



## **KINETIC STUDIES AND MECHANISM EVOLUTION OF THE METHYLATION OF PHENOL OVER Al-Fe<sub>2</sub>O<sub>4</sub> CATALYST**

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### **ABSTRACT**

Kinetics of methylation of phenol to xylenol over catalyst has been studied over Al-Fe<sub>2</sub>O<sub>4</sub> catalyst in a differential flow fixed bed reactor in the temperature range 543-643 K. The partial pressures of methanol and phenol were varied and rates were measured for the formation of xylenol. Product selectivity as well as rate of formation of xylenol were influenced by partial pressure of reactants. The rate equation  $R = k K_P K_E P_P P_E / (1 + K_P P_P + K_E P_E)^2$  deduced, on the basis of adsorption of methanol and phenol in gas phase represented the data most satisfactorily.

**Key words:** Methylation, Differential flow fixed bed reactor, Adsorption, 2,6-xylenol.

### **INTRODUCTION**

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 material for the synthesis of commercially important products<sup>1</sup>. Zeolites<sup>2-13</sup>, metal phosphates<sup>14,15</sup>, hydrotalcites<sup>16</sup> and ferrites<sup>17,18</sup> have been used as catalysts. Where zeolites lead to O-alkylated as well as C-alkylated products, we have noted that ferrites produce only ortho-C-alkylated products such as o-cresol and 2,6-xylenol.

There has been an upsurge on the alkylation of organic compounds over ferros spinel catalysts<sup>19-21</sup> having general formula AB<sub>2</sub>O<sub>4</sub>. Many ferrites have the spinel type structure, which can be described in terms of a nearly cubic close packed arrangement of anions with one half of the octahedral interstices (B site) and one eighth of the tetrahedral interstices (A site) filled with cation. Most of the ferrite properties depend upon the distribution of metal ions in the tetrahedral and octahedral sites within the spinel structure. The adequate

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selection of the substitution ion and the appropriate chemical composition changes the catalytic properties of the ferros spinels.<sup>22</sup> Depending upon the position of metals in the tetrahedral and octahedral sites ferros spinel can be normal  $A^{+2}[B_2^{+3}]O_4$ , inverse  $A^{+3}[A^{+2}B^{+3}]O_4$  or mixed spinel, in which the divalent cations are distributed between both sites. This type of cation distribution significantly affects acido-basic and surface properties of ferros spinels<sup>23,24</sup>.

A thorough literature survey on phenol methylation reveals that most of the published work on methylation of phenol is on process development. Although there are few reports on the kinetics of phenol alkylation over magnesium-aluminium calcined hydrotalcites<sup>16</sup>, Zeolite<sup>25</sup> and  $\gamma$ - $Al_2O_3$ <sup>26</sup>. This seems that there is no report available on the phenol methylation over aluminium ferrite catalyst. The present study was therefore undertaken with a view to (1) collect data on the kinetics of the vapour phase alkylation of phenol with methanol over  $AlFe_2O_4$  catalyst (2) to find a suitable rate law, which can explain the data satisfactorily, and (3) to predict a mechanism of the reaction.

## EXPERIMENTAL

### Catalyst preparation

$Al-Fe_2O_4$ , were prepared at low temperature, pH controlled co-precipitation route using aqueous solutions of ferric nitrate and aluminium chloride. NaOH was added to the mixture solution under stirring till a pH of 8.5 was obtained. The precipitate was washed, filtered, dried at 383 K and calcined at 873 K for 6 hrs in a current of air.

