



Original Research Article

**Effect of support nature on performance and kinetics of nickel nanoparticles
in toluene hydrogenation**

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ABSTRACT

The kinetics of toluene hydrogenation over Ni-supported catalysts with various supports was investigated under the wide range of conditions as 130 to 210 °C reaction temperature, 2.6×10^{-5} to 5.9×10^{-5} atm partial pressure of hydrogen and 1.4×10^{-9} to 3.7×10^{-8} atm partial pressure of toluene. For more study, two kinetics models were also selected and studied to describe the kinetics of this process. The modelling study indicates that the competitive adsorption mechanism provides a good fit towards the experimental data and allows to determine the kinetics parameters. According to these studies, Ni/HZSM-5(40 wt. %)-HMS catalyst has better performance than other prepared catalysts for the toluene hydrogenation process.

Keywords: Toluene; Mechanism; Zeolite; Modelling; Hydrogenation.

Introduction

Hydrogenation of aromatic compounds due to its importance in the production of chemical and petrochemical materials, converting the heavy oil into light oil and the reduction of carcinogenicity effects of aromatics has attracted the attention of many researchers [1, 2]. Toluene is one of the volatile organic compounds (VOCs) which is released in environment by several ways, including industrial and petrochemical activities. Because of the high volatility of toluene and its devastating effects on the health and environment, the reduction of toluene is one of the main challenges for researchers. One common method for reducing and eliminating the aromatic compounds is adsorption. For this purpose, the catalysts that selected for this reaction must have large surface area (as mesoporous materials) and high acidity (as zeolites) [3]. Among the various metals used for hydrogenation, nickel has been reported as a cost-effective metal with desired results. Nickel is highly remarkable in the industry due to its similar electronic structure to Pt and Pd [4, 5]. According to literatures [4, 6], the reaction rate of hydrogenation depends on different parameters as acidity of supports, particle size of active phase, number of active sites and preparation methods. The reported kinetics studies for toluene hydrogenation show that the adsorption mechanism can be competitive or non-competitive. In the case of non-competitive adsorption, acidity of supports plays an important role to increase the number of active sites [7].

To date, a lot of studies have been focused on toluene hydrogenation process, but there is still a long way to prepare the effective catalyst that has good activity in this reaction and high stability against deactivation.

In our previous works [8, 9], we examined the hydrogenation of a mixture of aromatics (as benzene, toluene and xylene). In these works, the activity of prepared catalysts was considered for the competitive hydrogenation of benzene in this mixture.

Accordingly, the objective of the present work is the study of catalytic hydrogenation of toluene, on different Ni supported micro-, meso- and micro/mesoporous materials. The purpose of this work is to gain some information about the relation between the catalytic activity, kinetics and the catalytic properties involving porous structure and acidity and so developing novel information about this reaction. In this work, the discrimination of two kinetics models for

toluene hydrogenation over a wide range of experimental conditions and also the role of hydrogen and toluene partial pressures in the hydrogenation of toluene were investigated.

Experimental

Materials and Catalyst Preparation. Nickel supported catalysts were prepared by wetness impregnation method and characterized as described in detail with our earlier reports [9, 10]. Briefly, the appropriate amounts (25 wt. %) of nickel nitrate hexa hydrate (Merck) were added to the following supports.

