

# A highly active anatase TiO<sub>2</sub> catalyst for alkylation of phenol with methanol

Aditi R. Gandhe<sup>a</sup>, Sajo P. Naik<sup>b</sup>, Sachin B. Kakodkar<sup>a</sup>, Julio B. Fernandes<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Goa University, Talegao Plateau, Goa 403 206, India

<sup>b</sup> Department of Chemical Engineering, Okubo University, Japan

Received 22 March 2005; received in revised form 14 September 2005; accepted 25 September 2005

Available online 10 January 2006

## Abstract

TiO<sub>2</sub> anatase sample was synthesized by sol–gel method and was evaluated as a catalyst for vapour phase methylation of phenol. It was found to be highly active and gave over 97% conversion under certain experimental conditions. The catalyst gave mainly 2,6-xyleneol and higher alkyl substituted products, which were identified by GC–MS. The activity selectivity profiles are discussed in terms of the acidic and basic properties of the catalyst and the BET surface areas.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Methylation; Methanol; Phenol; TiO<sub>2</sub>; Anatase; Rutile

## 1. Introduction

Alkyl phenols are important chemicals and chemical intermediates in the agrochemical and pharmaceutical industries. *o*-Cresol and anisole are intermediates in the synthesis of anethole in the beverage industry or herbicide in agro-industry, other methyl aryl ethers (MAE) are seen as octane boosters for gasoline. Dialkyl phenols such as 2,6-xyleneol is used in the manufacture of industrial grade plastics [polyphenylene oxide (PPO)] and paints. Trimethyl phenols are precursors for the synthesis of Vitamin E. Thus, the alkylation of phenol has received considerable attention [1–4].

Titanium dioxide is a versatile material with a wide number of technological applications due to its optical, chemical and mechanical properties [5]. Anatase, rutile and brookite are well-known phases of TiO<sub>2</sub> and their functional characteristics strongly depend on its phase [6]. We have recently reported the synthesis of an active rutile TiO<sub>2</sub>, which showed high *ortho*-selectivity ~100% under some experimental conditions [7]. It showed 40% conver-

sion to *o*-cresol and 2,6-xyleneol. In comparison the commercial rutile was less active (~18% conversion) and also showed the formation of several products. On the other hand the well-known photocatalyst Degussa P25 TiO<sub>2</sub> (70% anatase and 30% rutile) showed a phenol conversion of ~32% and predominant selectivities to cresols [8].

We report herein our findings on synthesized sol–gel TiO<sub>2</sub> anatase catalysts for the alkylation of phenol with methanol. An attempt is made to correlate the observed selectivity pattern with the acid base characteristics of the catalyst.

## 2. Experimental

### 2.1. Catalyst preparation

TiCl<sub>4</sub> was used as the starting material for the sol–gel route. Prior to the synthesis TiCl<sub>4</sub>, alcohol and acetone were cooled to near 0 °C in a refrigerator. Measured quantity of alcohol was taken in a beaker, which was placed in a tray with crushed ice. This was followed by drop-wise addition of pre-cooled TiCl<sub>4</sub> with constant stirring. Finally acetone was added in a likewise manner. A translucent yellow coloured gel was thus obtained. The resultant gel was

\* Corresponding author. Tel.: +91 832 2736206; fax: +91 832 2452889.  
E-mail address: [juliofernandes@rediffmail.com](mailto:juliofernandes@rediffmail.com) (J.B. Fernandes).

evaporated to dryness on a steam bath. The dry residue was then heated in a muffle furnace in continuous flow of dry air at 400 °C for 5 h to obtain the final sample.

## 2.2. Catalyst characterisation

The X-ray powder diffraction pattern (XRD) recorded on a Shimadzu LabX-700 diffractometer, using Ni filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) by step scanning with a scan rate of  $2^\circ 2\theta/\text{min}$ . The crystallite size (Scherrer formula) and the lattice parameters were determined from the same. The BET surface area was measured by nitrogen physisorption at liquid nitrogen temperature ( $-196^\circ\text{C}$ ) by taking  $0.162 \text{ nm}^2$  as the area of cross section of nitrogen molecule. The temperature programmed desorption (TPD) measurements using ammonia and carbon dioxide as probe molecules were carried out as per the procedure described elsewhere [9].