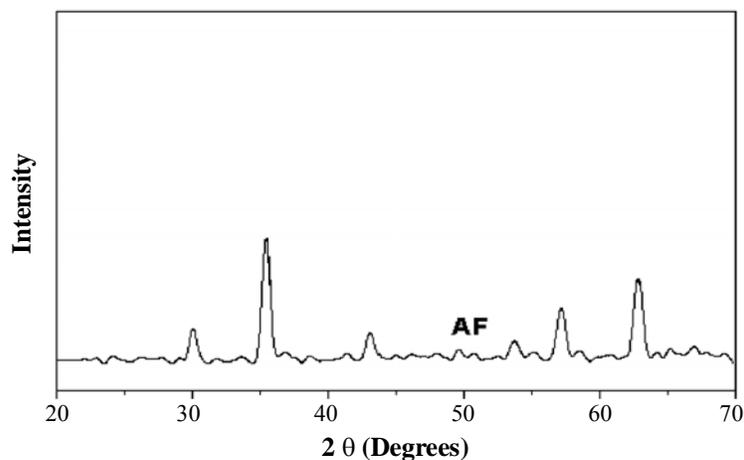
### Characterization

The XRD diffractogram of Al-ferrite was recorded on Rigaku diffractometer with  $Cu K_{\alpha}$  radiation (Fig. 1). All peaks in the pattern match well with the characteristic reflections of Al- ferrite (JCPDS No. 22-1012) and confirm the phase purity of the samples. The FTIR spectra of Al-ferrite catalyst was recorded on Perkin Elmer Series 1600 FTIR spectrometer (Fig. 2). Two broad bands appeared at 700 and 500  $cm^{-1}$  can be assigned to metal-oxygen stretching frequencies. On the basis of previous studies the band appeared at 700  $cm^{-1}$  is assigned to M-O stretching mode of tetrahedral group and that appeared at 500  $cm^{-1}$  is assigned to M-O stretching mode of octahedral group.

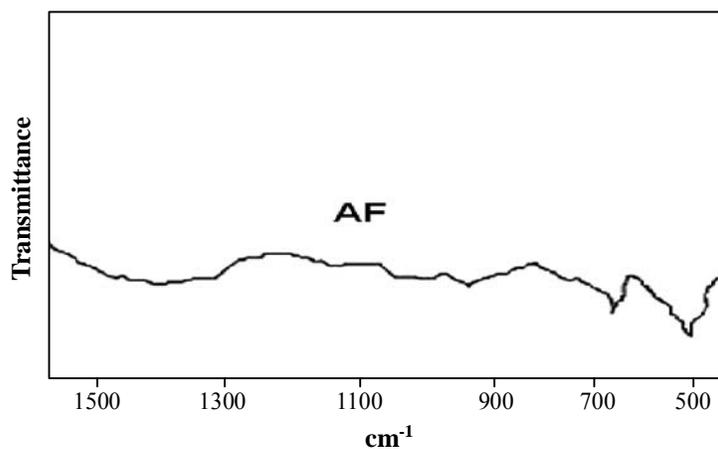
### Apparatus and procedure

Kinetic experiments were performed using a fixed bed down flow Pyrex glass tubular differential reactor (0.35 m in length and 0.8 cm ID) at atmospheric pressure. In this reactor, only a very small amount of catalyst is employed so as to keep the conversion level

low, and this affords direct evaluation of reaction rates. The contact time being small, the gas composition remains practically constant throughout the catalyst bed. The rates thus obtained are the initial rates. These initial rates are extremely helpful in simplifying the rates equations to make their applications. In addition; this technique appears to be the last resort in cases of reactions with large heat effect. The reactant partial pressure varied in the ranges as follows: Phenol (Pp) 4.21-9.92 kPa and methanol (Pm) 4.15-29.08 kPa. The measurements were made at three temperatures namely 543, 593 and 643 K. A 10 cm<sup>3</sup> pressure-equalizing funnel fed the mixture of phenol and methanol. The liquid products were condensed with the help of a cold-water condenser a cold trap and were analyzed by Shimadzu 14B Gas Chromatograph using SE-30 column and FID detector.



**Fig. 1: XRD diffractogram of Al-Ferrite**



**Fig. 2: FT-IR Spectrum of Al-Ferrite**

## Kinetic models

Because of small amount of catalyst, diffusion through the catalyst surface, mass transfer from the gas stream to the catalyst surface and desorption of products were not expected to be rate controlling. We suppose that adsorption of reactants and surface reaction were the rate controlling steps. Therefore, rate equations based on adsorption and surface reaction were derived. Such equations were solved for rate constants and adsorption equilibrium constants. A summary of different mechanisms and rate expressions derived are presented in Table 1. The mechanism for models 1 is the reaction between adsorbed phenol and adsorbed methanol on the catalyst surface and the slow step is the surface reaction. The mechanism of model 2 assumes the reaction between adsorbed phenol and methanol in gas phase as the slow and rate-controlling step. These two models are based on Langmuir adsorption as described elsewhere. Model 1 can be referred to as the Langmuir-Hinshelwood model, while Model 2 is the familiar Rideal-Eley model.

