Methylation of phenol over Degussa P25 TiO$_2$

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Abstract

Degussa P25 TiO$_2$ was evaluated as a catalyst for vapour phase methylation of phenol. It gave an optimum conversion of 32% at 450 °C and formed predominantly the *ortho-*, *para-* and *meta-*cresols. The activity selectivity profiles are discussed in terms of the acid–base properties of the catalyst and the BET surface areas. A new mechanism is proposed to explain the observed product selectivity.
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1. Introduction

Methylation of phenol is an industrially important reaction, as the products of methylation, such as *o*-cresol and 2,6-xylenol have high commercial value [1–6]. The reaction generally gives a mixture of products. We have recently reported synthesis of a highly *ortho*-selective rutile TiO$_2$ catalyst for the methylation of phenol in comparison to a commercial rutile TiO$_2$ (Loba Chemie, India). The commercial rutile sample showed low catalytic activity for alkylation of phenol ∼18% and also gave a large number of products like *o*-, *p*- and *m*-cresols, 2,6-xylenol, anisole and some higher C-alkylated products. The high *ortho*-selectivity of the synthesised rutile was attributed to the presence of a large number of weak basic sites [7]. The origin of these weak basic sites was related to the presence of urea in the synthesis route.

Degussa P25 TiO$_2$ (70% anatase, 30% rutile) is a well-known and widely investigated photocatalyst. Several studies have been dedicated to understanding the structure and synergistic effect in DP25 TiO$_2$. Bickley et al. [8] ascribed the activity of DP25 to a layer of rutile phase on the surface of anatase particles, which would aid in electron–hole separations. Their anatase and rutile model for DP25 was based on

the TEM studies. Recent morphological studies have showed that anatase and rutile particles exist separately in Degussa P25 [9]. Ohno et al. [10] suggested the existence of synergistic effects of anatase and rutile in its photocatalytic activity. It has been shown by numerous studies that there is a positive interaction between the anatase and rutile particles of TiO$_2$ [10–12], which enhances the electron–hole separations, and the photoefficiency.

This is a first report on the use of Degussa P25 TiO$_2$ as a catalyst for methylation of phenol. It is observed that unlike other TiO$_2$ catalysts, Degussa P25 TiO$_2$ showed lower alkylation activity. It also exhibited unique selectivity profiles producing mainly cresols. It is believed that a different methylation mechanism operates on it.

2. Experimental

2.1. Catalyst characterisation

The X-ray diffraction pattern of the Degussa P25 TiO$_2$ has been recorded on an ITAL Structures Diffractometric System APD2000 using Ni-filtered Cu Kα radiation. The BET surface area was measured by nitrogen physisorption at liquid nitrogen temperature (−196 °C) by taking 0.162 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 [13]. TPD measurements were carried out in a muffle furnace. A known weight of the catalyst was packed in a glass column. Ceramic beads were used as pre heaters. The catalyst was activated at 120 °C for about 2 h under flowing dry N_2. Before admitting the NH_3 vapours/CO_2 gas, the catalyst was allowed to cool to room temperature. Ammomia/carbon dioxide was passed over the catalyst for 60 min at a rate of 5 ml/h. After the physisorbed adsorbate was purged in N_2 flow, the catalyst was subjected to programmed heating at the rate of 5 °C per minute to cause desorption. The desorbed gases, viz. NH_3 or CO_2 were bubbled in 0.03 M HCl or 0.04 M NaOH, respectively. Thus, the amount of gas desorbed was quantified by back titration. This amount desorbed at various temperatures is a measure of the catalyst acidity or basicity and is expressed in micromoles per gram. The experiments were repeated to confirm reproducibility. While several data points were collected, only representative points at arbitrarily selected values have been shown. A Spline curve was then plotted using SigmaPlot software.