## 2.3. Methylation reaction

The alkylation reaction was carried out in a vertical flow reactor. Prior to the reaction the catalyst sample (1 g) 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 one hour prior to the reaction. A mixture of phenol and methanol in a mole ratio of 1:6 was fed into the reactor at predetermined flow rates through a Miclins (India) peristaltic pump. The reaction was further studied at an optimum flow rate of 5 ml/h and at temperatures between 250 and 480 °C. In all cases, the liquid products were condensed and analysed by a Chemito 8610 GC using a FID detector and a SE 30 column.

## 3. Results and discussion

Fig. 1 shows the XRD pattern of the catalyst. It showed a pure anatase crystal phase. The BET surface area, Scherrer crystallite sizes and the lattice parameters are also shown in the same. The lattice parameters are in good agreement with those reported in the literature [10].

### 3.1. Catalytic activity

The catalytic activity for methylation of phenol has been investigated at different phenol: methanol mole ratios, as well as temperatures and flow rates. The optimum conversion of phenol was observed at 1:6 phenol:methanol molar ratio at a flow rate of 5 ml/h. The change in flow rate to either 3 or 8 ml/h did not show any significant effect on either catalytic activity or product selectivity. Fig. 2 describes the catalytic activity in terms of percent conversion of phenol as well as selectivity patterns.

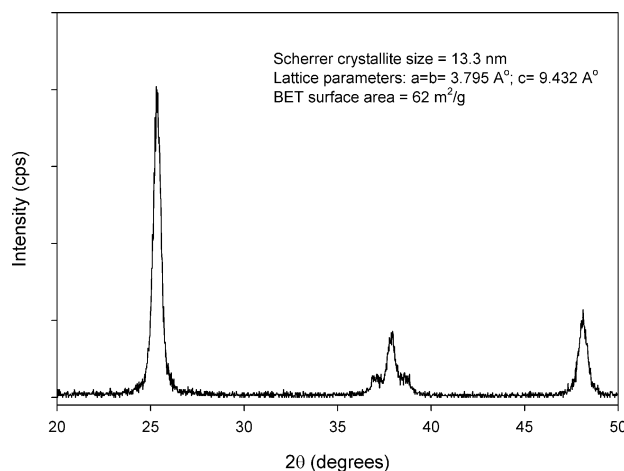


Fig. 1. XRD patterns of the sol-gel catalyst.

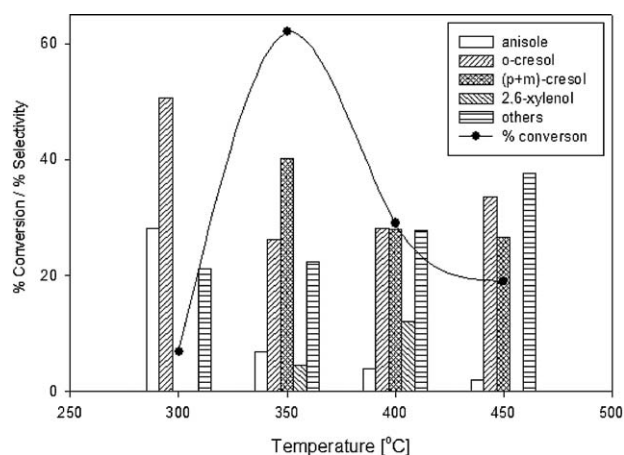


Fig. 2. Trend in percent conversions and percent selectivities for the catalyst at 350, 400 and 450 °C, respectively, with 1 g of catalyst, 1:6 phenol:methanol molar ratio and flow rate of 5 ml/h.

It is observed that percent conversion increased with temperature. The catalyst showed maximum alkylation activity ( $\sim 62\%$ ) at 350 °C and decreased at higher temperatures. The selectivity patterns at all the temperatures investigated showed formation of a mixture of several products. Although there were some internal variations products included anisole, cresols, 2,6-xyleneol and other higher C-alkylated products. It is observed that a decrease in selectivity towards anisole and cresols was accompanied by slight increase in the formation of 2,6-xyleneol as the temperature was raised from 350 to 400 °C. However, when the reaction was carried out at 450 °C, there was no formation of any 2,6-xyleneol. Instead tri and tetra methyl phenols were formed along with several higher C-alkylated products (collectively reported as others in Fig. 2). These were further identified by GC-MS analysis. The GC-MS analysis showed that these were compounds with very high molar mass ( $\sim 225$ ) such as alkyl substituted diphenyl ethers. These ethers are considered to be formed by the condensation of the tri and tetra methyl phenols

amongst themselves as well as cross condensation with the xylenols and cresols. A typical condensation product of molar mass 226 as identified by GC–MS, could be envisaged to be formed by reactions between 2,4,6-trimethyl phenol and *o*-cresol, in Fig. 3.