**Table 1: Models tested for alkylation of phenol with methanol**

Model	Mechanism	Resulting rate equation
1.	<p><b>Langmuir-Hinshelwood model</b></p> $\text{ROH} + \text{S} \rightarrow \text{ROH-S}$ $\text{CH}_3\text{OH} + \text{S} \rightarrow \text{CH}_3\text{OH-S}$ $\text{ROH-S} + \text{CH}_3\text{OH-S} \rightarrow \text{R-CH}_3 + \text{H}_2\text{O}$	$R = kK_pK_M P_p P_M / (1 + K_p P_p + K_M P_M)^2$
2.	<p><b>Rideal-Eley Model</b></p> $\text{CH}_3\text{OH} + \text{S} \rightarrow \text{CH}_3\text{OH-S}$ $\text{CH}_3\text{OH} + \text{S} + \text{ROH} \rightarrow \text{CH}_3\text{-R-OH}$ $\begin{array}{ccc} \text{OH} & & \text{OH} \\   & &   \\ \text{CH}_3\text{R} + \text{CH}_3\text{OH-S} & \longrightarrow & \text{CH}_3\text{-R-CH}_3 \end{array}$	$R = k K_M P_p P_M / (1 + K_M (P_M))$

\* R = C<sub>6</sub>H<sub>5</sub>, S = Surface, P<sub>M</sub> = Partial pressure of Methanol, P<sub>p</sub> = Partial pressure of Phenol, K = Equilibrium Constant, k = Rate Constant

## RESULTS AND DISCUSSION

### Effect of partial pressure of phenol

The effect of variation of partial pressure of phenol on the rate of formation of xylenol was studied at constant partial pressure of methanol. The results are listed (Table 2)

at temperatures of 543 and 593 K are shown graphically (Fig. 3) at 643 K. It was observed that the rates increased with partial pressure.

**Table 2: Effect of partial pressure of phenol on the rates**

Weight of catalyst : 0.1 g; Partial pressure of phenol: 4.21-9.92 kPa; Partial pressure of methanol : 4.15 kPa

S. No.	Partial pressures of Phenol (kPa)	Rate x 10 <sup>-6</sup> (moles s <sup>-1</sup> m <sup>-2</sup> )			
		543 K		593 K	
		Observed	Calculated	Observed	Calculated
1	4.21	0.0065	0.0063	0.1965	0.1931
2	7.09	0.009	0.0088	0.269	0.268
3	9.92	0.01	0.01	0.3122	0.32

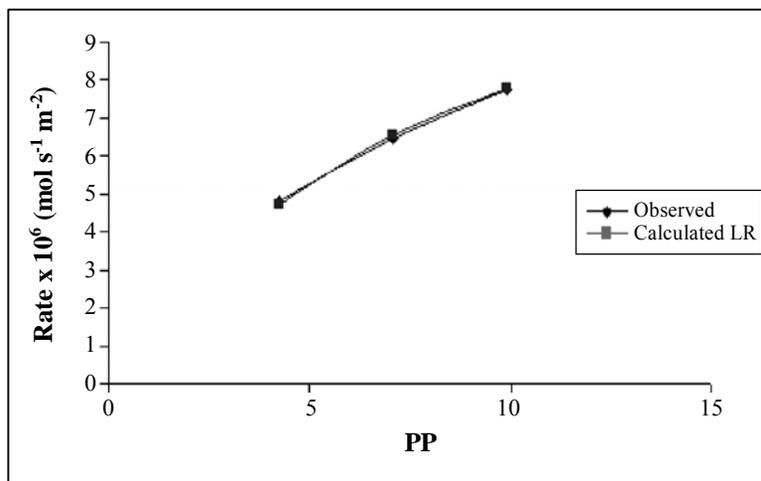
### Effect of partial pressure of methanol

The effect of partial pressure of methanol on the rates was studied at constant partial pressure of phenol and results are listed (Table 3) at temperatures of 543 and 593 K and are shown graphically (Fig. 4) at 643 K. The rates initially increased at low partial pressure of methanol and gave indications of a limiting rate being attained at higher partial pressure.