2.2. 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 sieved to get particles 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 °C 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.
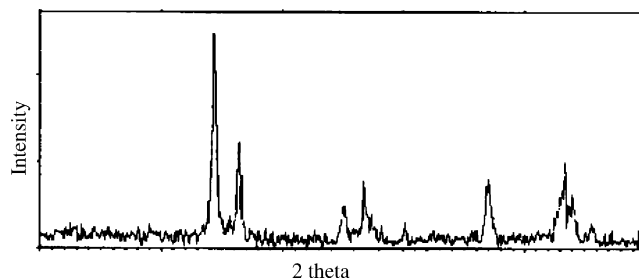

Fig. 1. XRD profile of Degussa P25 TiO$_2$.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the XRD pattern of the sample. The Scherrer crystallite size as calculated from the anatase 100 intensity peak was found to be 26.2 nm, while the BET surface area was 50 m^2/g and is in good agreement with that reported in literature [14,15].

The active centres for alkylation reactions are the acid and base sites on the catalyst surface. It can be seen from Table 1 that Degussa P25 TiO$_2$ catalyst has a very low concentration of active sites in comparison to the rutile catalysts as reported earlier [7]. Further, as evident from Fig. 2, the acid sites could be classified as moderate (M) and strong (S). On the other hand, the basic sites were weak (W), M and S.

The M acid sites were in the temperature range of ~200–350 °C and were of two different strengths. In this temperature range, generally dehydroxylation of the catalyst takes place [16,17] and the total acidity is often a measure of Lewis acidity only. Also, the methylation reactions are studied at temperatures above 250 °C. It is thus assumed that the catalytic activity is predominantly due to Lewis sites. However the low temperature peak ~200 °C (Fig. 2) is believed to be a composite peak due to Bronsted and Lewis acid sites. The predominant Lewis acidity in anatase and rutile TiO$_2$ samples has been subsequently confirmed by in situ FTIR studies with adsorbed pyridine [18]. The catalyst also shows a distinct weak basic site at 140 °C. Such a weak basic site has been reported by Sato et al. [3] on CeO$_2$ catalysts exhibiting

Table 1
Comparison of catalytic activity of the Degussa P25 TiO$_2$ catalyst in relation to pure rutile catalysts R1 and R2 [7]

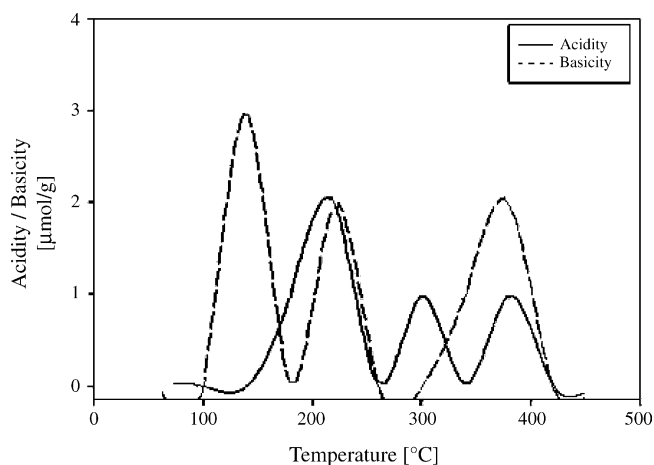| Sample	Crystal phase	Acid sites (μmol/g)	Base sites (μmol/g)	Conversion (%)	Selectivity
R1	Rutile	230	74	13	Mixture of several products including 2,6-xylenol
R2	Rutile	240	126	40	*Ortho*-products cresols and 2,6-xylenol
DP25	Mixed	5	8	32	Only cresols

Fig. 2. TPD profiles of Degussa P25 TiO$_2$ for the desorption of pre-adsorbed NH$_3$ and CO$_2$ showing profiles due to acidic and basic sites of the catalyst.

predominant *ortho*-selectivity. A similar peak has also been reported in R2, which was an *ortho*-selective methylation catalyst [7].

