



A highly *ortho*-selective TiO₂ catalyst for the methylation of phenol

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Abstract

The investigation describes alkylation of phenol with methanol over an active rutile TiO₂ catalyst in relation to a commercial rutile form. The catalysts were characterized by XRD, surface areas and temperature programmed desorption studies with NH₃ and CO₂ as probe molecules. Alkylation reactions were carried out in the temperature range 250–480 °C to investigate the conditions that would favour the formation of *ortho* products viz. *o*-cresol and 2,6-xylenol. The synthesized rutile sample was more active than the commercial sample under identical conditions of temperature, WHSV and molar ratio of reactants. It showed 100% *ortho* selectivity at 480 °C. In comparison the commercial rutile gave mixed selectivity. The selectivity profiles of the catalysts are explained on the basis of their acid–base characteristics.

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1. Introduction

Alkylation of phenol with methanol has gained considerable attention over the years as the products are of great importance in the industry. While anisole formed by the O-alkylation of phenol is used as an intermediate in the synthesis of anethole in the beverage industry, the C-alkylated products like *ortho*-cresol and 2,6-xylenol are used in the synthesis of industrial grade plastics and paints. A wide range of materials have been investigated as catalysts for the process; these included pure and doped metal oxides, mixed metal oxides, sulphates, metal phosphates and zeolites.

The activity–selectivity patterns as well as optimum reaction temperature of a catalyst is primarily governed by its acid–base properties. Depending upon the type of acid sites viz. Bronsted or Lewis, the phenol molecule undergoes either horizontal or vertical adsorption [1]. Hence depending upon the orientation of the phenol molecule the product selectivity varies. Perpendicular

dissociative adsorption of the phenol molecule on a Lewis acid–base pair site makes its *ortho* position more susceptible to attack, leading to high *ortho*-selectivity. While horizontal adsorption of the phenol molecule makes all the positions of its aromatic ring viz. *o*-, *p*-, and *m*-susceptible to attack, thus resulting in mixed selectivity. A typical acid–base mechanism for the methylation of phenol has been proposed by several workers [1–6]. Based on these reports, the existing mechanism for alkylation of phenol on methanol could be summarized as in Fig. 1.

Most present day catalysts give mixed selectivities forming both O- and C-alkylated products, others showed unsatisfactory stability with time on stream due to coking [1,5]. Hence search for appropriate catalyst continues. In the present investigation, we report our findings on pure rutile TiO₂ catalysts, as the rutile form is known to be more stable than other forms of TiO₂ at higher temperatures.

Titanium dioxide is a versatile material with a wide number of technological applications due to its optical, chemical and mechanical properties [7]. Anatase, rutile and brookite are well known phases of TiO₂ and their functional characteristics strongly depend on its phase

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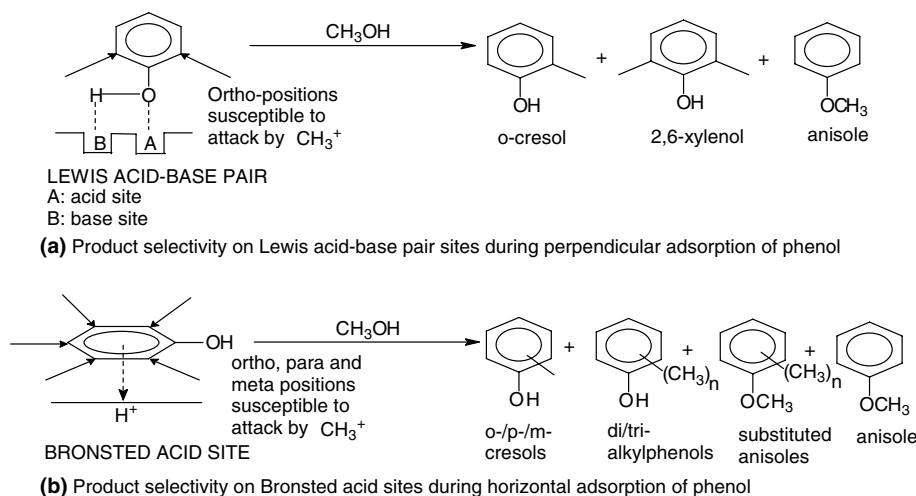


Fig. 1. Mechanism of alkylation of phenol with methanol.