**Table 3: Effect of partial pressure of methanol on the rates**

Weight of catalyst: 0.1 g; Partial pressure of methanol: 4.15-29.08 kPa; Partial pressure of phenol: 1.41 kPa

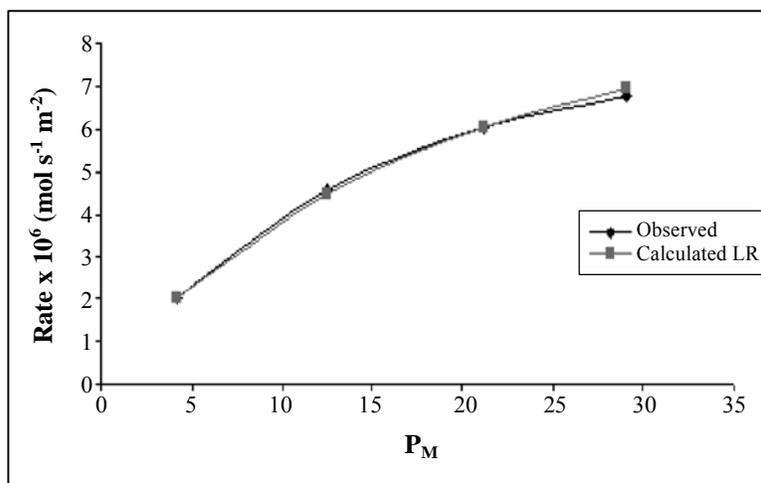
S. No.	Partial pressures of Methanol (kPa)	Rate x 10 <sup>6</sup> ( moles s <sup>-1</sup> m <sup>-2</sup> )			
		543 K		593 K	
		Observed	Calculated	Observed	Calculated
1	4.15	0.0027	0.0027	0.0812	0.0815
2	12.46	0.0061	0.006	0.1861	0.181
3	21.15	0.0082	0.0081	0.2402	0.242
4	29.08	0.0094	0.0094	0.2734	0.278



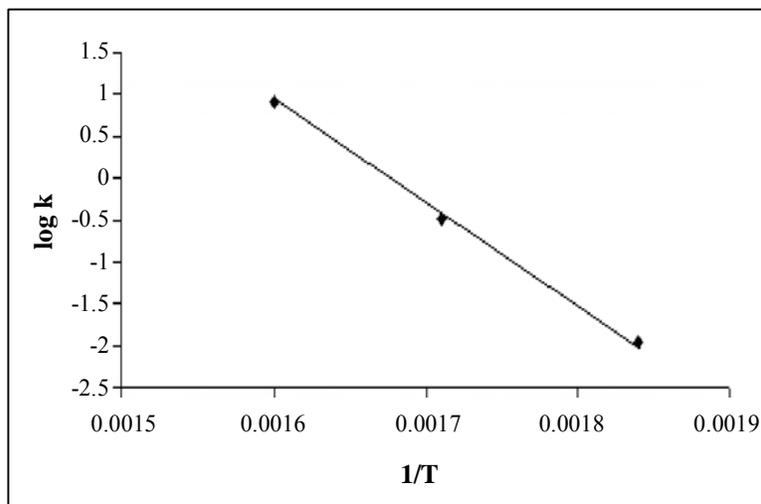
**Fig. 3: Effect of partial pressure of phenol (PP) on rate of formation of xylene temp. 643 K**

### Effect of temperature

The effect of temperature on the rates was investigated between 543 and 643 K and at various partial pressures of phenol and methanol. The results are presented (Tables 2 and 3, Figs. 3 and 4). As it is evident, the rates were increased with increase in temperature. Arrhenius plot is shown (Fig. 5). The rate constants and activation energy are listed in (Table 4). The activation energy was computed to be 25.3 kcal/mol.