3.2. Phenol conversion activity of the Degussa P25 TiO$_2$ catalyst

Table 1 gives the observed activity and product selectivities of this catalyst in relation to the previously reported rutile catalysts R1 and R2 [7].

Fig. 3 describes the catalytic activity in terms of percent conversion of phenol. It also describes the trend in selectivity as a function of temperature in the range 350–450 °C. It can be seen that percent conversion increased with temperature and reached a maximum of 32% at 400 °C. The activity decreased
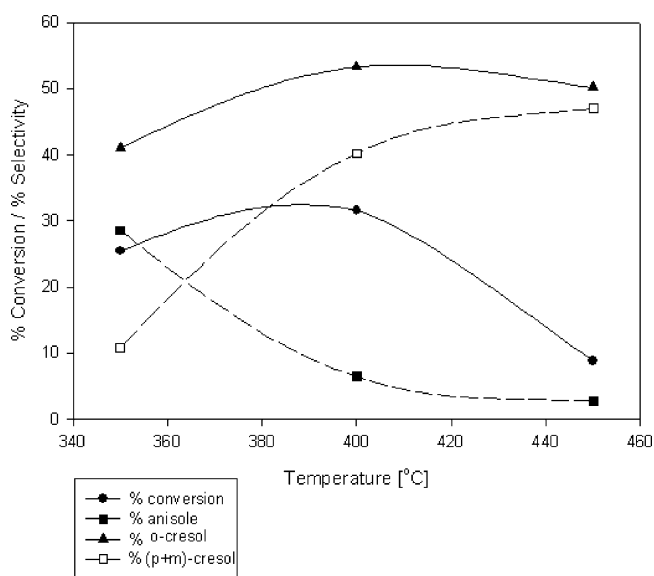

Fig. 3. Trend in percent conversion and selectivity as a function of temperature, with 1 g of catalyst, 1:6 phenol:methanol molar ratio and flow rate of 5 ml/h during methylation of phenol on Degussa P25 TiO2 catalyst.

thereafter at still higher temperatures. Similar decrease in activity was also observed on other TiO$_2$ catalysts, both rutile and anatase [7,18]. That phenol conversion passes through a maximum at higher temperatures was also observed on a similar basic catalyst, such as CeO$_2$ and has been attributed to decomposition of methanol [3]. In the present case, the decrease in activity is believed to be due to gradual desorption of phenol beyond 400 °C and also due to partial decomposition of methanol at these elevated temperatures. The TiO$_2$ catalysts investigated [18] did not show any carbon deposition, which usually occurs on zeolite catalysts, such as HZSM-5. Hence, the decreasing activity was not attributed to deactivation by carbon deposition.

As can be seen from Fig. 3, the catalyst showed formation of four products, viz. anisole and the three cresols: *o*-cresol, *p*-cresol and *m*-cresol. Anisole gets formed by O-alkylation, where the OH of phenol is converted to OCH$_3$. On the other hand, the cresols are C-alkylated products, where substitution occurs in the aromatic ring.

