) \quad (4)$$

where r_B , r_C , r_H are the initial rates of hydrodealkylation, hydrocracking and hydrogenation respectively. S_C and S_H can be calculated in a similar manner. It should be noted that

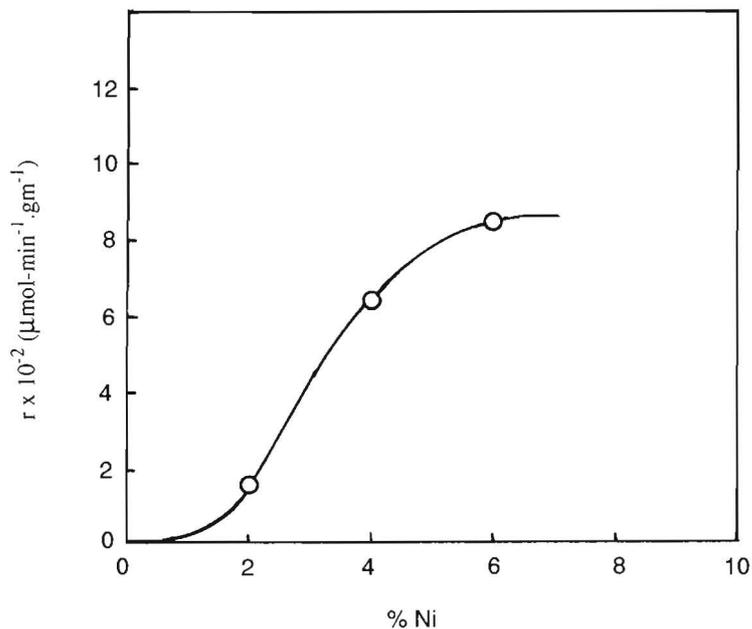


Fig. 2. Effect of the Ni content on the initial reaction rate.

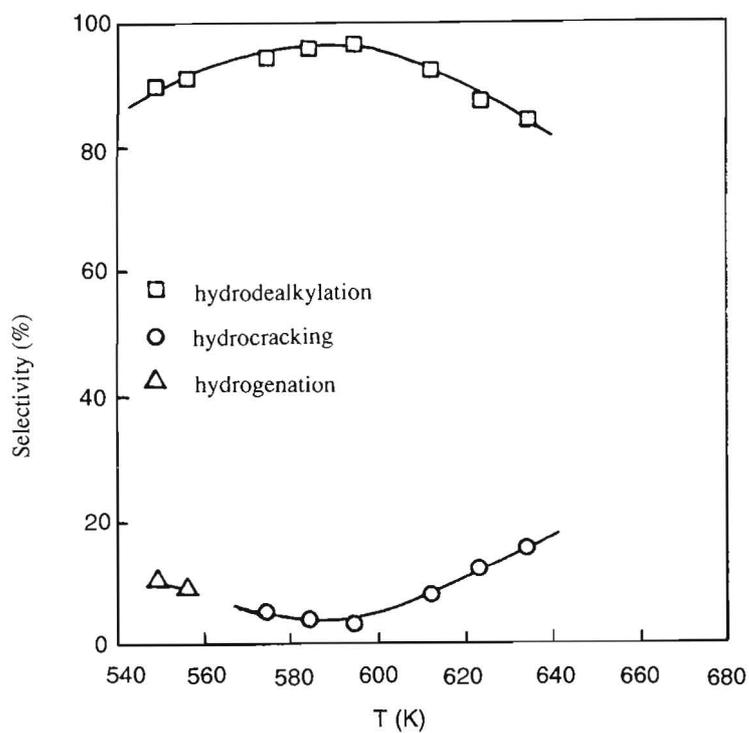


Fig. 3. Effect of temperature on the selectivity of the reaction using 6% Ni/Al₂O₃.

$$r_c = ((\infty_M - \infty_B) / 7) \times (F/w) \quad (5)$$

where ∞_M and ∞_B are the mole fractions of methane and benzene, respectively. From 574 to 634 K, hydrocracking of the different aromatic carbon-carbon bonds takes preference over hydrogenation with a corresponding increase in selectivity (5.4-15.6%) as the temperature gets higher. The hydrodealkylation reaction has been maintained at around 90% selectivity at the temperature range covered with an optimum at 593 K. Subsequent kinetic runs were then conducted at this temperature where the unwanted hydrogenation is eliminated and hydrocracking of the aromatic ring is minimal.