The selectivity of particular products is known to depend on acid–base characteristics of the catalyst. This is because of certain preferred orientation of the phenol molecule on the surface of the catalyst. Thus phenol molecule is adsorbed horizontally on catalysts having Bronsted acid sites, whereas there is vertical dissociative adsorption of the phenol molecule on Lewis acid sites. Fig. 4 gives the acid–base profiles of the catalyst.

It can be seen from the figure, that the catalyst showed two types of acid sites, as evident from the peaks at 180 and at 350 °C with total acidity of 123  $\mu\text{mol/g}$ . On the other hand, the total basicity was comparatively less, 84  $\mu\text{mol/g}$ , with peaks at 220, 320 and 450 °C. An important feature of both the profiles is the dominance of the weak acid–base sites. This is clear from the peaks in the 180–220 °C temperature region.

As seen in Fig. 2 the catalysts showed formation of both O and C alkylated products. This is envisaged by considering phenol molecule undergoing horizontal adsorption on the surface of the catalysts making all the positions on the ring susceptible to attack. Since substantial amount (>30%) *ortho* substituted products (*o*-cresol and 2,6-xyleneol) are also formed one could predict simultaneous perpendicular dissociative adsorption on the Lewis acid–base pair sites. To further elucidate the role of acid sites in the in the orientation of phenol on the catalyst surface, the catalyst was steamed in situ by taking water in the feed. This is done to transfer some of the  $\text{Ti}^{4+}\text{-O}^{2-}$  acid–base pairs into Bronsted acid sites by hydroxylation. Thus, the experiments were performed by taking water in the feed. The feed composition was water:phenol:methanol 1:1:6 molar ratio, 5 ml/h flow rate and temperature of 350 °C. Fig. 5 shows the comparative selectivity with and without water in the feed. As can be seen from the figure the percent conversion goes down by ~10%. The selectivity towards *o*-cresol and 2,6-xyleneol collectively decreased by about 9%, while there was an increase in selectivity towards higher alkylated products.

These results suggest that steaming decreased the number of available Lewis acid–base pairs. This would consequently result in decrease in perpendicular dissociative

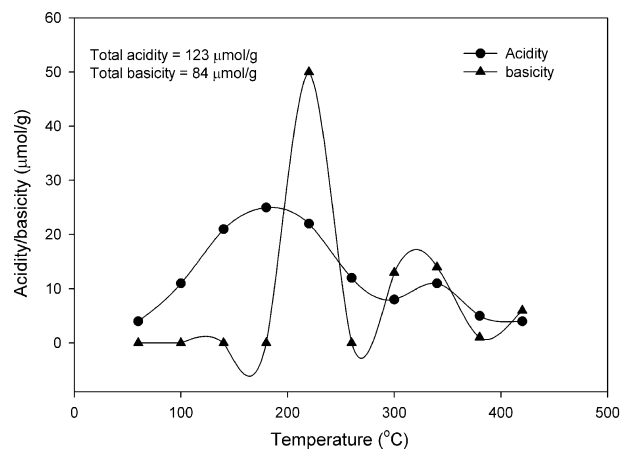


Fig. 4. TPD profiles for the desorption of pre-adsorbed  $\text{NH}_3$  and  $\text{CO}_2$ .

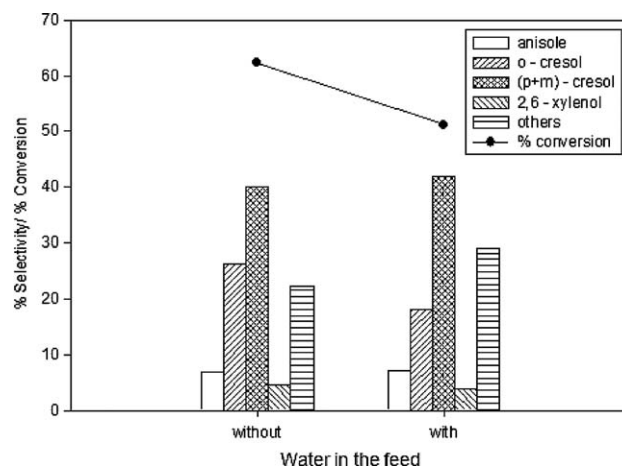


Fig. 5. Effect of water in the feed on alkylation of phenol [with 1 g of catalyst at 350 °C and a flow rate of 5 ml/h; without water in feed (phenol:methanol = 1:6) and with water in feed (phenol:water:methanol = 1:1:6)].

adsorption and hence decrease formation of the *ortho*-products, *o*-cresol and 2,6-xyleneol as observed.