The selectivity towards *o*-cresol varied from 41% to about 53% in the temperatures range studied. The selectivity towards anisole changed in an interesting manner. Thus, as the selectivity towards anisole decreased, there was a concomitant increase in *para*- and *meta*-selectivity. This was thought to be due to the possible conversion of anisole to *para*- and *meta*-cresols with the rise in temperature. It is known that anisole can undergo intramolecular reaction to form cresols [2,19,20]. To confirm the hypothesis of anisole conversion to cresols, alkylation of anisole was carried out with a pre-optimized feed composition of anisole:methanol (1:6) passed at 5 ml/h and at 400 °C. However, the present catalyst did not show any alkylation activity under these conditions. The reaction was then repeated with some phenol in the feed; the anisole:phenol:methanol feed composition being 1:0.5:6 molar ratio at 5 ml/h flow rate and 400 °C. It was observed that anisole remained unchanged at the end of the reaction. On the other hand, there was a decrease in percent phenol content in the products and consequent formation of *o*-, *p*- and *m*-cresols in small proportions. These results indicated that the cresols were formed on this catalyst independently from phenol itself and not through any intramolecular rearrangement of anisole as thought of on the basis of the selectivity profiles or as reported on other catalysts [21,22]. It is also reported that anisole can act as alkylating agent to convert phenol into cresols [2,4,23]. In the present case, however, we also rule out this possibility of alkylation by in situ generated anisole, as the formation of anisole is favoured on acidic catalysts and that too at lower temperatures (below 300 °C). The present catalyst behaves more as a basic catalyst and produces maximum conversion at 400 °C. Further, alkylation of phenol by anisole is also known to produce methyl anisole in addition to cresols. However, no methyl anisole was observed among the products. Therefore, it appears that there could be an alternate mechanism to form cresols possibly by some preferential orientation of phenol on the catalyst surface. It is therefore felt necessary to examine the existing
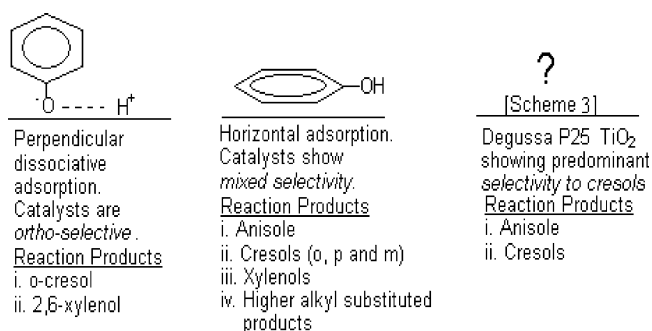
Scheme 1. Orientation of phenol molecule as per the observed selectivity profile.

theories regarding the adsorption and activation of phenol and methanol.

3.3. Adsorption of phenol

The observed selectivity for the methylation of phenol reaction on a particular catalyst is governed predominantly by orientation of the phenol molecule on the surface of the catalyst. The orientation is governed by the acid–base properties of the catalyst. There are two main mechanisms which have been proposed so far to correlate the type of acid–base properties of the catalyst surface to the orientation of the phenol molecule and, thus, the selectivity. These have been illustrated in Scheme 1.

Thus, as can be seen, when phenol is oriented vertically, its *ortho*-positions being closer to the surface are susceptible to attack by the methylating species, resulting in high *ortho*-selectivity to give *o*-cresol or 2,6-xylenol. Horizontal or parallel orientation, on the other hand, is known to give a mixture of several products including dimethyl and trimethyl phenols. This is because all the positions of the phenol molecule in contact with the catalyst can be activated and are hence prone to attack by the methylating species.

Degussa P25 TiO$_2$ does not seem to fall into either of these two mechanistic patterns, as it selectively produces cresols. As no 2,6-xylenol was detected even in trace quantities on Degussa P25 TiO$_2$ at any of the temperatures investigated, we rule out the mechanism involving a perpendicular adsorption of phenol.

Further, since only monoalkylated products, viz. cresols are obtained, it can be safely assumed that there is no possibility of horizontal adsorption. Hence, it appears that the phenol molecule is oriented neither vertically nor horizontally. If latter was the case, there would have been at least some traces of C-alkylated products like xylenols or trimethyl phenols detected under some of the experimental conditions.

As discussed in the preceding section, the cresols could not be obtained either by intramolecular rearrangement of the initially formed anisole or by it acting as an alkylating agent for phenol. The selectivity profiles on Degussa P25 (i.e. producing only cresols) thus indicate that the phenol molecule is oriented on the surface of the catalyst in such

a way that the *ortho*-, *para*- and *meta*-positions of only one side of it are closer to the surface for activation and hence more prone to attack by the methylating species.

Therefore, based on the existing evidence an alternative mechanism is being proposed here wherein the methylating species attacks a possibly edge-on adsorbed phenol, i.e. the aromatic ring is not truly parallel to the surface but slightly inclined.