Table 2. Kinetic runs at 593 K for the toluene hydrodealkylation using 5% Ni/Al₂O₃ catalyst

Run No.	Partial Pressure (Torr)		Rate $\mu\text{L}\cdot\text{min}^{-1}\cdot\text{gm}^{-1}$	K
	P _{Tol}	PH ₂		
1	15	710	110.5	6.818
2	22	710	140.0	6.744
3	30	710	170.0	6.701
4	33	710	191.8	7.108
5	40	710	203.8	6.670
6	25	84	125.0	7.760
7	25	100	130.0	7.852
8	25	140	140.4	8.042
9	25	190	148.4	8.101
10	25	234	144.2	7.617

Table 2 gives the kinetic data at 593 K. Plotting $\log r$ vs $\log P_T$ at constant P_H for the first five group of runs resulted in a fairly good straight line, having a slope $m = 0.65$. Similar plot of $\log r$ vs. $\log P_H$ is also linear, with slope $n = 0.16$. These results indicate that an empirical equation;

$$r = kP_T^{0.65} P_H^{0.16} \quad (6)$$

is able to correlate the kinetic findings. A k value can be calculated for each run and by averaging the 10 results, eq. (6) becomes;

$$r = 7.3413P_T^{0.65} P_H^{0.16} \mu\text{L}\cdot\text{min}^{-1}\cdot\text{gm}^{-1} \quad (7)$$

Dependence of rate on temperature was studied in a separate run from 549 to 643 K (Fig. 4). The corresponding k -values obtained by eq. (6), were employed for an Arrhenius plot (Fig. 5) conforming to the following equation;

$$k = 2.4 \times 10^9 e^{-97943/RT} \quad (8)$$

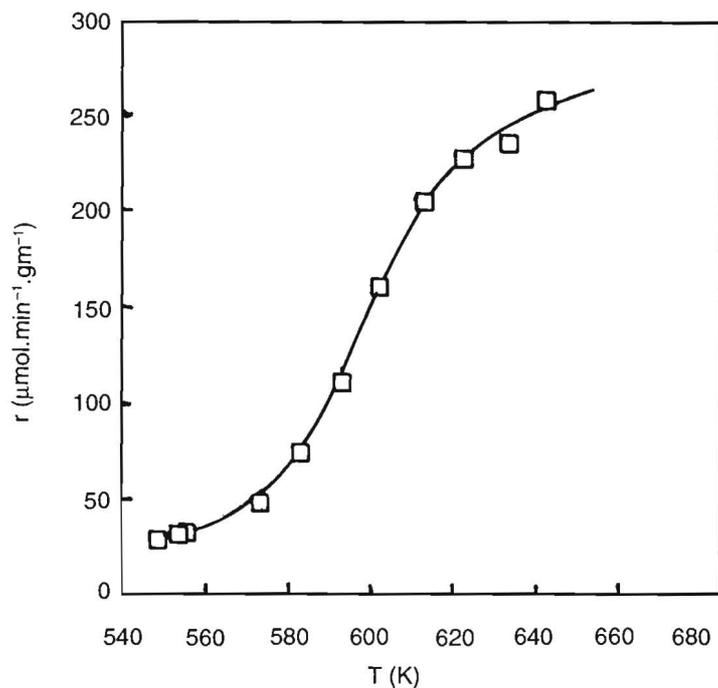


Fig. 4. Effect of temperature on the rate of reaction using 6% Ni/Al₂O₃.