In order to preparation γ -alumina [9, 11], 13.3 M aqueous solution of ammonia was added to 1.7 M solution of ammonium nitrate until the pH of solution equal to 6. Also, silica was prepared by adding 6% sulphuric acid solution at room temperature to a solution of 10% sodium silicate to reach pH=4-5. For preparing HMS [9, 12] and HZSM-5/HMS [9, 13], a certain amounts of ethanol (Merck), tetra ethyl ortho silicate (Merck), 0.5 ml HCl (1 M) (Merck), dodecyl amine (Merck) and deionized water were used. The hydrothermal method was used for preparing HZSM-5 (Si/Al=14). The obtained solid was washed with distilled water and calcined in air at 600 °C for 12 h. Then, decationization of Na-ZSM-5 powder was carried out by ion exchange four times using ammonium chloride solution. In preparation of the HMS [9, 12], the sol-gel method was used. In this procedure, the solid product was separated by filtration. To prepare the HZSM-5/HMS composite material, 1 g of HZSM-5 was added to a preformed HMS colloidal precursor according to the reported procedure [9, 13]. In all cases, the resulting gels were dried at ambient temperature for 18 h, calcined up to 600 °C and then cooled to 25 °C. The impregnated materials with nickel were dried at 110 °C and calcined in flowing air at 300 °C for 4 h [9].

Hydrogenation Experimental Method. The hydrogenation of toluene (Tu) to methyl cyclohexane was performed in a continuous fixed bed Pyrex micro reactor at atmospheric pressure and temperature range of $130 \leq T \leq 210$ °C. This process was conducted over 0.5 g of each loaded catalyst with toluene in the presence of hydrogen as a gas mixture feed. Before the catalytic test, each of the prepared catalysts was reduced under hydrogen stream with 40 ml min⁻¹ flow rate in 400 °C for 2 h. The used feed was injected into the reactor with the space velocity in the range of 500-3900 h⁻¹. The catalytic tests were carried out at various temperatures (130-210 °C) over each catalyst. The samples were heated at a rate of 20 °C h⁻¹. The obtained results from catalytic

performance were recorded by online gas chromatograph (Agilent Technologies 7890A equipped with a flame ionization detector). Also for investigating the stability of catalysts versus the effective factors in the deactivation of catalysts as coke deposition, all catalysts were tested at 190 °C for 72 h under feed stream.

Kinetics studies in the vapour-phase were carried out over prepared catalysts with the reaction mixture of toluene and H₂ in the previous described reactor. The toluene conversions were kept below 10% by varying catalyst weights in order to avoid the limitative effects of transport phenomena (heat and mass transfer) on the kinetics of toluene hydrogenation. The performed tests showed the absence of these transfer limitations. The toluene hydrogenation was also performed to determine the orders of reaction and activation energies obtained with the prepared catalysts. Accordingly, the order of reactants was evaluated by changing the partial pressure dependency on hydrogen in the range of 2.6×10^{-5} to 5.9×10^{-5} atm as well as changing the partial pressure dependency on toluene from 1.4×10^{-9} to 3.7×10^{-8} atm, in the gas phase at a constant temperature in 130-210 °C range and ambient pressure.

Results and Discussions

Experimental Results of Toluene Hydrogenation. Hydrogenation of toluene was used to study the catalytic activity of the nickel supported samples. Figure 1 presents the results for this investigation at 130-210 °C over the prepared catalysts. The analyses show that the main product in all catalytic tests is methyl cyclohexane and other products are very negligible. The obtained results (Figure 1) for all catalysts present a maximum activity at 190 °C. At higher temperature, the decrease in activity can be observed for all catalysts. This observation is due to the nature and tendency of hydrogenation reaction to carry out at low temperatures. After a certain temperature, this reaction is replaced by its reverse reaction (dehydrogenation). Among the used catalysts, the maximum activities were obtained for Ni/ZH-40 that is a composite catalyst of microporous (HZSM-5) and mesoporous (HMS) materials. The catalytic activities in terms of conversion, selectivity and yields (Figure 1 (a-c)) to the desired product follows the below sequence:



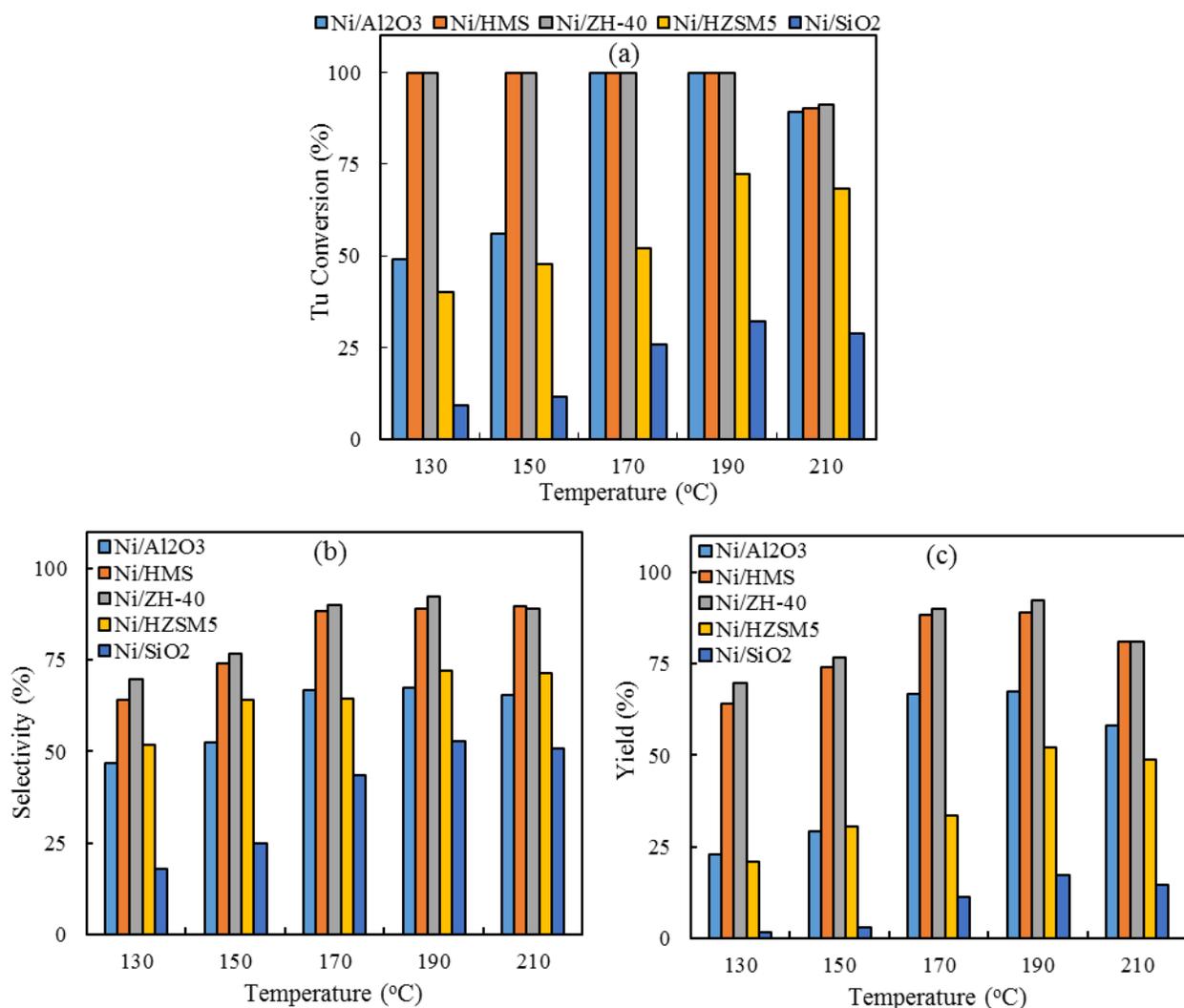


Figure 1. The effect of reaction temperature on (a) toluene conversion, (b) selectivity to methyl cyclohexane and (c) reaction yield over Ni-supported catalysts.

This trend does not follow a separate structural property that was reported for these prepared catalysts in our previous work [9]. This observation can be explained by the effect of a combination of the structural properties (as nickel particle size, catalytic surface and acidity) on the obtained results.