Recent in situ FTIR studies of phenol adsorbed on DP25 TiO$_2$ catalyst [24] throw interesting light on the adsorption modes of phenol. Whereby, bands at 1288 cm^{-1} and 3616 cm^{-1} were attributed to the presence of adsorbed phenol. These bands disappear beyond 500 °C indicating desorption of phenol at these high temperatures. The infra-red spectrum also showed a sharp band at 1491 cm^{-1}. It is attributed to the interaction between Ti^{4+} of the catalyst with the π electron system of the aromatic ring of surface adsorbed phenol. This interaction will therefore tend to favour parallel adsorption of phenol.

Sato et al. [3] have shown that catalysts with weak basic sites produce *ortho*-selectivity due to phenol undergoing perpendicular adsorption. The unique selectivity profiles on Degussa P25 catalyst, which also shows such predominant weak basic sites, therefore lead us to propose a unique edge-on adsorption of phenol. In this mode, the aromatic ring could, therefore, neither be or but slightly inclined from the parallel position on one side. This is possible by polarization of the π electron cloud by interaction with Ti^{4+} and held in that position by repulsion of the electron cloud by the unique weak basic sites of the catalyst.

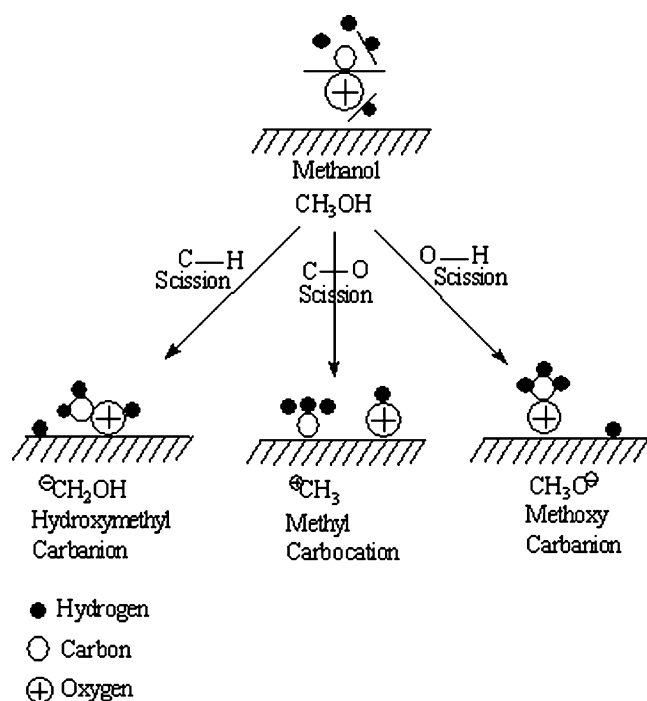### 3.4. Formation of methylating species

The type of active centers on the catalyst surface is a decisive factor for the nature of methylating species formed on a particular catalyst system.

The formation of methylating species involves scission of certain bonds in methanol following adsorption. Hence, accordingly there could be three possible modes of scission in methanol molecule:

i. C–O scission leading to a carbocation, $CH_3^{(+)}$;
ii. O–H scission leading to a methoxy group, $CH_3O^{(-)}$;
iii. C–H scission leading to a hydroxymethyl species, such as $^*CH_2OH$ radical or $^{(-)}CH_2OH$ type enolate formation.

The modes of scission in methanol and consequent methylating species are as depicted in Scheme 2.

Similar scheme has also been proposed very recently by Greeley and Mavrikakis [25–27] on the basis of DFT calculations of adsorbed methanol on Pt(1 1 1) surfaces. They concluded that the initial C–H and O–H bond scissions in methanol though have comparable energy barriers show very different thermodynamics and that steps connecting the two pathways are competitive. These studies suggested preferential formation of hydroxymethyl species.