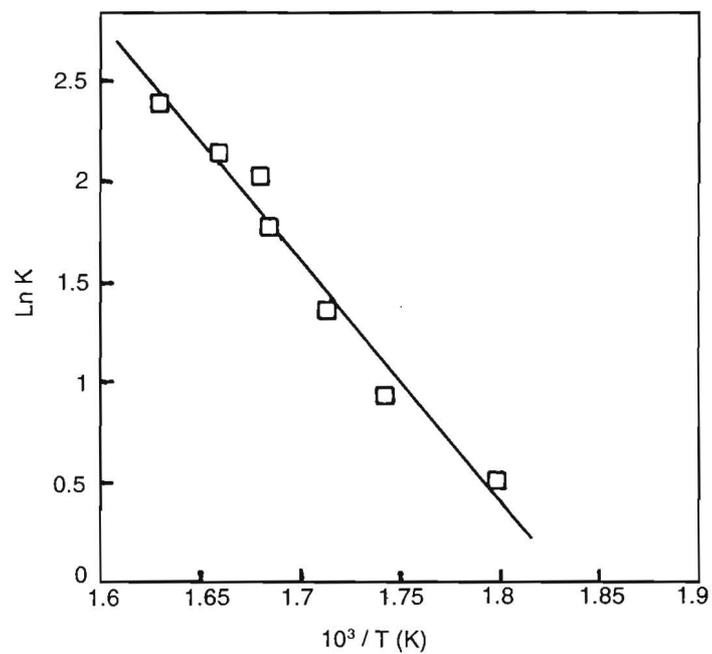


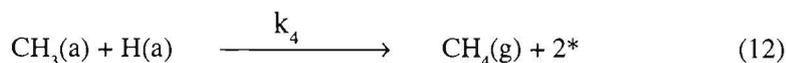
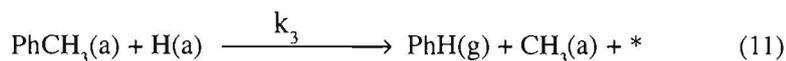
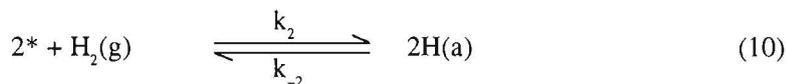
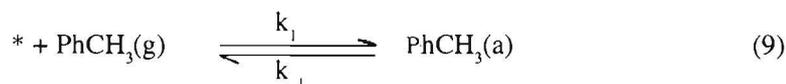
Fig. 5. Arrhenius plot for the coefficient of equation (6).

Comparison of these results with those of Grenoble (1979a) who obtained an apparent activation energy of 130 kJ/mol and reaction orders of 0.34 for toluene and -0.15 for hydrogen indicates that the catalyst may possibly be proceeding via a new and energetically favorable pathway. Correlating the results in Table 2 with those calculated using equation (7) gave an average relative deviation $(r_{\text{calc}} - r_{\text{exptl}})/r_{\text{exptl}}$ of only 0.58% (Fig. 6a). This clearly support the validity of the proposed equation within the limit of temperature and pressure studied. However, to gain more informations on the mechanism of reaction, other kinetic equations have been sought.

The observed partial reaction orders of 0.65 and 0.16 for toluene and hydrogen, respectively, points to a process controlled by the surface reaction. The competitive adsorption of the two reactants for the same surface active sites is clearly inferred by the Langmuir-Hinshelwood correlation in Fig. 7 obtained by plotting the initial reaction rate against the varying pressure of one of the reactants while at the same time maintaining the other reactant at a constant pressure. As a result of these observations, a Rideal-Eley type reaction as proposed by Grenoble (1979b) with one reactant in the gas phase attacking the other reactant adsorbed on the catalyst surface, appear to be in contradiction to this findings.

Of the several possibilities by which hydrodealkylation may proceed on $\text{Ni}/\text{Al}_2\text{O}_3$ surfaces, the probabilities may be limited to three pathways namely: 1) adsorption to same sites by the two reactants proceedings simultaneously to form benzene, 2) adsorption to the same sites but the reaction proceeding sequentially and 3) reaction by either atomic or molecular form of hydrogen with the toluene. These various modes by which hydrodealkylation may be achieved were examined by deriving the particular Langmuir-Hinshelwood type equations and evaluating their validity

Hydrodealkylation can be viewed to proceed via mechanism wherein atomic rather than molecularly adsorbed hydrogen is involved in a sequential reaction with adsorbed toluene molecule in a sequence as follows;



