Chapter-2

Synthesis of $p$-tert-butyl catechol by liquid phase alkylation of catechol with tert- butyl alcohol over WO$_x$/ZrO$_2$

"An invasion of armies can be resisted, but not an idea whose time has come"

Victor Hugo
Nomenclature

A → Catechol (CAT)

B → tert-butyl alcohol (TBA)

C → p-tert-butyl catechol (4-TBC)

D → 4, 6-Di-tert-butyl catechol

W → Water

k₁ → rate constant for reaction 1 (g/mol min)

k₂ → rate constant for reaction 2 (g/mol min)

k₃ → rate constant for reaction 3 (g/mol min)

k₄ → rate constant for reaction 4 (g/mol min)

k₅ → rate constant for reaction 5 (g/mol min)

K₁ → Adsorption constant of A (CAT) (dm³/ g)

K₂ → Adsorption constant of B (TBA) (dm³/ g)

K₃ → Adsorption constant of C (4-TBC) (dm³/ g)

K₄ → Adsorption constant of D (4, 6-Di-tert-butyl catechol) (dm³/ g)

K₅ → Adsorption constant of water (dm³/ g)

-rAS → rate of reaction of Catechol at the surface (alkylation) (mol/ g min)
2.1 Introduction

Alkylation reaction of catechol (CAT) with tert-butyl alcohol (TBA) is an industrially important reaction. The product, 4-tert-butyldocatechol (4-TBC) has widespread applications as antioxidants, polymerization inhibitors and also as stabilizer of many organic compounds [1]. This is a Friedel-Crafts reaction and is generally carried out using acids such as ZnCl₂, HCl and FeCl₃ as catalysts [2]. The use of these catalysts poses many problems such as handling, safety, corrosion and waste disposal. Thus, it is essential to develop a suitable alternate eco-friendly and commercially viable catalyst system. Although numerous studies have been reported on selective synthesis of phenol derivatives, there are limited reports available for the selective synthesis of 4-TBC using solid catalyst. The butylation of CAT to form 4-TBC is commonly carried out with TBA [3-11], methyltertiarybutyl ether [12-16] and isobutene [17-20] as alkylating agents.

The most commonly employed catalysts when TBA is used as the alkylating agent includes acidic zeolites like H-Y [3], H-USY, H-ZSM-5 [4] and Hβ [5], clay-based porus montmorillionite heterostuructures (PMH) solid acid catalysts [6-8], SO₃H-functionalised ionic liquid [9] and Co-napthenate and ZnCl₂ mixture [10]. Anand et al. [3] have studied the vapor phase alkylation in the temperature range 120 - 200 ºC using a fixed-bed vertical flow reactor at 1:3 molar ratio of CAT: TBA over HY and dealuminated HY zeolites, they showed marked increase in conversion of CAT and selectivity of more than 86 % towards 4-TBC with moderately steam-treated HY zeolites (steamed at 550 and 700 ºC). Among the various micorporous acidic zeolite catalysts like H-USY, Hβ, γ– alumina and H-ZSM-5 studied by Yoo et al. [4], H-ZSM-
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5 showed a conversion of more than 90 % and selectivity higher than 84 % for 4-TBC at 170 °C using fixed-bed vertical flow reactor at 1:3 molar ratio of CAT: TBA. Hβ zeolite was found to be very efficient catalyst for the alkylation with conversion of CAT about 87 % and selectivity towards 4-TBC was 99 % at 1:4 molar ratio of CAT: TBA [5]. Chunhui et al. have reported the liquid phase alkylation of CAT with TBA over meso and nanoporous clay composites [6-8]. In their work on H-exchanged montmorilonite and novel mesoporous acidic montmorilonite heterostructure catalysts [6], they observed best CAT conversion of 83.3 % and 4-TBC selectivity of 80.6 % under the optimized reaction condition of 137 °C, 1:2 molar ratio of CAT: TBA for 8 h. Under the same reaction condition over the synthetic nanoporous silicoaluminium montmorillonite hetero structured composites [7], CAT conversion of 76.8 % and 4-TBC selectivity of 85.2 % was observed. Recently, Xiaowa et al. [9] have studied the catalytic properties of several SO3H-functionalised ionic liquids for CAT alkylation with TBA by combination of experimental and computational techniques. They achieved the best CAT conversion of 41.5 % and 4-TBC selectivity of 97.1 % in 8h under the optimized reaction condition of 150 °C at 1:2 molar ratio of CAT: TBA.