[8]. TiO_2 is widely investigated as a support in catalysis [9,10] and recently $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ is used as a SCR catalyst for the abatement of NO_x from waste gases [11]; however reports of TiO_2 as a direct catalyst for heterogeneous reactions are few although it has wide applications as a photocatalyst in waste degradation [12]. TiO_2 by itself is reported to have low acid strength, but the strength of acid sites and the catalytic activity is found to increase in its binary and ternary mixed forms such as $\text{SiO}_2\text{-TiO}_2$, $\text{Al}_2\text{O}_3\text{-TiO}_2$ and $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ [13,14]. Further Ti^{4+} ions are reported to be the active Lewis acid sites in these catalysts [15]. Alkylation of phenol with methanol has been reported on $\text{AlPO}_4\text{-TiO}_2$ [16] and $\text{V}_2\text{O}_5\text{-TiO}_2$ [17] systems and these composite systems have been found to be more active than the pure titanium oxides. Generally, TiO_2 rutile phase is found to be more stable but not appreciably active as compared to the anatase form [18].

Herein we report the synthesis of an active rutile TiO_2 and its activity for alkylation of phenol in comparison to that of a commercially available rutile form. This is probably the first systematic effort towards the investigation of alkylation reaction of phenol with methanol on titanium dioxide. The investigation was carried out with the aim of selectively producing *o*-cresol and/or 2,6-xyleneol.

2. Experimental

2.1. Catalyst synthesis

The catalyst R2 was synthesized by drop wise addition of dilute nitric acid to a 15% TiCl_3 solution until the solution turned from violet to colourless followed by the addition of urea such that the TiCl_3 :urea molar ratio in the final solution was 1:2. The resultant solution was

evaporated to dryness on a steam bath. The dry residue was heated in a horizontal muffle furnace at 400 °C under continuous flow of dry air for 5 h to obtain the final sample. R1 is a commercial TiO_2 obtained from Loba Chemie (India). R3 is prepared in the same way as R2, but without the use of urea.

2.2. Catalyst characterization

The X-ray powder diffraction patterns (XRD) have been recorded on a Shimadzu LabX -700 diffractometer, using Ni filtered Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$) by step scanning with a scan rate of $2^\circ 2\theta/\text{min}$. The crystallite size was determined by Scherrer formula. The weight percent of anatase in the rutile phase was obtained from the equation [19]

$$X_A = [1 + 1.26(I_R/I_A)]^{-1},$$

where X_A is the weight fraction of anatase in the mixture, I_R and I_A are obtained from the peak areas of the characteristic anatase (101) and rutile (110) diffractions, respectively. The BET surface area was measured by nitrogen physisorption at liquid nitrogen temperature (-196°C) The temperature-programmed desorption (TPD) measurements were carried out using ammonia and carbon dioxide as probe molecules as per the procedure described elsewhere [20].

2.3. Catalytic studies

The alkylation reaction was carried out in a vertical flow reactor. Prior to the reaction 1 g of the catalyst sample was pelletized and crushed and then loaded in a glass reactor (i.d. = 30 mm). The catalyst was activated in flowing air for about 5 h at a temperature of 450 °C. The temperature was then brought down to the desired reaction temperature in dry nitrogen. Once the reaction

temperature was attained the catalyst was allowed to remain at that temperature for 1 h prior to the reaction. In a typical reaction, a mixture of phenol and methanol in a molar ratio of 1:6 was fed into the reactor at pre-determined flow rates through a peristaltic pump. The reaction was studied at a fixed flow rate of 5 ml/h and at temperatures between 250 and 480 °C. The products were condensed and analysed by a Chemito 8610 GC using a FID detector and a SE 30 column.