**Fig. 4: Effect of partial pressure of methanol ( $P_M$ ) on rate of formation of xylene temp. 643 K**



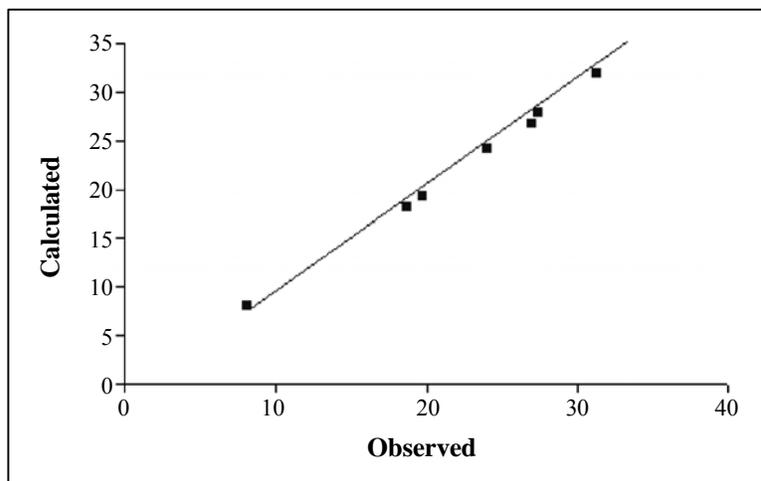
**Fig. 5: Arrhenius plot for the methylation of phenol with methanol over Al-ferrite**

**Table 4: Rate constants and activation energy**

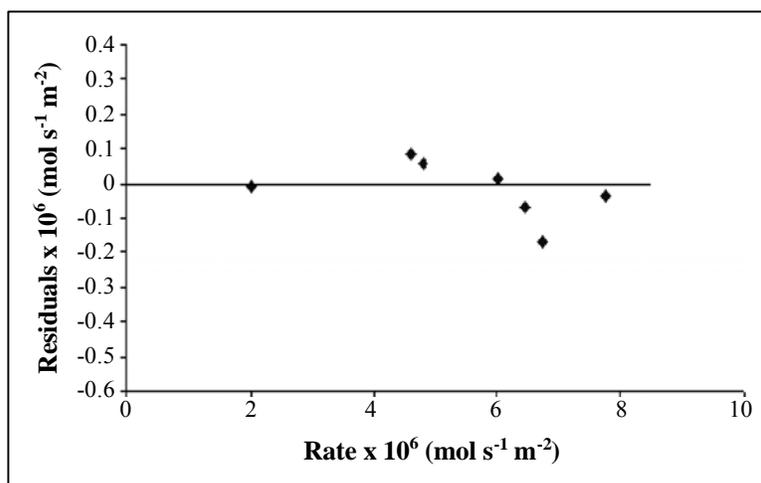
Constants	Temperature (K)			Activation energy (Kcal/mol)
	543	593	643	
k	0.011455	0.331534	8.265109	
k <sub>A</sub>	0.137596	0.133970	0.140272	25.3
k <sub>B</sub>	0.057930	0.060517	0.060405	

### Reaction mechanism

Since the constants involved in models 1 and 2 are physical quantities, their value should be positive. Rate equations for model 1 and 2 shown (Table 1) were solved for rate or adsorption equilibrium constants by method of least squares and the mechanisms giving a negative coefficient in the rate equation were rejected. While model 1 came out with negative constant, positive coefficients were found for model 2. The correlation of data is illustrated (Fig. 6), where observed rates are plotted along with calculated rates for different partial pressures of phenol and methanol. A plot of residuals versus calculated rates is shown (Fig. 7).