The alkylation of catechol with MTBE has been reported over acid-functionalized ionic liquid [12]. The results indicated that under optimized reaction condition of 120 °C; 2h; n (catechol) : n (MTBE) : n (IL) = 1:3 : 0.02, the conversion of catechol and the selectivity of p-tert-butylcatechol (4-TBC) were 87.4 % and 65.3 % respectively. Gao et al. [13] reported the alkylation of catechol with MTBE catalyzed by H2SO4. The results indicated that under optimized reaction condition of 110 °C, 1.5 h, n (catechol): n (MTBE) = 1 : 1.5, the yield of 4-TBC was 72 %. Use of H2SO4 may
cause equipment corrosion and environmental pollution. Hence, the challenge to obtain solid acid catalysts with acid sites of comparable strength to those of conventional liquid acids is still open in an attempt to eliminate environmental concerns caused by the use, regeneration, transportation and storage of liquid acids [21].

In recent years, solid superacid catalysts based on doping tungsten oxides on zirconia support (WO\textsubscript{x}/ZrO\textsubscript{2}) is considered to have better application prospects for alkylation of aromatics compared to many other solid super acids such as, sulfate supported ZrO\textsubscript{2}, SbF\textsubscript{5}, TiO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} super acids. This is because WO\textsubscript{x}/ZrO\textsubscript{2} catalyst system is stable at very high temperature and in a solid-liquid system [21, 22]. Since, it was first reported by Hino and Arata [21], it has been employed by researchers for many versatile catalytic reactions like alkylation of hydrocarbons, liquid-phase alkylation of phenol with long-chain olefins, acetylation of alcohols and isomerization of light alkanes and nitration of aromatics [23-29]. This prompted us to choose WO\textsubscript{x}/ZrO\textsubscript{2} catalyst for selective alkylation of CAT with TBA to form 4-TBC. To investigate the influence of WO\textsubscript{3} loading on the conversion and selectivity towards various products during alkylation of CAT with TBA, we have prepared pure zirconia and 1, 5, 15, 25 and 50 wt. % tungsten oxide on zirconia.

Considering the industrial importance of this reaction system, a systematic study has been made, which includes preparation of the above mentioned catalysts, detailed physicochemical studies and catalytic performance for the alkylation of CAT with TBA. We have also made an attempt to correlate the physico-chemical properties towards the catalytic activity. The catalyst with highest activity has been used to study the effect of reaction parameters, such as reaction temperature, molar ratio of the reactants and catalyst loading on the conversions and product selectivity for this
reaction. Further, we have developed L–H–H–W surface reaction controlled kinetic model and estimated the model parameters. From the estimated rate constants at different temperatures, the activation energy of the CAT alkylation reaction with TBA was determined.

2.2 Experimental

2.2.1 Catalyst preparation

Precipitate of Zr(OH)$_4$ was obtained by slow addition (around 1 ml/min) of aqueous ammonium hydroxide (10 % w/v) to an aqueous solution of 100 g of zirconium oxychloride (ZrOCl$_2$ · 8H$_2$O) at room temperature with vigorous stirring until the pH of the mother liquor reached 10. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected by AgNO$_3$ solution, and was dried at 120 ºC for 12 h. Catalysts containing series of WO$_x$/ZrO$_2$ loading (1–50 wt. % of zirconium oxyhydroxide) were prepared by adding Zr(OH)$_4$ powder into aqueous solution of ammonium metatungstate [(NH$_4$)$_6$(H$_2$W$_{12}$O$_{40}$)·nH$_2$O] (Aldrich) followed by drying at 120 ºC for 12 h and calcining at 700 ºC for 5 h. This series of catalysts were denoted by xWZ, where x represents wt. % of tungsten oxide, W represents tungsten oxide, Z represents zirconia. For instance 5WZ represents ZrO$_2$ that was dried at 393 ºC and doped with 5 wt. % tungsten oxide. ZrO$_2$ is the pure support calcined at 700 ºC for comparison purpose. Further, the catalyst 15WZ was calcined at different temperatures (600 ºC and 800 ºC for 5 h) to study the impact of calcination temperature on the catalyst performance. Tungsten content in all the prepared catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The results are reported in Table 2.1.
2.2.2. Catalyst characterization

The following characterization has been made on the calcined catalyst materials. Tungsten content in all the prepared catalysts was determined by Spectro Cirros Inductively coupled plasma optical emission spectrophotometer. The samples were digested before spraying to the ICP through the CEM MARS microwave digester with the following acid composition HCl/HF/HClO$_4$/HNO$_3$ (1:1:1:4). The acids used were of high pure Merck grade. The Milli Q distilled water was used unless otherwise mentioned. The digested catalyst samples were diluted to 50 cm$^3$ with suitable internal standard (Scandium). The calibration standards (5-50 ppm) were prepared using tungsten (W-1000 ppm) from Accu standard. The ICP-OES was used in cross flow nebulizer mode at 1400 W plasma power. Coolant, nebulizer and auxiliary flow were maintained at 14 l/min, 0.8 l/min and 1.0 l/min respectively.