Further due to the generation of these Bronsted acid sites, the proportion of phenol molecule undergoing horizontal adsorption increases. Hence higher C-alkylated products are being formed due to horizontal adsorption of phenol.

The reaction was carried out with 3 g of the catalyst. Fig. 6 shows selectivity patterns. It is observed that anisole

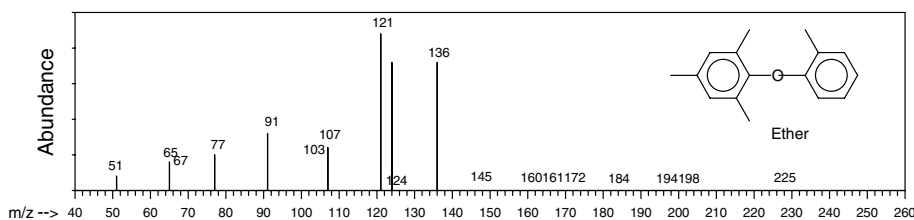


Fig. 3. GC–MS pattern of the high molecular weight compound envisaged to be formed from 2,4,6-trimethyl phenol and *o*-cresol.

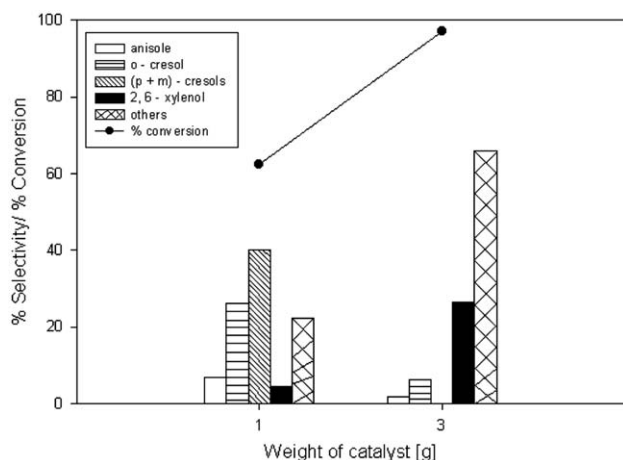


Fig. 6. Selectivity profile of the catalyst as a function of the catalyst weight, at 350 °C (1:6 phenol:methanol molar ratio and flow rate of 5 ml/h).

and cresols almost vanished. Instead there was increased formation of 2,6-xyleneol ~25% and higher C-alkylated products ~75%.

The selectivity is known to depend on the contact time. Thus, when the weight of the catalyst is increased, the length of the catalyst bed increases and as a result of which the contact time between the reactants and the catalyst increases. Since the reactant phenol and methanol now

spend more time on the surface of the catalyst there is formation of higher C-alkylated compounds.

#### 4. Conclusions

A highly active TiO<sub>2</sub> anatase catalyst for the methylation of phenol has been synthesized, with over 97% conversion.

#### Acknowledgements

This research work was sponsored by UGC, New Delhi vide F-540/04/DRS/2003 (SAP-III).

#### References

- [1] B. Viswanathan, Bull. Catal. Soc. India 10 (2000) 1.
- [2] E. Santacesaria, D. Graso, D. Gelosa, S. Carra, Appl. Catal. 64 (1990) 83.
- [3] S. Sato, K. Koizumi, F. Nozaki, J. Catal. 178 (1998) 264.
- [4] E. Santacesaria, D. Grasso, Appl. Catal. 64 (1990) 83–99.
- [5] Y. Yan, S.R. Mater, D.G. Chen, A. Sarkar, Chem. Mater. 7 (1995) 2001.
- [6] R. Debnath, J. Chaudhuri, J. Mater. Sci. Lett. 10 (1991) 494.
- [7] A.R. Gandhe, J.B. Fernandes, Cat. Commun. 5 (2004) 89.
- [8] A.R. Gandhe, J.B. Fernandes, J. Mol. Cat. 226 (2005) 171.
- [9] S.P. Naik, J.B. Fernandes, Thermochim. Acta 332 (1999) 21.
- [10] M. Schuisky, A. Harsta, A. Aidla, K. Kukli, A. Keisler, J. Electrochem. Soc. 147 (2000) 3319.