3. Results and discussions

3.1. Structural and surface properties of titania samples

Fig. 2 shows the XRD patterns of the TiO₂ samples used in this work. The commercial TiO₂ R1 as well as the synthesized samples R2 and R3 showed rutile crystal phase containing small amounts of anatase phase. The crystallite sizes based on Scherrer formula, weight percent of anatase in the rutile samples and the BET surface areas are as reported in Table 1. It can be seen from the table that all the three samples showed comparable acidity (~230 μmol/g). However as evident from Fig. 3(a), the strength of acid sites were different. While the commercial rutile R1 showed well resolved peaks at

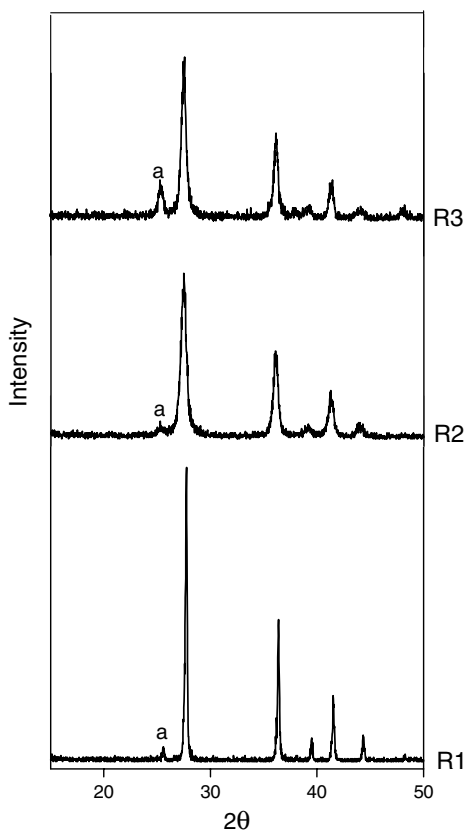


Fig. 2. XRD patterns of catalysts R1, R2 and R3, where 'a' shows the anatase phase in the rutile samples.

180 and 300 °C, R2 showed a different pattern with a peak at 250 °C and a broad peak in the 260–380 °C region. The distinctive features of R2 are also evident from its TPD-CO₂ profile (Fig. 3(b)) showing the basic sites. While R1 showed lower basicity of ~70 μmol/g with moderate and strong basic sites, R2 showed higher basicity of 125 μmol/g with a unique presence of a low temperature peak at about 150 °C in the basicity profile corresponding to weak basic sites. This low temperature peak is conspicuous by its absence in the TPD profile of the R3 as discussed in the forgoing Section 3.3.

3.2. Catalytic activity and selectivities

The alkylation reactions were carried out at pre-determined optimum conditions of 1:6 phenol: methanol molar ratio and a flow rate of 5 ml/h. Fig. 4 gives the activity–selectivity profiles of the two catalysts in the temperature range 350–450 °C. As can be seen from the figure, the commercial TiO₂ catalyst gave poor alkylation activity. It showed a maximum of only 18% conversion of phenol at 350 °C and thereafter the percent conversion decreased at higher temperatures. On the other hand the synthesized catalyst R2 showed high activity at higher temperatures. Although its activity was initially low, ~5% at temperatures below 400 °C, it increased to a maximum of 42% at 450 °C and then slightly decreased to 40% at 480 °C. The higher activity of R2 appeared to be in agreement with the trend in particle size and surface areas of the catalysts. Thus, R2 having smaller particle size and larger surface area (36 m²/g) gave maximum conversion of 42%. R1 on the other hand having comparatively larger particle size and lower surface area (15 m²/g) gave a much lower conversion being only 18%. At the same time R2 showed larger amounts of acidic as well as basic sites. Hence we propose that acid–base site mechanism is involved during alkylation of phenol on R2.

The commercial rutile catalyst R1 showed mixed selectivity with formation of O-alkylated product, anisole, as well as several C-alkylated products. These later products being *o*-, *p*-, and *m*-cresol and 2,6-xyleneol. In addition, other higher C-alkylated products were also formed in significant proportions. This mixed selectivity also continued when the reaction was investigated at higher temperatures though with some internal variations. On the other hand R2 showed high *ortho*-selectivity forming only two products *o*-cresol and 2,6-xyleneol at 450 °C and above. Further R2 also showed interesting temperature-dependent selectivity variations.