Total surface acidity of all the catalysts were determined by Metrohm-736 autotitrator using indicator and reference electrode system. The surface acidity of the catalyst is determined by treating known excess amount of n-butylamine (0.1 N) in dry benzene and back titrating the residual n-butylamine with 0.1 N HClO$_4$ in acetic acid. Known weight (~0.1g) of the catalyst was taken in stoppered round bottom flask in 5 cm$^3$ dry benzene. To this flask 20 cm$^3$ of n-butyl amine in dry benzene was added and set aside for overnight shaking. The unreacted n-butylamine was back titrated using HClO$_4$ in acetic acid pre-standardized by potassium hydrogen phthalate. The difference in volume of HClO$_4$ consumed for the total n-butylamine and the catalyst provides the surface acidity of the catalyst. Powder X-ray diffraction patterns was measured on a Philips X-ray diffractometer with Ni filtered Cu-K$\alpha$ radiation over the range of 20 from 20 to 40° with the intensity data for each point being collected at a 4 second interval.
Surface area, pore volume and pore size distribution presented in this research were measured by nitrogen adsorption at -196 °C with an ASAP-2010 porosimeter from Micromeritics Corporation (Norcross, GA). Surface area was measured by the BET method. The mesopore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.5 by assuming that all the mesopores were filled with condensed nitrogen in the normal liquid state. Pore size distributions were estimated using the Barrett, Joyner, Halenda (BJH) algorithm (ASAP 2010 built-in software from Micromeritics). The samples were degassed at 100 °C at 10⁻⁵ torr overnight prior to the adsorption experiments. IR spectra were recorded in-situ at room or elevated temperatures by a Perkin Elmer FTIR instrument, equipped with a conventional evacuation-gas manipulation ramp (10⁻³ Pa). The FTIR instrument was typically operated at a resolution of 4 cm⁻¹ after averaging over 500 scans per spectrum. All the samples were subjected to a standard pretreatment involving heat treatment at 500 °C for 6 h under vacuum (10⁻⁵ mbar). The quantitative analysis was carried out after 3 h pyridine adsorption at room temperature followed by evacuation at 150 °C for 30 min under vacuum (10⁻⁵ mbar) for 30 min. The Brönsted (B) and Lewis (L) acidity was calculated from the area under the peaks at 1540 cm⁻¹ and at 1445 cm⁻¹ respectively. Raman spectra presented in this study were recorded at ambient temperature on a Nicolet FT-Raman 960 Spectrometer with a range of 4000-100 cm⁻¹ and a spectral resolution of 2 cm⁻¹ using the 1064 nm exciting line (~600 mV) of a Nd:YAG laser (Spectra Physics, USA). Finely powdered samples were contained in a 5 mm outer diameter sample tube. X-ray photoelectron spectroscopic measurements were carried out for the catalysts were characterized by achromatic Mg Kα (hμ = 1253.6 eV) X-rays
in an Omicron ultra-high vacuum (UHV) surface analysis system (ESCAPROBE MK II) with a base pressure < 10^{-10} Torr. System consisted of a sphaera electrostatic energy analyzer operated in constant analyzer energy mode, with a pass energy set at 5 eV, and a 7-channel detector. Catalyst powders were smeared onto a conducting copper tape mounted on a standard sample holder supplied with the system. Analyses were conducted in the surface normal mode. Samples corrected for surface charging against C1s peak corresponding to C-C/C-H species (~ 284.6 eV). Spectral data were subjected to background subtraction and subsequently analyzed using a least squares fitting method with Casa XPS software. Binding energies of various photoelectron peaks were compared against spectral reference database from national institute of standards and technology (NIST) V. 3.5. To observe possible morphological changes and also to know the shapes of the catalyst particles, some of the catalyst samples were investigated by SEM technique on a QUANTA 250 (FEI make), additional elemental analysis was performed via energy-dispersive analysis of the x-rays (EDAX) emitted by the sample. The solid samples were mounted on a aluminum stub with the help of a carbon adhesive tape to make the sample surfaces conductive, it was coated with carbon of about 1-2 nm thickness. Back scattered electron micrographs was recorded while scanning electron microscope was operated at 20 kV accelerating voltage with different magnification.