The stability of the catalysts activity under the experimental conditions for toluene hydrogenation was assessed by on-stream reaction tests lasting over 12 h at a selected temperature (190 °C). As can be seen in Figure 2, all prepared catalysts except Ni/SiO₂ have the most decreasing in activity for the first 4 h of the reaction. As the time increases, the decrease

continues slowly until it remains relatively stable at a level of activity. Among the prepared catalysts, the activity of Ni/SiO₂ has a minimum amount of reduction. It could be found from the results that the main factor in reducing the activity of catalysts is their deactivation by the coke deposition on catalysts surfaces. The measured coke amounts are as follows;

Ni/γ-Al₂O₃ (0.79 wt. %) > Ni/HZSM-5 (0.64 wt. %) > Ni/ZH-40 (0.62 wt. %) > Ni/SiO₂ (0.34 wt. %) > Ni/HMS (0.27 wt. %)

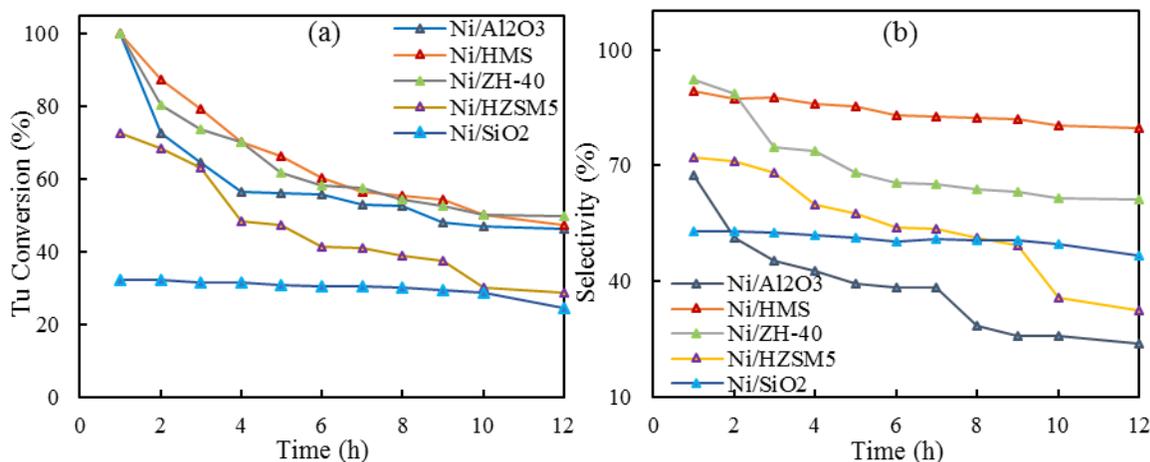


Figure 2. Changes of conversion and catalytic selectivity to desired product in toluene hydrogenation vs. time of reaction at 190 °C.

The reaction kinetics were modelled by the empirical power rate model (PRM) at 130-210 °C temperature range based on the following equation;

$$r = k P_{Tu}^m P_{H_2}^n \quad (1)$$

Where k represents the experimentally determined apparent rate constant, P_{Tu} and P_{H_2} are the partial pressures of toluene and hydrogen, and m and n are the orders of the reaction with respect to the toluene and hydrogen partial pressures, respectively.

For the experimental study of this work, the initial partial pressures of toluene and hydrogen were varied from 1.4×10^{-9} to 3.7×10^{-8} atm and from 2.6×10^{-5} to 5.9×10^{-5} atm, respectively. Under these conditions, the toluene conversion was obtained 0.6 to 8.9%. It shows that the reaction proceeds in the kinetics regime. The observed reaction rates as a function of the partial pressures of the reactants in the logarithm form were shown in Figure 3 (a). The results show that

the reaction rate increases with an increasing pressure of H_2 , whereas the reaction rate decreases slightly with an increasing pressure of toluene.