As can be seen from Fig. 4, at the temperature of 350 °C, R2 showed high selectivity to *o*-cresol (~70%). Anisole was only 30%. This high selectivity to *o*-cresol remained almost unchanged at all the three temperatures investigated from 350 to 450 °C. However the initial selectivity to anisole changed in an interesting

Table 1
Structural properties of the titania samples

Sample	Phase	Weight percent of anatase	XRD particle size (nm)	BET surface area (m ² /g)	Total acidity (μmol/g)	Total basicity (μmol/g)
R1	Rutile	2.2	27.26	15	230	74
R2	Rutile	3.5	9.09	36	240	126
R3	Rutile	13.1	15.14	32	225	49

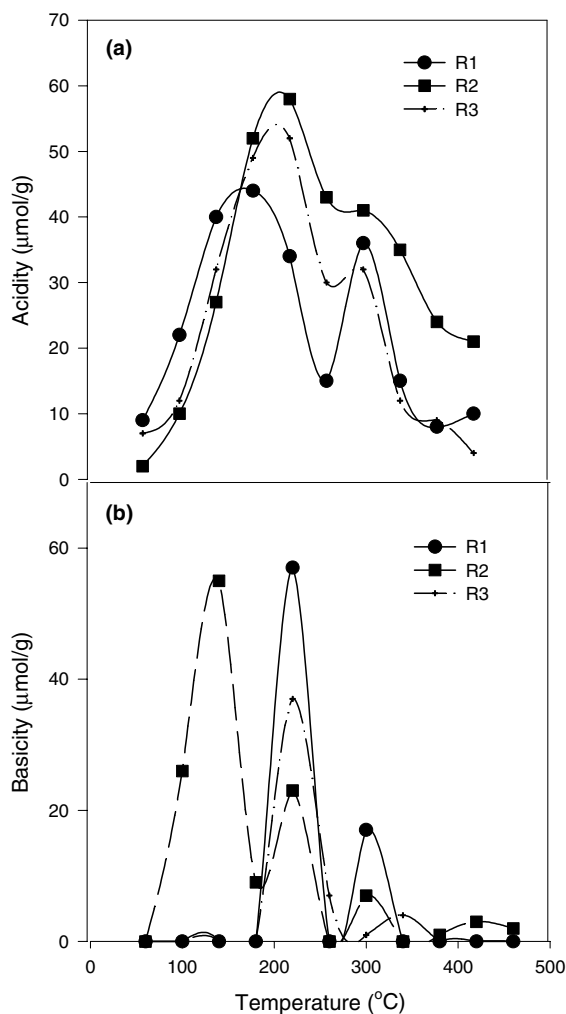


Fig. 3. TPD profiles. (a) R1 and R2 and R3 for the desorption of pre-adsorbed NH₃ and (b) R1, R2 and R3 for desorption of pre-adsorbed CO₂.

manner. The amount of anisole gradually decreased as temperature was increased from 350 °C. As the selectivity towards anisole decreased, there was a concomitant increase in the formation of 2,6-xylenol. Thus as we go from 350 to 480 °C, anisole selectivity dropped by ~29% and *o*-cresol dropped by ~11%. At the same time the 2,6-xylenol selectivity increased from 0 to about 40%. Thus, 2,6-xylenol could be considered to be formed on catalyst R2 through intermediate formation of (i) anisole predominantly and (ii) *o*-cresol to some extent. That two pathways could exist for 2,6-xylenol formation is reported earlier [3]. In order to confirm the above