2.2.3. Reaction conditions

Catalytic activity studies for liquid phase reactions were carried out in round bottom flask fitted with a reflux condenser, equipped with a magnetic stirrer and immersed in a thermostated oil bath. The catalyst was activated at 500 ºC for 2 h in
flow of dry air and cooled to the reaction temperature prior to its use in the reaction. The reactor was filled with reactants at a pre-determined molar ratio and fixed amount of catalyst and the temperature was set using the control panel while the cold water was circulated through the water condenser. The reactants–catalyst mixture was continuously agitated with the help of a stirrer. The stirrer speed was maintained at 500 rpm. The clear solution of the reaction mixture was withdrawn periodically, centrifuged and analyzed for product compositions by GC analysis as per the following procedure. GC analysis for the current research was conducted on liquid samples (diluted in HPLC grade dichloromethane to obtain around 1 mg/cm³ concentration) using a Shimadzu 2010 GC for quantitative estimation, while GC-MS (Shimadzu QP 5500) was used for confirmation of products. The column used for the current research was a HP-5 (methyl 5% Phenyl Polysiloxane) 30 metre, 0.32 mm diameter and of 0.25 μm film thickness; oven was temperature programmed from 60 to 300 ºC at 10 ºC/min heating rate and held at 300 ºC for 10 min; helium was used as carrier gas at a flow rate of 1 cm³/min. The injector and detector were maintained at 290 ºC and split ratio was 100:1. For the GC-MS analysis, GC operating conditions was maintained for injector and column, with the mass spectrometer operating in electron-impact mode (EI) at 70 eV, in the scan range 40–800 Da. All the test runs were repeated twice to check the reproducibility.

2.3 Results and discussion

2.3.1 Physicochemical properties

The XRD pattern of the catalysts with different WO₃ loadings calcined at 700 ºC along with 15WZ calcined at different temperatures are shown in Fig. 2.1. Highly
crystalline materials were obtained after calcination at 700 °C. It can be observed that even a small loading of tungsten exhibited mixtures of monoclinic (\(2\theta = 28.2^\circ, 31.5^\circ\)) and tetragonal (\(2\theta = 30.3^\circ\)) \(\text{ZrO}_2\) \([30,31]\). The fraction of tetragonal zirconia becomes dominant with subsequent loading of tungsten and under the present treatment conditions tetragonal phase was clearly dominant for \(\text{WO}_3\) loadings of 15 wt. %, (Fig. 2.1). Thus, the added \(\text{WO}_3\) stabilizes the tetragonal phase of zirconia. X-ray diffraction lines characteristic of monoclinic \(\text{WO}_3\) (\(2\theta = 23.2^\circ, 23.6^\circ\) and \(24.5^\circ\)) are observed for sample containing above 15WZ loading. This indicates that \(\text{WO}_3\) is highly dispersed on the support for samples with less than 15WZ loading and the crystalline \(\text{WO}_3\) peaks are observed when the \(\text{WO}_3\) loading exceeds the monolayer coverage. The XRD of the 15WZ catalyst calcined at 600 °C, 700 °C and 800 °C shows that \(\text{ZrO}_2\) exists mainly in the tetragonal phase at all the calcination temperatures. There was no crystalline \(\text{WO}_3\) peaks observed at calcination temperatures at and below 700 °C, indicating that \(\text{WO}_3\) is highly dispersed on the \(\text{ZrO}_2\) support. When the calcination temperature is increased beyond 700 °C new peaks at \(2\theta\) of 23.2°, 23.6° and 24.5° was observed. These characteristic peaks of \(\text{WO}_3\) indicate that \(\text{WO}_3\) crystallises at temperatures higher than 700 °C reducing the dispersion of \(\text{WO}_3\) at higher calcination temperature [32, 33].
Fig. 2.1 X-ray diffraction pattern for WO$_3$-ZrO$_2$ containing different WO$_3$ loading calcined at 600 °C, 700 °C and 800 °C. T and M indicate tetragonal and monoclinic phases, respectively.

The BET surface area and BJH mean pore diameters of WO$_x$/ZrO$_2$ samples are also included in Table 2.1. The results indicate that an increase in the specific surface area for all the tungsten doped samples. Surface area becomes maximum at 15 WZ (ca. 67 m$^2$ g$^{-1}$), and thereafter, further loading of WO$_3$ leads to decrease in the surface area. This confirms that the surface area stabilizing effect is due to strong interaction of WO$_3$ species with ZrO$_2$ crystallites. The presence of monoclinic WO$_3$ as indicated from the XRD pattern for samples with higher concentration of tungsten species could be correlated to decrease in the surface area due to sintering of particles. Further, it is
also observed that pore size of pure zirconia (without the use of promoter), is little wider compared to the W (promoted) samples. These values are in good agreement with the results reported in the literature [31]. The surface density shown in the Table 2.1 of W is calculated as per the following formula.

Surface density of \( W = \frac{[\text{WO}_3 \text{ loading (wt. %)/100}] \times 6.023 \times 10^{23}}{[231.8 \text{ (formula weight of WO}_3\text{)} \times \text{BET surface area (m}^2 \text{g}^{-1}) \times 10^{18}]}\}.