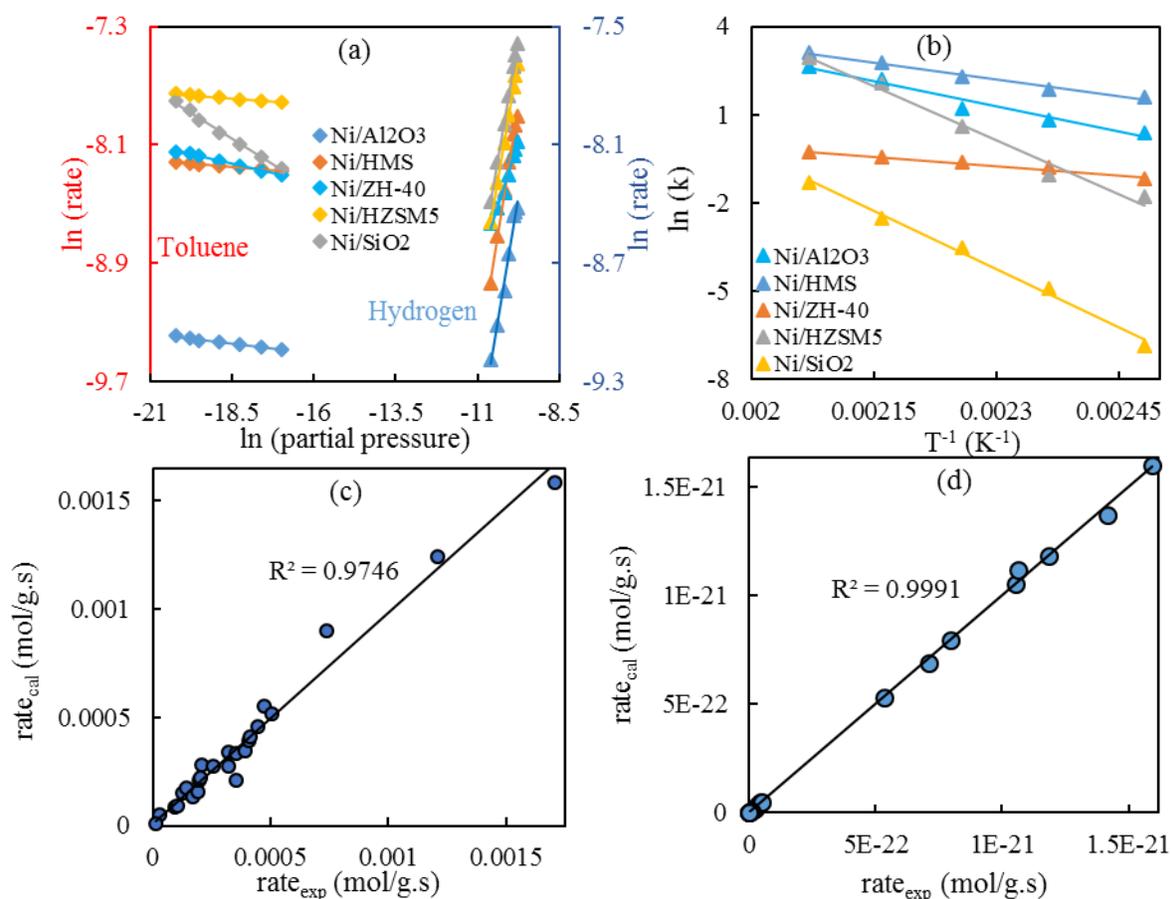


Figure 3. (a) Logarithm plots of the reaction rate over Ni-supported catalysts in toluene hydrogenation at 190 °C as a function of partial pressure of toluene and hydrogen, (b) Arrhenius plots, and comparison of experimental rate with values calculated using (c) the power rate model and (d) kinetics model equation (Eqn. (2)).

