



Kinetics of the alkylation of phenol with methanol over magnesium–aluminium calcined hydrotalcites

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Abstract

Vapour phase alkylation of phenol with methanol over magnesium–aluminium calcined hydrotalcites (MgAl-CHT) with an Mg/Al atomic ratio of 3–10 has been investigated in detail and reported previously. This study concerns the evaluation of the kinetic parameters such as the activation energy (E_a) and Arrhenius frequency factor ($\ln A_0$) for the disappearance of phenol employing the Power law equation assuming pseudo first order kinetics. The kinetic parameters were found to be in good agreement with the specific activity of the catalysts. The existence of the compensation effect between E_a and $\ln A_0$ has been tested.

Keywords: Alkylation; Hydrotalcite; Kinetics

1. Introduction

Hydrotalcites are a class of layered materials of current interest. They consist of positively charged brucite-like layers separated by charge balancing hydrated anions. A wide range of compositions of the type $[M(II)_{1-x}M(III)_x(OH)_2(A^{n-})_{x/n}y \cdot H_2O]$, where M(II) and M(III) are divalent and trivalent cations, A^{n-} is the interlayer exchangeable anion and $x = 0.1–0.33$ can be successfully synthesized. Thermal calcination of these materials around 450°C results in the formation of highly active mixed metallic oxides which are found to be versatile base catalysts for the synthesis of variety of fine chemicals [1,2].

Alkylation of phenol with methanol is an industrially important reaction since alkyl phenols such as *o*-cresol and 2,6-xylenol are used as raw materials for the

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synthesis of many commercially important products [3]. Our recent investigations on the alkylation of phenol with methanol over MgAl-CHTs showed that these catalysts are more efficient for the synthesis of 2,6-xylenol compared to MgO, γ -Al₂O₃ or zeolites [4]. On the other hand, substitution of Mg²⁺ or Al³⁺ by other bivalent or trivalent cations in the HT frame work resulted in an increase in the selectivity for *o*-cresol [5].

The present study has been focused on the evaluation of energy of activation (E_a) and Arrhenius frequency factor ($\ln A$) for phenol conversion over a series of MgAl-CHT, employing Power law Eq. (6) assuming a pseudo first order kinetics and then to check if a correlation exists between these parameters.

2. Experimental

[Mg_{1-x}Al_x(OH)₂]^{x+}(CO₃²⁻)_{x/2} with $x = 0.1-0.33$ were synthesized by the coprecipitation method and their physicochemical properties were studied in detail. The vapour phase alkylation of phenol with methanol was carried out at atmospheric pressure using a vertical flow type reactor, packed with 1.5 g of powdered calcined hydrotalcite (450°C/8 h). From the preliminary experiments the optimum phenol to methanol feed ratio was found to be 1:7 (where the rate of phenol conversion was independent of the concentration of methanol) with a space velocity of 9.0 mol h⁻¹ kg⁻¹. The kinetic parameters (E_a and $\ln A_0$) were evaluated from the phenol conversion values in the temperature range 250–350°C, where the diffusion and mass transfer effects were found to be insignificant. Detailed procedures on the synthesis, characterization and catalytic studies can be obtained from our earlier reports [4,7].

3. Results and discussions

The results of alkylation of phenol with methanol over a series of MgAl-CHT with an Mg/Al atomic ratio of 3–10 have already been reported [4]. To determine the reaction rate parameters for the conversion of phenol, the following differential equation was established to describe the reaction system in a plug flow reactor by assuming a pseudo first order kinetics,

$$-dC_{\text{phenol}}/d(W/F) = kC_{\text{phenol}} \quad (1)$$

where W is the weight of the catalyst (kg) and F is the flow rate of the feed (mol of phenol h⁻¹). Integration of Eq. (1) yields,

$$-\ln(1-x) = k(W/F) \quad (2)$$

The plot of $-\ln(1-x)$ against W/F over MgAl 4.0-CHT gave a straight line passing through the origin as illustrated in Fig. 1 ($k = 8.87 \cdot 10^{-4}$ mol s⁻¹