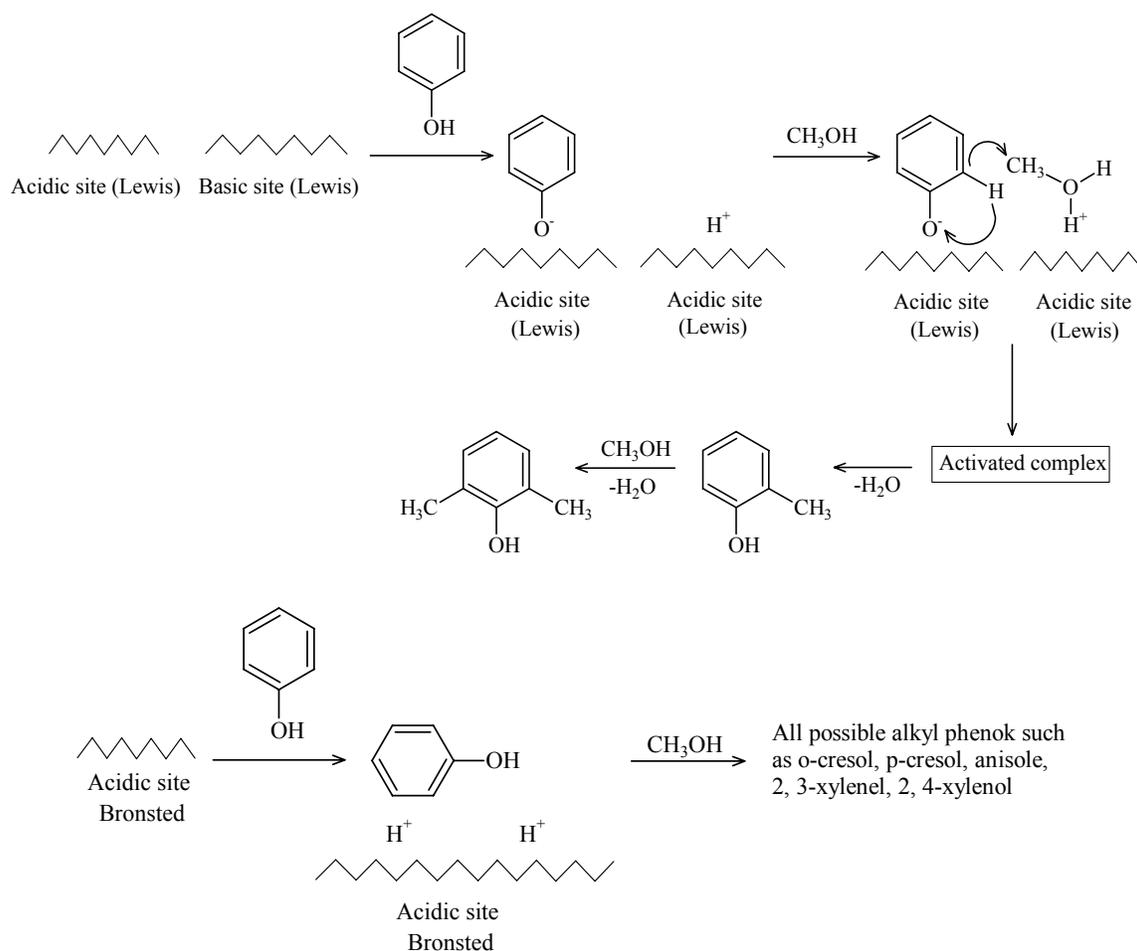
**Fig. 6: Calculated and observed rate (Rate x 10<sup>7</sup> mole s<sup>-1</sup>m<sup>-2</sup>) for formation of xylenol**



**Fig. 7: Residuals vs rate of formation of xylenol**

The plot does not show any heteroscedic pattern. It can be seen that best correlation is shown by Rideal-Eley model. Thus, we conclude that our kinetics measurement suggests a Rideal-Eley type mechanism and the reaction is first order in phenol as well as methanol with a total order of two under the present experimental conditions. Product analysis confirmed total absence of o-, p- and -m substituted products. o-cresol and 2,6-xylenols were found to be only products. One the basis of present kinetics studies and product distribution,

it can be concluded that phenol is vertically adsorbed on the surface with oxygen attached to a lewis acid site and hydrogen with the neighboring lewis base site and methanol remains in the gas phase. Methanol abstract a proton from phenol, get protonated and converted to carbonium ion by releasing water molecule. An electrophilic attack by carbonium ion on the ortho position of phenoxide ion leads to formation of o-cresol and completing the catalytic cycle. Further adsorption by o-cresol and methanol leads to the formation 2,6-xyleneol. The alkylation of phenol is a consecutive reaction on the catalyst surface. The presence of negative charge on the ion requires a strong acidic site for its adsorption. This seems to be the reason for increase of ortho products. The mechanism is shown in Fig. 8.