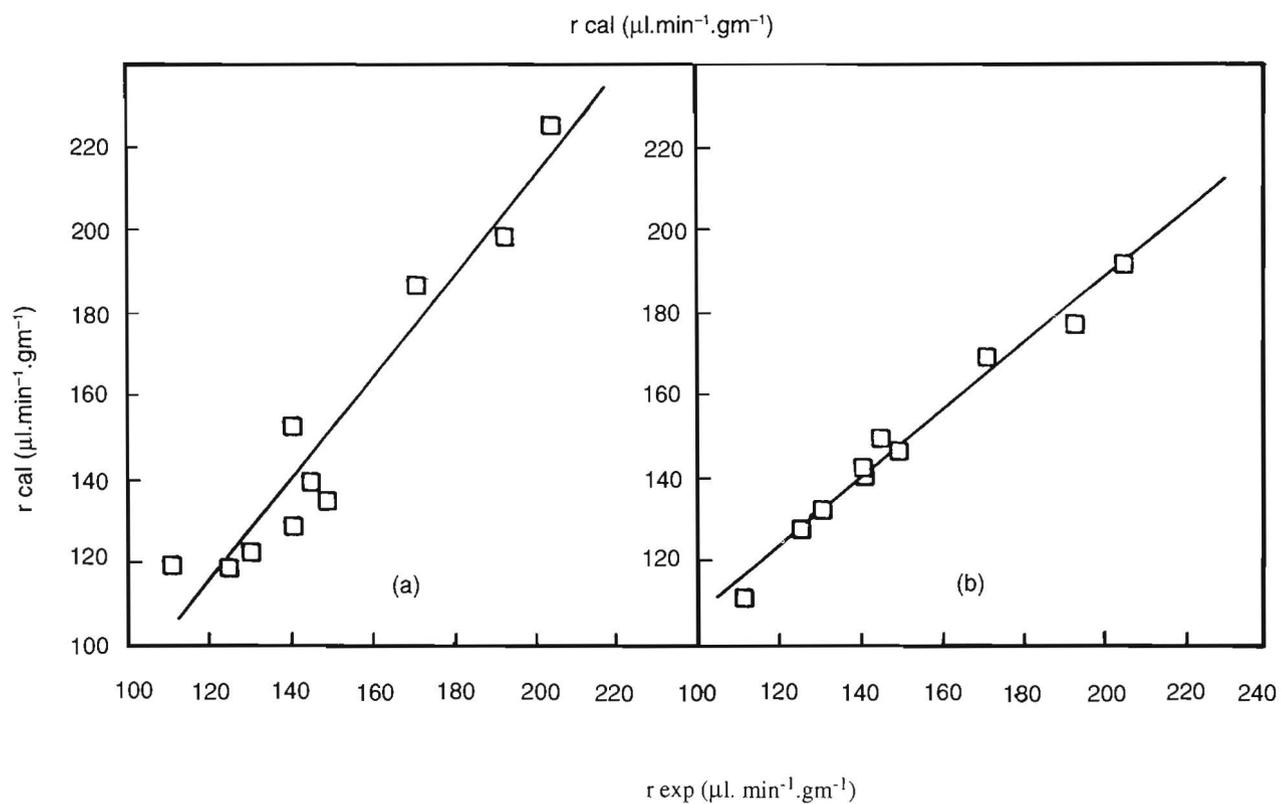


Fig. 6. Experimental values of Table 1 vs. initial reaction rates calculated by (a) equation (7) and (b) by equation (18).

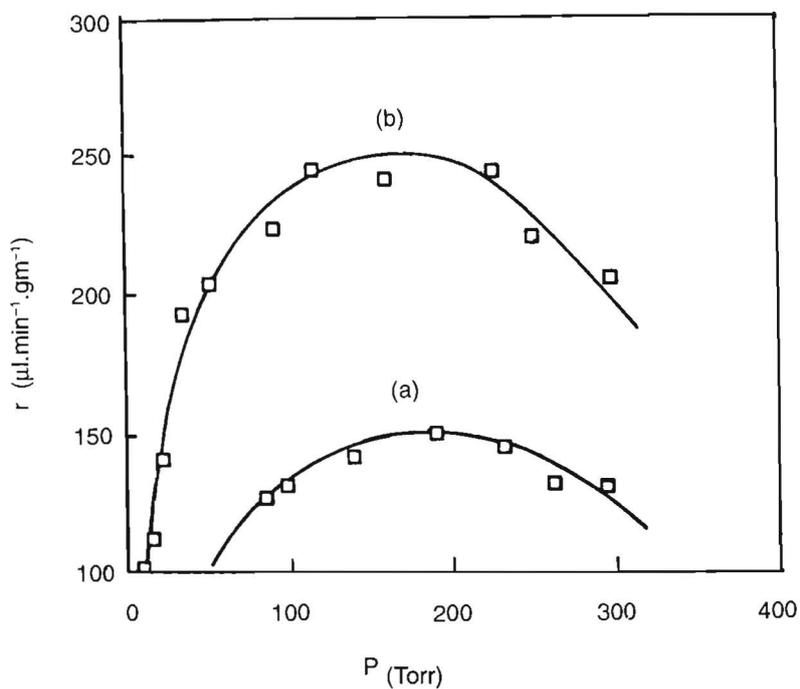


Fig. 7. Effect of (a) hydrogen ($P_T = 25$ Torr) and (b) toluene ($P_H = 710$ Torr) partial pressure on the initial reaction rate.