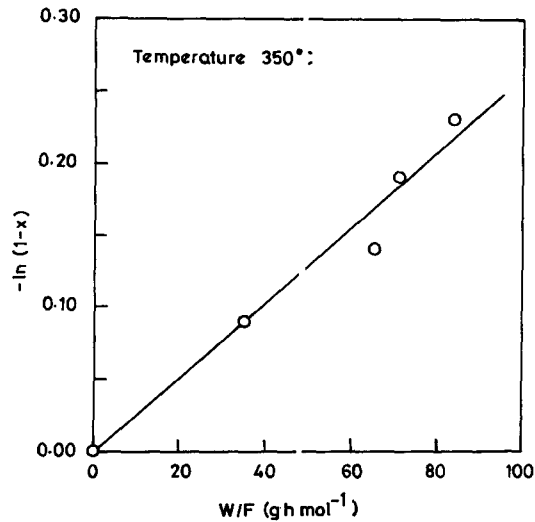


Fig. 1. Pseudo first order kinetic plot for the conversion of phenol over MgAl 4.0-CHT

kg^{-1}). The rate of the phenol conversion is, therefore, first order with respect to phenol and zero order with respect to methanol. Hence the rate equation can be written as,

$$r = kC_{\text{phenol}} \quad (3)$$

employing the equation from Power law kinetics [6], the rate of the reaction for the present system would be,

$$r = A \exp(-E_a/RT)C_{\text{phenol}} \quad (4)$$

where E_a is the activation energy and A is the Arrhenius frequency factor. For a reaction in a plug flow reactor, since, $r = (F/W)x$, Eq. (4) can be modified as

$$(F/W)x = A \exp(-E_a/RT)C_{\text{phenol}} \quad (5)$$

writing the C_{phenol} in terms of initial concentration of phenol [$C_{(\text{phenol})_0}$] and rearranging the equation, we obtain,

$$\ln(x/1-x) = \ln A_0 - E_a/RT \quad (6)$$

where $\ln A_0$ is the apparent Arrhenius frequency factor which includes a constant such as W/F as well as $C_{(\text{phenol})_0}$ and E_a is the apparent activation energy. From Eq. (6), it is clear that, a plot of $\ln(x/1-x)$ against $1/T$ would give a straight line from which E_a and the $\ln A_0$ can be obtained.

The representative Arrhenius plots for the phenol conversion employing Eq. (6) are shown in Fig. 2. The values of E_a and $\ln A_0$ derived from these plots are collected in Table 1 along with specific activity of the catalysts at 300°C. It can be seen that the E_a evaluated in the present study is in good agreement with the specific activity of the catalysts. MgAl 4.0-CHT which was found to be the most

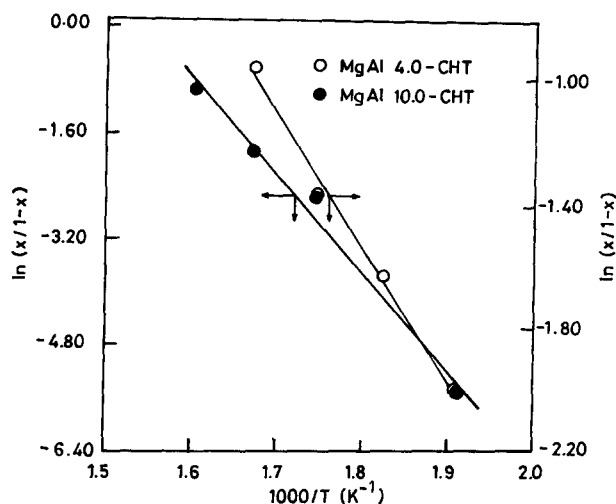


Fig. 2. Representative Arrhenius plots for phenol conversion over MgAl-CHT

active catalyst (nearly 20% phenol conversion at 300°C) showed the lowest E_a of 36 kJ mol⁻¹, while the least active MgAl 10.0-CHT (nearly 10% phenol conversion at 300°C) showed the highest E_a of 123.7 kJ mol⁻¹.

The experimental results were also checked for zero order and second order with respect to phenol using appropriate kinetic expressions derived from Eq. (1) and Eq. (5). The linear regression analysis showed ($r > 0.99$) that the experimental data fits the first order kinetic equation satisfactorily. Hence, it can be stated that under the experimental conditions employed in the present study, the results do not fit into any other kinetic expressions.