Surface density of W on the catalyst depends on both the WO\(_3\) loading and the calcination temperature. When the calcination temperature is increased from 600 °C to 700 °C, the surface density increases from 5.48 to \(~6\) W-atoms nm\(^{-2}\), which is equivalent to the surface density of W in the monolayer [32]. Also, when the calcination temperature is further increased beyond 700 °C to 800 °C, the surface density increased to 6.69 W-atoms nm\(^{-2}\), because WO\(_x\) species agglomerate into monoclinic WO\(_3\) crystallites and becomes less effective sintering inhibitors of underlying amorphous zirconia support. Our observations are similar to other reported literature values [32-35].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Calcination Temp (°C)</th>
<th>Measured WO(_3) (%)</th>
<th>Surface area (m(^2)/g)</th>
<th>Pore size (Å)</th>
<th>Surface acidity (m.eq./g)</th>
<th>Surface density (W-atoms/nm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO(_2)</td>
<td>0.0</td>
<td>23.02</td>
<td>163.8</td>
<td>0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1WZ</td>
<td>700</td>
<td>1.1</td>
<td>23.37</td>
<td>126.7</td>
<td>0.52</td>
<td>1.22</td>
</tr>
<tr>
<td>5WZ</td>
<td>700</td>
<td>5.2</td>
<td>53.24</td>
<td>81.8</td>
<td>1.11</td>
<td>2.53</td>
</tr>
</tbody>
</table>
Table 2.1 Surface area, pore size, surface acidity and surface density of the catalyst with varying WO$_3$ loadings.

To study the surface topography and to assess the surface dispersion of the active components over the support, we performed SEM investigations on all the samples calcined at 700 °C. Although, 5 % crystalline WO$_3$ can be detected by SEM, however, in our study, no particle corresponding to crystalline WO$_3$ is observed sample up to 15 wt.% WO$_3$ (Fig. 2.2, a - b) and only large angular particles of ZrO$_2$ were observed for 5 WZ and 15 WZ. This observation indicates thorough dispersion of tungsten species throughout zirconia by the method of synthesis adapted by us and therefore presumably it could not crystallize separately. The sample containing 25 wt. % WO$_3$ shows appearance of prominent monoclinic WO$_3$ and 50 % WO$_3$ shows highly agglomerated WO$_3$ particles as seen in Fig. 2.2 c and d respectively.
Thus, the presence of monoclinic WO$_3$ for samples containing beyond 15 wt.% of WO$_3$ as indicated from the XRD and SEM pattern could be the reason for the decrease in the surface area for higher loadings of WO$_3$. Thus, at higher concentrations of WO$_3$ loadings, the crystallization of WO$_3$ must have resulted in sintering of particles and hence decrease in the surface area, but in the case of samples with lower loadings of WO$_3$ (<15 wt. % loadings), strong interaction of WO$_3$ species with ZrO$_2$ crystallites helps in inhibiting sintering of ZrO$_2$[29-31].

Total surface acidity of different tungsten loaded catalyst samples are shown in Table 2.1. It can be seen from figure that total acidity increased up to 15 wt. % WO$_3$ loading and then decreased with further increase in WO$_3$ loading. From the acidity curves of various samples with different WO$_3$ loading, it can be easily said that sample with 15 wt. % W possesses comparably higher acidity than other samples.
However, this particular observation is noticed for samples only up to 15 wt.% W and beyond this concentration, the acidity curve indicates a decrease in the number of acid sites. In an attempt to estimate the type of acidity, we performed the FT-IR studies of pyridine adsorbed on WO$_3$–ZrO$_2$ samples. Adsorption of pyridine as a base on the surface of solid acids is one of the most frequently applied methods for the characterization of surface acidity. The use of FT-IR spectroscopy to detect adsorbed pyridine enables us to distinguish among different acid sites. Representative FT-IR pyridine adsorption spectra of catalyst with 15 % WO$_3$ loading calcined at 700 ºC is shown in Fig. 2.3. The catalysts showed Brönsted (B) and Lewis (L) acidity at 1539 cm$^{-1}$ and at 1445 cm$^{-1}$, respectively. Peak at 1489 cm$^{-1}$ is attributed to both Brönsted (B) + Lewis (L) site [24].

**Fig. 2.3** Representative FTIR spectra of pyridine adsorption on 15WZ-700 ºC calcined catalyst.

Fig. 2.4 shows the i) total acidity ii) Lewis and iii) Brönsted acidity of WZ catalysts at different WO$_x$ loadings calcined at 700 ºC, that is attributed to the crystal structure of ZrO$_2$ phase, the type of tungsten oxide species and the interaction
between the surface tungsten oxide layer and ZrO$_2$ support [30,31]. The above results of total acidity can be correlated with the trends observed in XRD, SEM and surface area results.

**Fig. 2.4** Total acidity, Lewis and Brönsted acidity of WZ catalysts at different WO$_x$ loadings and calcined at 700 °C.