**Fig. 8: Mechanism of the alkylation of phenol with methanol over  $\text{AlFe}_2\text{O}_4$  catalyst**

**REFERENCES**

1. Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim (2003) p. 642.
2. P. D. Chantal, S. Kaliaguine and J. L. Grandmaison, *Appl. Catal.*, **18**, 133-145 (1985).
3. R. Pierantozzi and A. F. Nordquist, *Appl. Catal.*, **21**, 263-271 (1986).
4. S. C. Lee, S. Lee, W. K. S. Kim, T. J Lee, D. H. Kim and J. C. Kim, *Catal. Today*, **44**, 253-258 (1998).
5. M. Marczewski, J. P. Bodibo and M. P. Guisnet, *J. Mol. Catal.*, **50**, 211-218 (1989).
6. L.Garcia, G. Giannetto, M. R. Goldwasser, M. Guisnet and P. Magnoux, *Catal. Lett.*, **37**, 121-123 (1996).
7. S. Balsama, P. Beltrame, P. L. Beltrame, P. Carniti, L. Forni and G. Zuretti, *Appl. Catal.*, **13**, 161-170 (1984).
8. P. Beltrame, P. L. Beltrame, P. Carniti, A. Castelli and L. Fomi, *Appl. Catal.*, **29**, 327-334 (1987).
9. R. F. Parton, J. M. Jacobs, H. V. Ooteghem and P. A. Jacobs, *Stud. Surf. Sci. Catal.*, **46**, 211-221 (1989).
10. S. Namba, T. Yashima, Y. Itaba and N. Hara, *Stud. Surf. Sci. Catal.*, **5**, 105-112 (1980).
11. Z. H. Fu and Y. Ono, *Catal. Lett.*, **21**, 43-47 (1993).
12. G. Moon, W. Böhringer and C. T. O'Connor, *Catal. Today*, **97**, 291-295 (2007).
13. M. D. Romero, A. Ovejero, A. Rodriguez, J. M. Gomez and I. Agueda, *Ind. Eng. Chem. Res.*, **43**, 8194-8199 (2004).
14. G. Sarala Devi, D. Giridhar and B. M. Reddy, *J. Mol. Catal.*, **181**, 173-178 (2002).
15. F. M. Bautista, J. M. Campelo, A. Garcia, D. Luna, J. M. Marinas, A. Romero, J. A. Navio and M. Macias, *Appl. Catal. A*, **99**, 161-173 (1993).
16. S. Velu and C. S. Swamy, *Appl. Catal. A*, **145**, 141-252 (1996).
17. R. Bal, B. B. Tope and S. Sivasanker, *J. Mol. Catal. A*, **181**, 161-171 (2002).
18. V.V. Rao, V. Durga Kumari and S. Narayanan, *Appl. Catal.*, **49**, 165-174 (1989).
19. S. Velu and C. S. Swamy, *Appl. Catal. A*, **162**, 81-89 (1997).

20. K. Sreekumar, T. Raja, B. P. Kiran, S. Sugunan and B. S. Rao, *App. Catal. A*, **182**, 327-336 (1999).
21. K. Sreekumar, T. M. Jyothi, T. Mathew, M. B. Talawar, S. Sugunan and B. S. Rao, *J. Mol. Catal.*, **159**, 327-334 (2000).
22. K. Sreekumar, T. Mathew, B. M. Devassy, R. Rajgopal, R. Vetrivel and B. S. Rao, *Appl. Catal. A.*, **205**, 11-18 (2001).
23. V. S, Reddy A. Radheshyam, R. Dwivedi, R. K. Gupta, V. R. Chumbhale and R. Prasad, *J. Chem. Technol. Biotechnol.*, **79**, 1057-1064 (2004).
24. J. P. Jacobs, A. Maltha, J. G. H. Reintjes, J. Drimal, V. Ponec and H. H. Brongersma, *J. Catal.*, **147**, 294-300 (1994).
25. K. Ojha, N. C. Pradhan and A. N. Samanth, *Chem. Engg. J.*, **112**, 109-115 (2005).
26. M. Marczewski, G. Perot and M. Guisnet, *React. Kinet. Catal. Lett.*, **57**, 21-27 (1996).

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