By fitting the apparent rate constant results for the different catalysts to the Arrhenius equation (Figure 3 (b)) [9], the apparent activation energies set out in Table 1 have been estimated for the temperatures ranging of 130 to 210 °C. From the slope of these plots, the apparent activation energies were approximated to be in the range of 17.32-109.76 kJ mol^{-1} . These values show almost the observed conversion trend. As stated about activity results, it does not seem that a parameter such as catalytic surface area, catalysts acidity and acid strength independently effect on these results, but the interaction of these parameters is effective on the results. These obtained data are very sparse, such as the activation energies available in the literatures [14-16] for the gas-phase hydrogenation of toluene. For example, Frauwallner et al. [14] reported the activation

energies of approximately 58.1 kJ mol^{-1} on molybdenum carbide catalyst at $150\text{-}325 \text{ }^\circ\text{C}$. Pushkarev et al. [15] reported activation energies for the toluene hydrogenation over Pt/SBA-15 catalysts with $1.5\text{-}5.2 \text{ nm}$ Pt particle sizes at temperatures between 70 and $125 \text{ }^\circ\text{C}$ to be $32\text{-}39 \text{ kJ mol}^{-1}$, whereas activation energies in the range of 153 to 163 kJ mol^{-1} were reported by Castaño et al. [16] in the toluene hydrogenation over Pt/HZSM-5 and Pt/ Al_2O_3 -HZSM-5 catalysts at temperatures ranging from 250 to $450 \text{ }^\circ\text{C}$.

Table 1. Kinetics parameters calculated by PRM model for toluene hydrogenation.

Temp.	Ni/ Al_2O_3		Ni/HMS		Ni/ZH-40		Ni/HZSM5		Ni/ SiO_2	
	n_{H_2}	m_{Tu}	n_{H_2}	m_{Tu}	n_{H_2}	m_{Tu}	n_{H_2}	m_{Tu}	n_{H_2}	m_{Tu}
$130 \text{ }^\circ\text{C}$	0.98	-0.05	0.99	-0.02	0.99	-0.14	0.80	-0.03	0.39	-0.10
$150 \text{ }^\circ\text{C}$	1.01	-0.04	0.99	-0.02	0.99	-0.14	0.83	-0.02	0.52	-0.07
$170 \text{ }^\circ\text{C}$	1.03	-0.03	0.99	-0.02	0.99	-0.14	0.95	-0.02	0.69	-0.06
$190 \text{ }^\circ\text{C}$	1.06	-0.02	0.99	-0.02	0.99	-0.13	1.05	-0.01	0.91	-0.05
$210 \text{ }^\circ\text{C}$	1.09	-0.02	0.99	-0.01	0.99	-0.13	1.13	-0.01	1.09	-0.04
$E_{\text{app}}^{\text{act}}(\text{kJ mol}^{-1})$	47.36 ± 0.21		31.39 ± 0.09		17.32 ± 0.07		101.84 ± 0.32		109.76 ± 0.22	

Three parameters of the PRM (k , m and n) were determined by multiple regression analysis (Table 1), and the experimental reaction rates were compared to the values calculated by Eqn. 1 in Figure 3 (c). The fitness of the PRM to the experimental data is evidenced by the slope of unity and correlation coefficient ($R^2=0.97$). The measured values of n and m from this model show a slight negative reaction order for toluene (-0.01 – -0.14) and a value in the range of 0.39 – 1.13 for hydrogen as the reaction temperature was raised from 130 to $210 \text{ }^\circ\text{C}$. The surface dehydrogenation reactions at high temperatures leads to an increase in the hydrogen order. The observed results indicate that toluene and hydrogen adsorb competitively on the same type of active sites on the Ni-supported catalysts. The negative rate exponents of toluene show the inhibitory effect of this compound and its strong adsorption on catalysts surfaces in relation to the adsorption of hydrogen.

The PRM is a simple statistical model versus numerical adjustment. Since this model does not consider the adsorption of molecules on catalytic surfaces, its results is unreal. Accordingly, to better estimate, other kinetics models were proposed for the study of toluene hydrogenation. These models can be classified into two groups as non-competitive and competitive models. In the first model, the reaction is performed on two different active sites and in other model on only one type of active site.