In the above sequence * is a special site in the metal catalyst capable of chemisorbing toluene or hydrogen. If the equilibria (9) and (10) are established rapidly compared with the removal of adsorbed reactants in the reactions (11) and (12) the appropriate Langmuir equations may be applied to obtain the surface coverages of toluene and hydrogen. Thus

$$\theta_T = K_T P_T / (1 + K_T P_T + K_H^{1/2} P_H^{1/2}) \quad (13)$$

$$\theta_H = K_H^{1/2} P_H^{1/2} / (1 + K_T P_T + K_H^{1/2} P_H^{1/2}) \quad (14)$$

where $K_T = k_1/k_{-1}$ and $K_H = k_2/k_{-2}$. Accordingly the rate of toluene hydrodealkylation, r_B , is given by;

$$r_B = k_3 \theta_T \theta_H$$

$$r_B = k_3 K_T P_T K_H^{1/2} P_H^{1/2} / (1 + K_T P_T + K_H^{1/2} P_H^{1/2})^2 \quad (15)$$

In order to examine the validity of the derived equations for the observed pressure dependence, Eq. (15) is transformed to;

$$(P_T/r_B)^{1/2} = (1 + K_H^{1/2} P_H^{1/2}) / (k_3 K_T K_H^{1/2} P_H^{1/2})^{1/2} + K_T P_T / (k_3 K_T K_H^{1/2} P_H^{1/2})^{1/2} \quad (16)$$

which provides a linear relationship between $(P_T/r_B)^{1/2}$ and P_T under the condition of constant P_H . A similar transformation of Eq. (15) with respect to hydrogen gives;

$$(P_H^{1/2}/r_B)^{1/2} = (1 + K_T P_T) / (k_3 K_T K_H^{1/2} P_T)^{1/2} + K_H^{1/2} P_H^{1/2} / (k_3 K_T K_H^{1/2} P_T)^{1/2} \quad (17)$$

where a linear relationship between $(P_H^{1/2}/r_B)^{1/2}$ and $P_H^{1/2}$ exists under the condition of constant P_T . Fairly good linear plots of the observed values for the above mentioned relationships shown in Figs. 8a and 8b. Calculation of the adsorption coefficients K_T and K_H from the numerical values of the slopes and intercepts obtained by regression analysis gave positive values. Eventually Eq. (15) could be written for the temperature of 593 K as;

$$r = 4.104 P_T P_H^{1/2} / (1 + 0.037 P_T + 0.086 P_H^{1/2})^2 \quad (18)$$

Reaction rates calculated using Eq. (18) were correlated with experimental results giving an average relative deviation of 0.68% and is shown in Fig. 6b. All these observations verify the validity of Eq. (15), hence the mechanism suggested.

Similar treatments have been carried out for other possible reaction pathways for the THD reaction. Among those investigated are: adsorption on different sites on the surface; simultaneous reaction sequence for toluene and hydrogen; and the adsorption of molecular hydrogen on the catalyst surface. It is interesting to note that these attempts resulted either in very far correlation between the experimental and calculated rate values, or the unacceptable negative values for some or all of the kinetic parameters/adsorption coefficients calculated from the derived Langmuir reaction rate equations.

Conclusion

Kinetic equations have been suggested and the relevant parameters determined that represent very well the behaviour of the system on the 6% Ni/A1203 catalysts for conversions less than 10% at 593 K. The kinetics are consistent with the reaction mechanism in which the rate determining step is the sequential reaction between toluene and hydrogen atom adsorbed on similar sites on the surface of the metal catalyst.