Recently Li et al. [8] have reported the E_a value of 115.0 kJ mol⁻¹ for the conversion of phenol over Manganese oxide catalyst, while Bautista et al. [9] have found it to be 20–60 kJ mol⁻¹ over various anions loaded AlPO₄-Al₂O₃.

Table 1
Catalytic activity and kinetic parameters for a series of MgAl-CHT

Catalyst	Surface area (m ² g ⁻¹)	Specific activity ^a		Kinetic parameters	
		(mmol h ⁻¹ m ⁻²) 10 ³	(mmol g ⁻¹)	E_a (kJ mol ⁻¹)	ln A_0
MgAl 3.0-CHT	125	7.89	107	52.0	9.5
MgAl 4.0-CHT	176	8.36	157	36.0	6.3
MgAl 5.0-CHT	150	5.58	90	69.3	12.9
MgAl 7.0-CHT	149	3.12	50	109.4	20.4
MgAl 10.0-CHT	124	2.25	30	123.7	23.1

^a Temperature = 300°C.

$$\text{Specific activity (mmol h}^{-1} \text{ m}^{-2}) = \frac{\% \text{ phenol conversion (g}^{-1}) \times \text{flow rate of phenol (mmol h}^{-1})}{\text{surface area (m}^2 \text{ g}^{-1})}$$

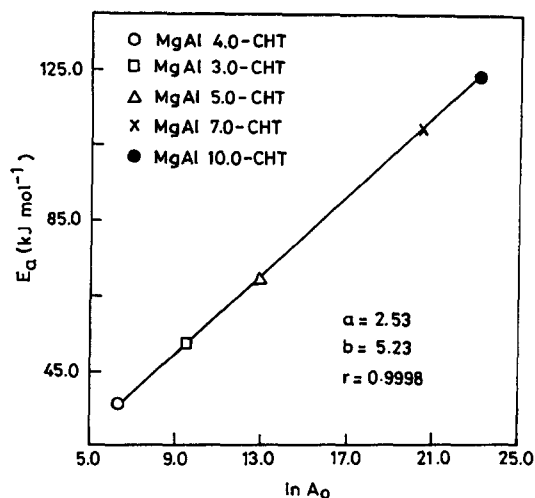


Fig. 3. Compensation plot for phenol conversion over a family of MgAl-CHT

However, Santacesaria et al. [10] have estimated the same to be 50–70 kJ mol⁻¹ over the H-ZSM-5 zeolite. The E_a calculated in the present study also varies in the same range (30–130 kJ mol⁻¹) indicating the validity of the model assumed for the evaluation of kinetic parameters.

It has been shown by several authors that a good correlation exists between E_a and $\ln A$ for a single reaction taking place over different catalysts or different reactions taking place over one catalyst [11–13]. Such a correlation is represented as ‘compensation effect’ or ‘isokinetic effect’ or ‘linear free energy relationship’ and can be written as [13]

$$E_a = a + b \ln A \quad (7)$$

where ‘ a ’ and ‘ b ’ are constants called compensation parameters. A plot of E_a versus $\ln A_0$ for the family of MgAl-CHT gave a straight line (Fig. 3) with a very high linear regression coefficient (r) of 0.9998 indicating the existence of a good compensation effect. The values of ‘ a ’ and ‘ b ’ evaluated from this plot are 2.53 and 5.23 kJ mol⁻¹, respectively. Further work is in progress to understand the mechanism of the alkylation of phenol with methanol over a series of hydrotalcite derived catalysts and to evaluate the kinetic parameters.

4. Conclusions

1. The apparent activation energy E_a and Arrhenius frequency factor $\ln A_0$ for the disappearance of phenol showed a good correlation with the specific activity of these catalysts.
2. The values of E_a vary in the same range (30–130 kJ mol⁻¹) as reported recently by several authors for phenol conversion over different catalyst

systems indicating the validity of the power law equation employed in the present study.

3. The existence of a good compensation effect between E_a and $\ln A_0$ for the family of MgAl-CHT has been evidenced.

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