According to the obtained results, it seems that these data are consistent with the competitive model. In this model, a competitive adsorption occurs between toluene and hydrogen on metal sites.

A preliminary investigation of kinetics data obtained from PRM suggests that the molecules adsorption on active sites has been done competitively. Using different assumptions, researchers have provided various equations for expressing this model. Among the different reported equations [7], the empirical obtained data were shown more consistent with the follow equation;

$$r = \frac{kK_{H_2}P_{H_2}K_{Tu}P_{Tu}}{(1+K_{H_2}^{1/2}P_{H_2}^{1/2}+3K_{Tu}P_{Tu})^3} \quad (2)$$

Where k is the rate constant, K_{H_2} and K_{Tu} are the chemisorption equilibrium constants ($K_i = \frac{k_i}{k_{-i}}$) and P_{H_2} and P_{Tu} are the hydrogen and toluene partial pressures, respectively.

The estimated values of the kinetics parameters for the competitive adsorption model (Eqn. 2) and the fitting of this model with experimental data were presented in Table 2 and Figure 3 (d), respectively. The correlation coefficient of this plot ($R^2 \sim 1.00$) is more than PRM. This shows that the calculated data with this model has a closely trend to experimental results. The negative values of the adsorption heats for Tu (ΔH_{ads-Tu}) and H₂ (ΔH_{ads-H_2}) in Table 2 present exothermic nature of the reactions in hydrogenation process. The pre-exponential factors of adsorption for H₂ (A_{H_2}) and Tu (A_{Tu}) were also listed in Table 2.

Table 2. Kinetics parameters and activation energies estimated by Eqn. 2 in toluene hydrogenation.

Parameters	Ni/Al ₂ O ₃	Ni/HMS	Ni/ZH-40	Ni/HZSM5	Ni/SiO ₂
K					
E_{app}^{act} (kJmol ⁻¹)	77.6	48.8	44.4	99.9	181.9
A (mol/gs)	8.5×10 ⁻⁸	7.4×10 ⁻¹¹	9.9×10 ⁻¹³	1.8×10 ⁻⁴	2.7×10 ⁶
K_{Tu}					
$-\Delta H_{ads-Tu}$ (kJmol ⁻¹)	3.6	3.6	3.6	3.6	3.6
A_{Tu} (atm ⁻¹)	13.0	13.0	13.0	13.0	13.0
K_{H_2}					
$-\Delta H_{ads-H_2}$ (kJmol ⁻¹)	102.6	33.1	93.6	93.7	121.8
A_{H_2} (atm ⁻¹)	4.2×10 ⁻⁴	3.3×10 ⁻¹⁵	2.0×10 ⁻⁶	1.5×10 ⁻⁵	3.6×10 ⁻³

This factor for Tu is almost similar in all catalysts, and for hydrogen is in the range of 33-122 kJ mol⁻¹. The smaller pre-exponential factor probably implies a slower and weaker adsorption for respective component over the prepared catalysts. The calculated activation energies with this model for the catalysts are in the range of 44 and 182 kJ mol⁻¹.

These values are in good agreement with the reported works [7]. According to the kinetics data, the Ni/ZH-40 catalyst performs the toluene hydrogenation reaction fast and easily, because of its low activation energy compared to other catalysts.

Conclusions

A series of kinetics tests was performed with the Ni-supported catalysts under various operating conditions. The kinetics tests show that these catalysts (especially Ni/ZH-40) could perform the toluene hydrogenation process with appropriate rate. The activation energies calculated in this work confirm that this catalyst is an attractive support for toluene hydrogenation reaction. Furthermore, two kinetics models (power law and Eqn. 2) were tested in the kinetics study by first estimating kinetics parameters and then simulating rate amounts to be compared to experimental data, in order to validate the model. Our modelling study indicates that this process is good described by the Eqn. 2 model, suggesting is as the competitive adsorption mechanism.

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