Scheme 2. Possible bond scissions in methanol during formation of methylating species.

The methyl carbocation could be formed by activation of the methanol molecule by the acidic surface hydroxyls, viz. (i) the Bronsted acid sites of the catalyst surface or (ii) by the Bronsted acidity generated by the reactant phenol molecule during dissociative adsorption.

The surface of the TiO$_2$ catalyst is normally hydroxylated [16]. In fact, this is one of the factors, believed to govern the photocatalytic efficiency of these catalysts [28]. However, under the reaction temperatures >150 °C, these Bronsted acid sites get converted to Lewis acid sites [16,17]. This is due to dehydroxylation at these elevated temperatures. Hence, at the temperature under investigation, the formation of methyl carbocation by use of Bronsted acid sites from the catalyst surface does not appear probable. Recently, Gopinath and co-workers [29] have carried out detailed in situ FTIR investigation of adsorbed phenol on Cu$_{1-x}$Co$_x$ Fe$_2$O$_4$ catalyst and concluded that adsorbed phenol shows both dissociated and undissociated forms. Further, insitu FTIR studies of phenol adsorbed on the Degussa P25 TiO$_2$ catalyst have shown that the hydroxyl group of phenol is undissociated [24] and is present in a hydrogen bonded state. Therefore, significant CH$_3^+$ formation does not appear probable using OH proton of phenol, in agreement with the suggestion made by Sato et al. [3].

Hence, methylation should proceed by formation of either the methoxy or hydroxymethyl enolate type species. For formation of the methoxy species, there should be cleavage of the O–H bond. While for the hydroxymethyl enolate ion formation, there should be cleavage of the C–H bond. A comparison of the O–H and C–H bond strengths shows us that the

O–H bond (bond strength = 435 kJ mol^{-1}) is stronger than the C–H bond in methanol (bond strength = 393 kJ mol^{-1}). Thus, the cleavage of C–H bond is considered to be preferred over that of the O–H bond [30].

C–H bond activation of hydrocarbons is shown to occur on oxide catalysts [31,32] based on H–D isotope exchange reactions. Both acidic and basic sites on the catalysts are believed to be important in the C–H bond activation process. Recently, Suib and co-workers [33] have confirmed C–H bond activation in benzyl alcohol to form a species of the type Ph-$^{(+)}$CHOH on Lewis acid catalysts also by similar isotope exchange studies. Further, methanol dehydrogenation by preferential breaking of C–H bond is a well-accepted mechanism during anodic oxidation of methanol on platinum catalysts [34] wherein Pt-CH$_2$OH formation is the primary step. Moreover, if the methoxy species were formed there would have been possible formation of some methoxy phenols. But, since there were no methoxy phenols detected, methoxy species cannot be considered to be the alkylating species. Also, CH$_2$O is not the alkylating agent as it is known to produce hydroxymethyl phenol rather than cresols [3,35].

Therefore, we propose here the formation of a $^{(-)}$CH$_2$OH$_{(ads)}$ type hydroxymethyl species, in a manner similar to the formation of enolate ion in conventional base catalysed aldol condensation reactions. In fact, Sato et al. [3] have earlier explained *ortho*-selectivity during methylation of phenol by predicting formation of hydroxymethyl radical mediated by Ce^{4+}/Ce^{3+} redox couple.

3.5. Proposed mechanism

Summarising the preceding discussion:

i. phenol does not adsorb vertically, since 2,6-xylenol is not formed even in trace amount unlike other catalysts;
ii. phenol does not adsorb parallel to the catalyst surface, since neither formation of trimethyl phenols or other dimethyl phenols, such as 2,5-xylenol is detected.