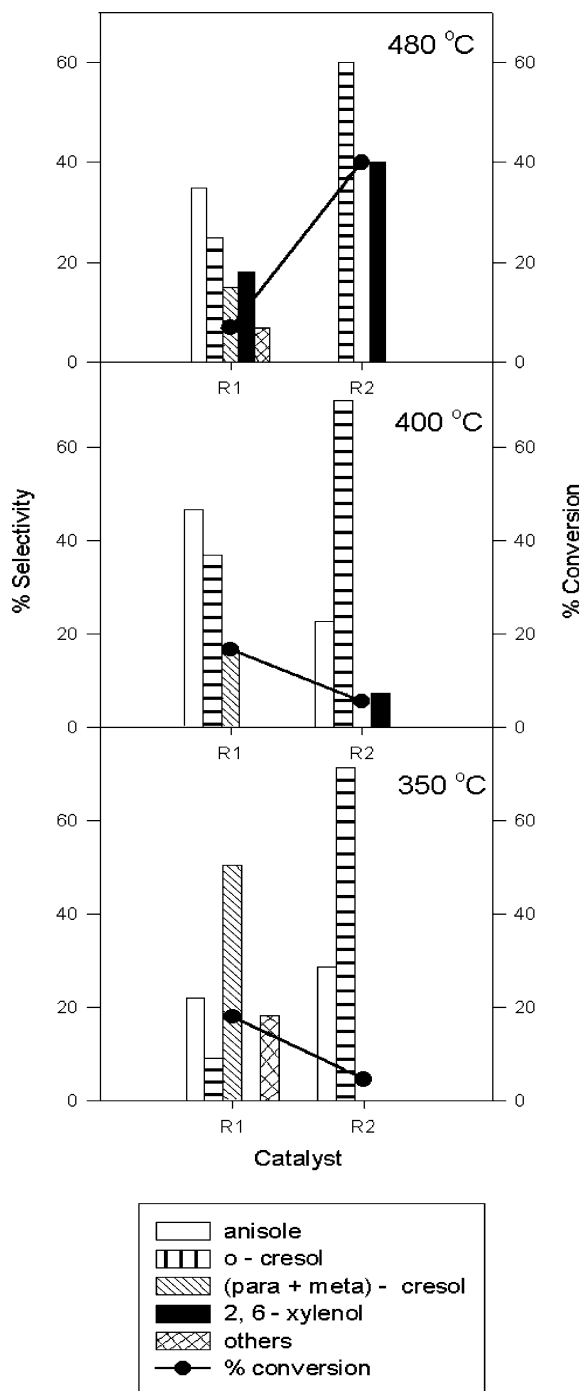


Fig. 4. Trend in percent selectivities and percent conversions for the catalysts at 350, 400 and 480 °C, respectively, with 1 g of catalyst, 1:6 phenol:methanol molar ratio and flow rate of 5 ml/h.

Table 2

Alkylation of anisole and *o*-cresol with methanol over the TiO₂ catalyst R2 with substrate to methanol molar ratio of 1:6 and flow rate 5 ml/h per gram of catalyst at 450 °C

S. No.	Reactants	Catalyst	% Conversion of substrate	% Selectivity			
				Anisole	<i>o</i> -Cresol	2,6-Xylenol	^a Others
1	Anisole + methanol	R2	3.5	–	0	100	0
2	<i>o</i> -Cresol + methanol	R2	17.5	22.7	–	77.3	0

^aOthers: higher C-alkylated products.

hypothesis on catalyst R2, separate experiments were conducted using mixtures of (i) anisole and methanol and (ii) *o*-cresol and methanol in the molar ratio 1:6 in both the cases. The experimental data in Table 2 substantiates the above hypothesis. Refer entry 1 in this table. It is seen that on R2 catalyst, anisole gives only 2,6-xylenol (100% selectivity) while *o*-cresol gives mixed selectivity to anisole and 2,6-xylenol. This result suggests that 2,6-xylenol could in fact be formed by phenol alkylation through three possible pathways

r_1 : phenol \rightarrow anisole \rightarrow 2,6-xylenol

r_2 : phenol \rightarrow *o*-cresol \rightarrow 2,6-xylenol

r_3 : phenol \rightarrow *o*-cresol \rightarrow anisole \rightarrow 2,6-xylenol

The reaction pathway on R2 catalyst could therefore be summarized as in Fig. 5.

3.3. Relation between acid–base sites and selectivity patterns

The high *ortho*-selectivity during methylation of phenol is believed to be due to acid–base pair mechanism involving an essential presence of weak basic sites at ~ 150 °C [21].