Raman spectra of the catalysts were recorded to find out the nature of the tungsten species present on different catalysts. Raman spectra of unpromoted and promoted zirconia samples are presented in Fig. 2.5. The assignment of Raman bands of metal oxide overlayers in supported oxide catalysts is typically based on comparisons with the spectra of structurally well characterized reference compounds. The signals corresponding to reported surface tungsten oxospecies were expected in the 700–1060 cm$^{-1}$ region for W–O–W and W=O stretching modes [36,37]. The Raman spectra of pure WO$_3$ have characteristic bands at 806, 714, and 287 cm$^{-1}$. Absence of these bands in samples suggests that microcrystalline WO$_3$ are not formed to detectable levels on
the surface of W-ZrO$_2$ catalyst and the impregnated oxides are strongly interacting with the zirconia.

**Fig. 2.5** Raman spectra of (a) WO$_3$ (b) 1% WO$_3$/ZrO$_2$, (b) 5% WO$_3$/ZrO$_2$ (c) 15% WO$_3$/ZrO$_2$ (d) 25% WO$_3$/ZrO$_2$ (e) 50% WO$_3$/ZrO$_2$ (f) pure ZrO$_2$.

Interactions with a support can dramatically change the properties of metals or metal oxides. We have measured the W (4f) and Zr (4p) XPS spectra of all the samples. Fig. 2.6 shows W 4f spectra of 15WZ sample calcined at 700 °C (as example). The characteristics peaks of W$^{6+}$ 4f7/2, 4f5/2 appear at 35.4 and 37.5 eV respectively and that of W$^{4+}$ 4f7/2, 4f5/2 appeared at 34.2, 36.3 eV respectively. The W4f7/2 binding energy measured for 15 WZ sample occurred at 35.7 eV and corresponds to tungsten in
the +6 oxidation state (WO$_3$). These values are in agreement with the characteristic peaks obtained for standard ZrO$_2$ and WO$_3$ samples (calcined at 700 ºC) and values reported in literature for tungstated zirconia [38].

Fig. 2.6 XPS spectra of W (4f) 15WZ calcined at 700 ºC.

2.3.2 Catalytic activity studies

The alkylation reaction of CAT with TBA is a typical example of Friedel-Craft acid-catalyzed electrophilic substitution reaction. Dehydroxylation of tert-butyl alcohol by the acid sites of the catalyst leads to the formation of tert-butyl cation species. The butyl carbocation reacts mainly at the para-position of the CAT to form 4-TBC, trace amount of 4, 6-di-tert-butyl catechol (DTBC) compounds are produced by further alkylation of 4-TBC (Scheme 1).
Scheme 2.1 tert-butylation of CAT over WO$_x$/ZrO$_2$.

The conversion of CAT is defined as moles of consumed CAT to the moles of CAT used for the reaction. The selectivity to specific product is defined as moles of specific product divided by moles of consumed CAT.

2.3.3. Effect of WO$_3$ loading

To investigate the effect of WO$_3$ loading on tert-butylation of CAT, 0-50 WZ catalysts calcined at 700 °C are used for alkylation reaction at 140 °C using equimolar ratio of TBA and CAT for 30 min. It is clear from Fig. 2.7, that pure ZrO$_2$ showed the least conversion of 4 %, and among the catalysts with different WO$_3$ loading, the conversion was found to increase with WO$_3$ loading, and the catalyst 15WZ gave the highest conversion of 99 %, as the WO$_3$ loading is further increased the conversion of CAT decreased to 80 % at 25 WZ and finally at 50 WZ it was found to be 63 %. Interestingly, 0WZ and 1 WZ catalysts under the same reaction condition, not only showed less conversion of CAT, but also produced more of DTBC. These observations are in good agreement with the characterization data and indicate that
reaction is highly sensitive to acidity, surface area and pore size of the catalyst. 15 WZ catalyst has the higher acidity (2.3 m.eq./g), higher surface area (68 m$^2$/g) and least pore size (62 Å) compared to other catalysts and is found to be most active in the tert-butylation of CAT with a 99 % conversion of CAT and 99 % selectivity towards 4-TBC. From the Fig. 2.4, it can also be observed that DTBC is formed up to 36 % in pure ZrO$_2$ and 25 % with 1WZ. This could mainly be attributed to the pore size, which is found to be almost double for ZrO$_2$ (163 Å) and 1WZ (127 Å) compared to catalysts with WO$_3$ loading of 5 % (81.8 Å) and above (Table 2.1). Thus, it can be concluded that the formation of di-alkylated product from the mono-alkylated products favored only when the steric hindrance is less, i.e. the catalyst has large pores to allow the bulky alkylated products to travel out [39]. At and beyond 5 % tungsten loading, the pore size of all the catalysts reduces drastically to below 82 Å, hence, in spite of higher acidity in the catalysts with WO$_3$ loading of more than 5 %, the selectivity towards the di-alkylated product is significantly low (< 3 %) under the same reaction conditions. These observations clearly indicate that addition of WO$_3$ has a significant role in promoting the catalytic performance of ZrO$_2$ for the tert-butylation of CAT with TBA.
Further for the catalyst 15WZ calcined at different temperatures (600 °C, 700 °C and 800 °C) to study the impact of calcination temperature on the catalytic performance. It was found that calcination temperature also affects the catalytic performance. The conversion of CAT at 600 °C, 700 °C and 800 °C was (92.9 %, 99 %, and 97.2 %) and the selectivity towards 4-TBC was found to be (93, 99 % and 91 %) respectively. The 15WZ catalyst with very high specific surface area and good balance of acid strength and pore size distribution was found to be the most efficient for the synthesis of 4-TBC. Therefore, the 15WZ catalyst was used to study the different reaction parameters.