Therefore, only one side of phenol has to be adsorbed on the catalyst surface. Therefore, an edge-on adsorption of phenol is proposed on Degussa P25 TiO$_2$ catalyst. This assumption is supported by the evidence available from in situ FTIR studies of adsorbed phenol on the Degussa P25TiO$_2$ catalyst [24]. Such an adsorption can lead to activation of *ortho*- and *meta*-sites to produce the corresponding cresols. Edge-on chemisorption assisted by repulsion from weak basic sites could occur by donation of π electrons of the benzene ring of phenol to the vacant d-orbitals of the catalyst, Ti^{4+} acting as Lewis acid centers, as depicted in Scheme 3 with respect to attack at the *meta*-position. In a similar manner, methylation could occur at the *ortho-* or *para*-positions. The cresols are then obtained by the nucleophillic attack of the hydroxymethyl species at the now electron deficient aromatic ring, the nucleophile being generated by activation with the basic sites.
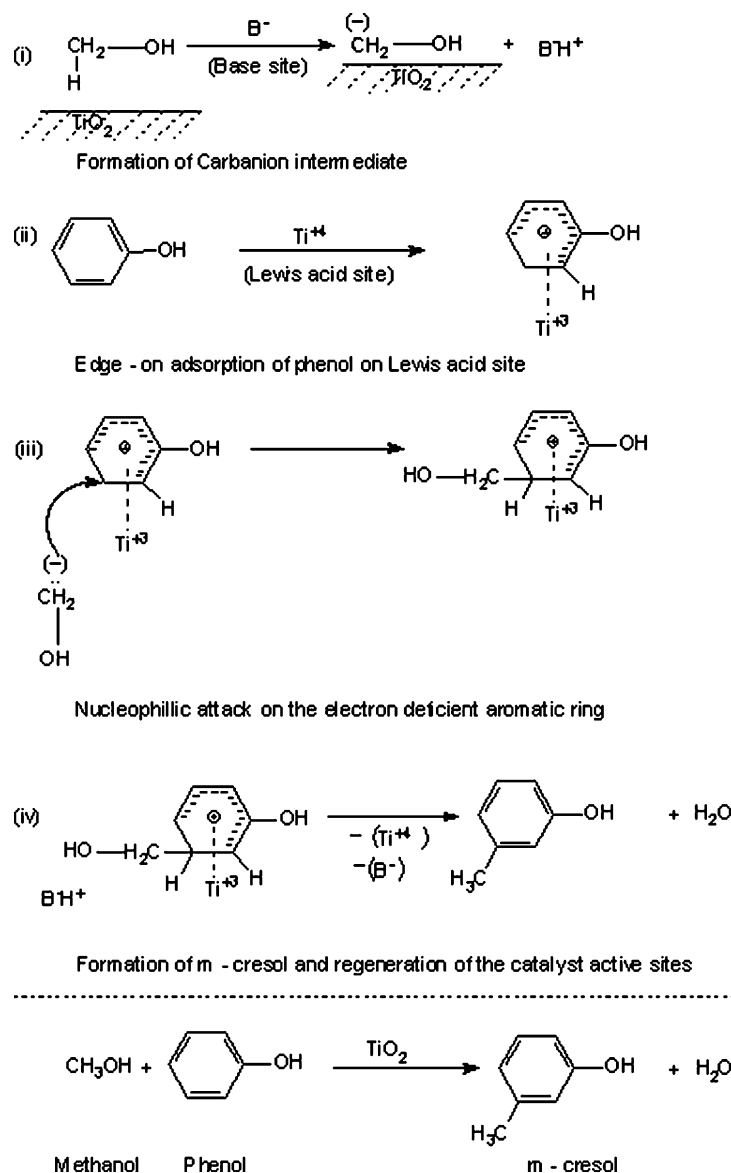
Scheme 3. Proposed mechanism for formation of *m*-cresol on Degussa P25 TiO$_2$ catalyst.

4. Conclusions

Degussa P25 TiO$_2$ has been investigated as a methylation catalyst. It gave an optimum 32% conversion at 400 °C, with predominant selectivity to cresols. An edge-on adsorption of the phenol molecule has been proposed to explain the observed selectivity.

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