Thus a phenol molecule interacts with a Lewis acid–base pair, dissociatively adsorbing as a phenolate ion on the acid site while its proton interacts with the adjacent

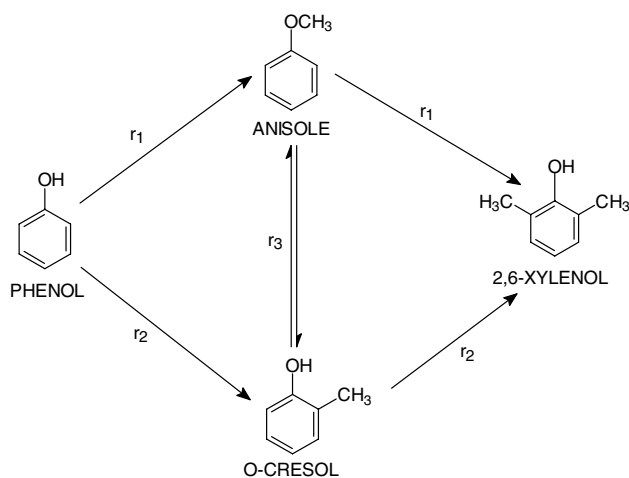


Fig. 5. Proposed reaction pathway for formation of 2,6-xylenol on the TiO₂ catalyst R2 during alkylation of phenol with methanol.

basic site. This proton is mobile enough to activate the molecule of methanol, resulting in the formation of the methyl carbocation. The *ortho*-positions of the phenolate ion are closer to the surface of the catalyst and thus more susceptible to attack by the carbocation. This resulted in the observed high *ortho*-selectivity to *o*-cresol and 2,6-xylenol.

As mentioned earlier the catalyst R1 showed only moderate and strong basic sites as evident from the two peaks in the temperature range 220–350 °C (Fig. 3(b)). On

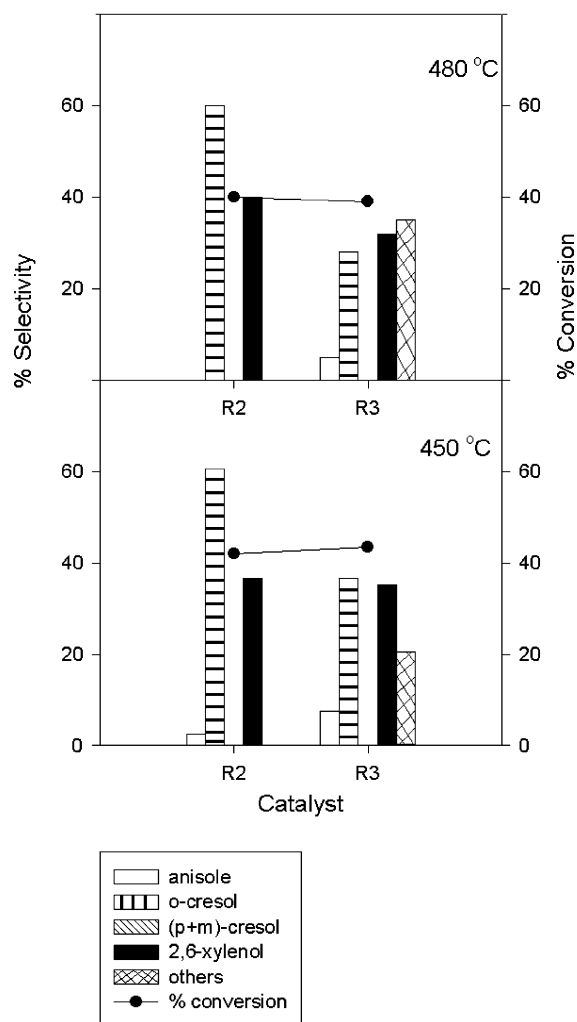


Fig. 6. Trend in percent selectivities and percent conversions over the TiO₂ catalysts R2 and R3 at 400 and 450 °C, respectively, with 1 g of catalyst, 1:6 phenol:methanol molar ratio and flow rate of 5 ml/h.

the other hand R2 showed a unique presence of a large peak at ~ 150 °C corresponding to high concentration of weak basic sites. Further the high temperature peaks of R2 greatly decreased in intensity in comparison to R1. This implied that moderate and strong basic sites might not be responsible for the observed high *ortho*-selectivity.