2.3.4. Effect of catalyst loading
To investigate the optimum amount of catalyst required for the reaction, reactions were carried out with the most active catalyst 15 WZ at 140 °C for 30 mins with 1:1 mole ratio of CAT: TBA. The catalyst loading was varied from 0 % (without catalyst) to 20 % (w/w) with respect to CAT. There was no reaction observed in the absence of the catalyst (i.e. at 0 wt. %). Fig. 2.8 suggests that as the catalyst loading is increased, conversion of CAT also increases. The conversion of CAT was found to be 83.0 % with 5 wt.% catalyst, which increased substantially to 94.0 % with 10 wt. % and to about 99.0 % with 15 % catalyst, and further increase to 20 %, had only marginal effect on conversion of CAT. The conversion of CAT at 20 % is about 99.5 %. Hence, 15 % loading appears to be optimum under the prevailing reaction conditions.

In the heterogeneous catalysis, the reactants are expected to react on the surface of the catalyst. Hence, the conversion is expected to increase with increase in the catalyst loading as there is availability of more surfaces for the reactants. Also, this behavior suggests that catalyst loading is an effective parameter which can influence the conversion if the catalyst loading is less than 15 %.

The catalyst loading does not seem to have any significant effect on the selectivity of the products. This is because though we have more active surfaces with increased catalyst loading, we have limited amount of TBA. The moles of TBA is same as that of CAT, hence it leads to selective formation of 4-TBC (mono product). The di-alkylated product is less than 1 % for all the catalyst loading as can be seen in Fig. 2.8.
Fig. 2.8 Effect of catalyst loading (w.r.t. Catechol) on conversion of catechol and selectivity of products at 140 °C 1:1 mole ratio of catechol: TBA for 30 minutes.

2.3.5. Effect of molar ratio of Catechol: TBA

The effect of the molar ratios of the reactants has been studied using 15WZ as the catalyst and about 15 % catalyst loading (w/w) with respect to CAT, at 140 °C for 30 min. The molar ratio of CAT to TBA was varied from 1:1 to 1:3. Fig. 2.9 shows that there is no significant effect of increasing the moles of TBA on the conversion of CAT. The conversion of CAT was in the range of 99.0- 99.9 %. However, it can be seen from the figure that as the molar ratios (CAT/TBA < 1) is increased, the selectivity towards 4-TBC decreases considerably from 99.02 % at 1:1 to 73 % at 1:2 and finally to 65 % at 1:3 mole ratio of CAT: TBA, with corresponding increase in
the dialkylated product. The increase in dialkylated product could be attributed to the availability of excess TBA. As there is more TBA in the reaction the possibility of unreacted TBA and 4-TBC (mono product) to collide at the active surface is higher, leading to formation of more dialkylated products. Hence, it can be concluded that the increase in the molar ratio (CAT/TBA < 1) of TBA does not have a significant effect on conversion but decreases the selectivity towards the desired product 4-TBC.

**Fig. 2.9** Effect of moles of TBA (w.r.t. Catechol) on conversion of catechol and selectivity of products at 140 °C 15 % loading (w.r.t catechol) of 15WZ for 30 minutes.

**2.3.6. Effect of temperature**
Increase in temperature leads to an increase in rate constants and hence we have carried out the experiments at seven different temperatures ranging from 80 to 160 °C, at equal moles of CAT: TBA using 15WZ catalyst loading. The samples were taken for GC analysis at 15 min interval for first hour and after an hour it was taken at an interval of 30 min. Fig. 2.10 shows the conversion of CAT at different temperatures. It can be observed from Fig. 2.10 that the conversion of CAT at lower temperature (80 °C) increases from 37.2 % at 15 min to 93.8 % at 90 min and finally reaches 94.4 % at 180 min. Thus, indicating that beyond 90 min the conversion does not change significantly. A very similar trend is also seen for conversion of CAT at temperatures of 90 °C, 100 °C and 100 °C. The conversion of CAT was observed to increases from 15 min to 90 min, from 55.6 % to 95.8 %, 74.9 % to 96.2 % and 84.8 % to 96.6 % for temperatures of 90 °C, 100 °C and 110 °C respectively. When the temperature is further increased to 120 °C, the conversion of CAT increases from 90.4 % at 15 min to maximum of 97.7 % at 60 min and remains almost constant beyond 60 min, while at the highest studied temperature of 140 °C, the conversion at 15 min is 99 % and it becomes constant beyond 15 min. Further, at reaction temperature of 160 °C, no significant increase in TBA conversion was observed. The temperature does not seem to have any significant impact on the selectivity of 4-TBC, as all the CAT was mostly converted to 4-TBC. The di-alkylated by-product was formed at a very low level of 1-2 % at all the studied temperatures.
Fig. 2.10 Effect of temperature on conversion of catechol at 1:1 mole ratio of catechol: TBA 15 % loading (w.r.t catechol) of 15WZ for 30 minutes.