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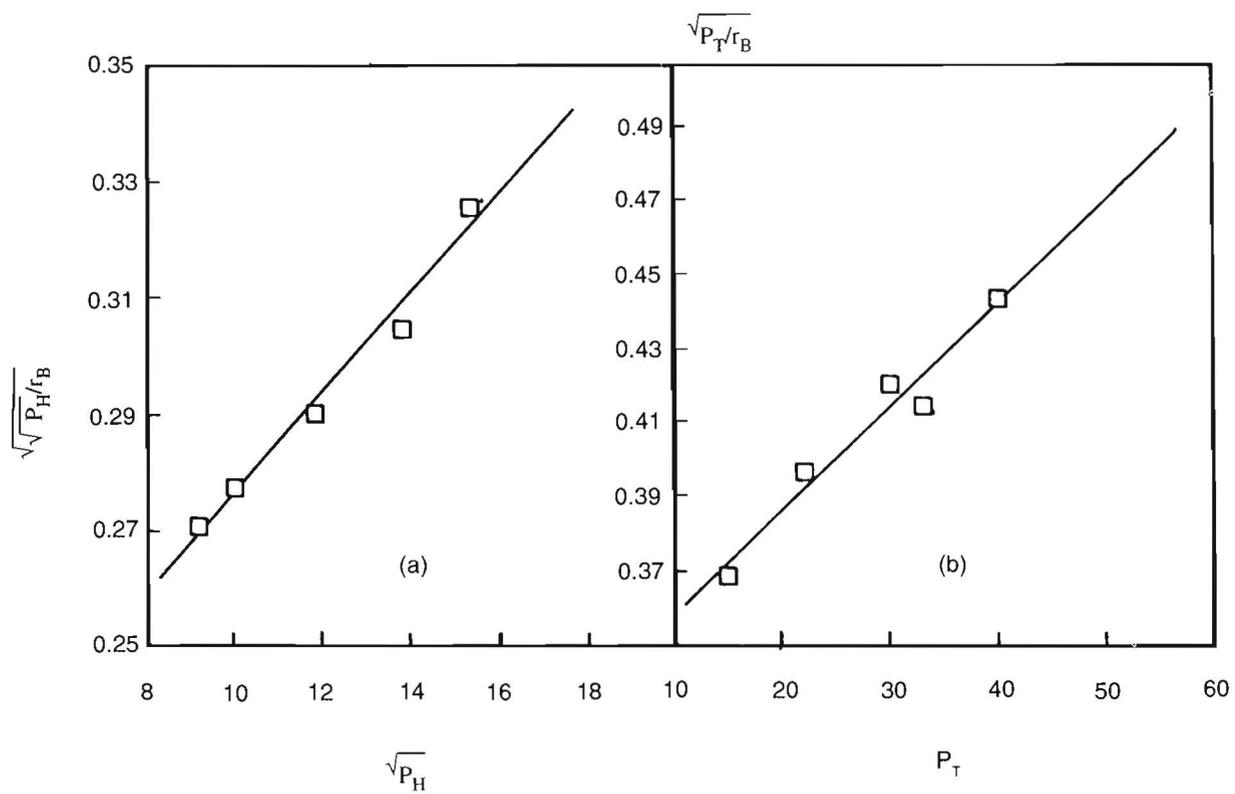


Fig. 8. Linear plots of (a) $\sqrt{P_H/r_B}$ vs. $\sqrt{P_H}$ and (b) $\sqrt{P_T/r_B}$

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حركية وميكانيكية نزع مجموعة الألكيل بهدرجة التولوين على حفاز النيكل المحمول على أكسيد الألومنيوم

سليمان بن حماد الخويطر

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ص.ب. (٢٤٥٥) - الرياض ١١٤٥١ - المملكة العربية السعودية

تمت دراسة نزع مجموعة الألكيل بهدرجة التولوين على حفاز النيكل المحمول على أكسيد الألومنيوم (6% Ni/Al₂O₃) باستخدام جهاز التدفق النبضي . ولقد وجد أن إنتقائية إنتاج البنزين تكون أعلى ما يمكن عند درجة حرارة (593 K) أما عند درجات حرارة أقل تحدث عملية هدرجة للحلقة العطرية بينما تحدث عملية تكسير لها عند درجات الحرارة العالية . كما وجد أن طاقة التنشيط لإنتاج البنزين تساوي (97.9) كيلو جول لكل مول .

كما تم إقتراح ميكانيكية للتفاعل حسب ميكانيكية لانجمور - هينشل وود - (Langmuir-Hinshelwood) تم إشتقاق قانون لسرعة التفاعل بالاعتماد على هذه الميكانيكية على أساس أن الخطوة المحددة لسرعة التفاعل هي التفاعل السطحي الذي يحدث بين جزيئة التولوين وذرة الهيدروجين الممتزتان على موقع متشابه على السطح .

$$r = 4.104P_T P_H^{1/2} / (1 + 0.037P_T + 0.086P_H^{1/2})^2$$

ثم تم تفسير النتائج الحركية عند تحويلات منخفضة للتولوين إلى بنزين
بالاعتماد على قانون سرعة التفاعل التجريبي :

$$r = K P_T^m P_H^n$$

والقانون السابق المشتق من الميكانيكية ، ولقد وجد تطابق جيد بين
القانونين عندما يكون التفاعل من الرتبة (n=0.16) بالنسبة للهيدروجين ومن
الرتبة (m=0.65) بالنسبة للتولوين .