It is believed that the presence of crucial weak basic sites on the surface of R2 have its origin in its urea related precursor during synthesis. To confirm the unique role of urea in making the crucial difference for R2, a catalyst R3 (also rutile phase) was synthesized following essentially the same procedure as R2 but without urea. The TPD-CO₂ profile of R3 (included in Fig. 3(b)) did not show any low temperature peak corresponding to weak basic sites. Alkylation reactions carried out on R3 failed to show the kind of *ortho*-selectivity as that of R2 although the percent conversion was almost same. Fig. 6 shows the percent conversion and selectivity profile of catalyst R3 in comparison to R2. As can be seen from this figure, the catalyst R3 showed formation of large quantities of higher C-alkylated products (grouped as others) at 480 °C while R2 showed formation of only 2 products, *o*-cresol and 2,6-xyleneol. Thus, the distinctive presence of weak basic sites in R2 alone, confirmed its high *ortho*-selectivity.

4. Conclusions

1. A rutile TiO₂ catalyst synthesized using TiCl₃-urea method was investigated as an alkylation catalyst for methylation of phenol. It showed 100% *ortho*-selectivity at 480 °C at 40% conversion of phenol. In comparison a commercial rutile form showed mixed selectivities under all experimental conditions.
2. The high *ortho*-selectivity of the synthesized rutile sample could be attributed to the unique presence of weak basic sites.

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References

- [1] E. Santacesaria, D. Graso, D. Gelosa, S. Carra, Appl. Catal. 64 (1990) 83.
- [2] C. Bezouhanova, M.A. Al-Zihari, Appl. Catal. A 83 (1992) 45.
- [3] S. Velu, C.S. Swamy, Appl. Catal. A 119 (1996) 141.
- [4] V. Murugesan, B. Arabindev, M. Palenichamy (Eds.), Recent Trends in Catalysis, Narosa Publishing House, New Delhi, India, 1999.
- [5] B. Viswanathan, Bull. Catal. Soc. India 10 (2000) 1.
- [6] K. Sreekumar, S. Sugunan, Appl. Catal. A 230 (2002) 245.
- [7] Y. Yan, S.R. Mater, D.G. Chen, A. Sarkar, Chem. Mater. 7 (1995) 2001.
- [8] R. Debnath, J. Chaudhuri, J. Mater. Sci. Lett. 10 (1991) 494.
- [9] S. Matsuda, A. Kato, Appl. Catal. 8 (1983) 149.
- [10] H. Bosch, F. Janssen, Catal. Today 2 (1988) 369.
- [11] J.C. Vedrine, Catal. Today 56 (2000) 329.
- [12] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
- [13] K.R. Pillai, K.V.C. Rao, Bull. Chem. Soc. Jpn. 64 (1991) 1920.
- [14] C. Lawhouse, F. Mauge, B. Bachelier, J.C. Lavalley, J. Chem. Soc. Faraday Trans. 91 (1995) 2907.
- [15] I.M. Fraser, J.R. MacCallum, J. Chem. Soc. Faraday Trans. I 82 (1986) 2747.
- [16] J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas, M.S. Moreno, Bull. Soc. Chim. Fr. 2 (1988) 283.
- [17] V.V. Rao, K.V.R. Chary, V. Durgakumari, S. Narayanan, Appl. Catal. 61 (1990) 89.
- [18] H. Gerischer, A. Heller, J. Phys. Chem. 95 (1991) 5261.
- [19] R.A. Spurr, H. Myers, Anal. Chem. 29 (1957) 760.
- [20] S.P. Naik, J.B. Fernandes, Thermochim. Acta 332 (1999) 21.
- [21] S. Sato, K. Koizumi, F. Nozaki, J. Catal. 178 (1998) 264.