It can be hence summarized that the optimum conditions for the synthesis of 4-TBC is by using 15 % loading of 15WZ at 140 °C and 1:1 mole ratio of CAT:TBA. Under these conditions within 30 min about 99 % conversion of CAT is observed with 99 % selectivity towards 4-TBC. The performance of WZ is compared with other reported catalysts for synthesis of 4-TBC in Table 2.2. It is evident that catalytic
performance of WZ is better than the other catalyst in terms of both conversion as well as selectivity.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Conversion of CAT</th>
<th>% Selectivity (4-TBC)</th>
<th>Reaction conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HY</td>
<td>86.0</td>
<td></td>
<td>120 - 200 ºC, 1:3(CAT:TBA)</td>
<td>[3]</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>90.0</td>
<td>84.0</td>
<td>170 ºC, 1:3(CAT:TBA)</td>
<td>[4]</td>
</tr>
<tr>
<td>H-β</td>
<td>87.0</td>
<td>99.0</td>
<td>1:4(CAT:TBA)</td>
<td>[5]</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>83.3</td>
<td>80.6</td>
<td>137 ºC, 8 hours, 1:2(CAT:TBA)</td>
<td>[6]</td>
</tr>
<tr>
<td>SO₂H functionalised Ionic liquid</td>
<td>41.5</td>
<td>97.0</td>
<td>150 ºC, 8 hours, 1:2(CAT:TBA)</td>
<td>[9]</td>
</tr>
<tr>
<td>WOₓ/ZrO₂(current study 15WZ)</td>
<td>99.0</td>
<td>99.0</td>
<td>140 ºC 30min, 1:1(CAT:TBA)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2 Comparison between the activity and selectivity of catalysts under optimum conditions.

2.4 Kinetic model - Determination of the rate equation for alkylation of CAT

Kinetic runs were conducted at four different temperatures 80, 90, 100 and 110 ºC. The reaction products were sampled at 15, 30, 45, 60, 90, 120, 150 and 180 min in order to have enough data points for evaluating the kinetic parameters with confidence. For the reaction studied at temperatures beyond 110 ºC, it was found that the reaction reached completion within 45 min, hence the temperatures beyond 110 ºC were not used for estimating the kinetic parameters. Langmuir-Hinshelwood-Hougen-Watson
approach was used to generate rate expression for the reaction scheme. The model considers the adsorption of TBA and CAT on the active sites of the catalyst. On the catalytic surface, CAT (A) combines with TBA (B) to form first the mono-alkylated products (C) 4-TBC. These monoalkylated products further undergo alkylation to form dialkylated product (D), if more TBA is available at the catalytic site to combine with the monoalkylated products. This model is represented by the following mechanism.

(a) Adsorption of the reactants

\[
\begin{align*}
A + S & \xrightleftharpoons[k_1]{k_1} AS \\
B + S & \xrightleftharpoons[k_2]{k_2} BS
\end{align*}
\]

(R1)

(b) Surface reaction

Formation of mono alkylated products (4-tert-butyl catechol)

\[
\begin{align*}
AS + BS & \xrightleftharpoons[k_3]{k_3} CS + WS
\end{align*}
\]

(R3)

Formation of dialkylated products

\[
\begin{align*}
CS + BS & \xrightleftharpoons[k_4]{k_4} DS + WS
\end{align*}
\]

(R4)

(c) Desorption of the products

\[
\begin{align*}
CS & \xrightleftharpoons[k_5]{k_5} C + S \\
DS & \xrightleftharpoons[k_6]{k_6} D + S \\
WS & \xrightleftharpoons[k_7]{k_7} W + S
\end{align*}
\]

(R5) (R6) (R7)
The rate of adsorption of various compounds can be written for the reactions (R1), (R2) and (R5-R7),

\[
\left(-r_A\right)_{Ad} = k_1 C_A C_S - k_1 C_{AS} \quad \text{(eqn 1)}
\]

\[
\left(-r_A\right)_{Ad} = k_1 \left(C_A C_s - \frac{k_1}{k_1} C_{AS}\right) \quad \text{(eqn 2)}
\]

\[
\left(-r_A\right)_{Ad} = k_1 \left(C_A C_s - \frac{1}{K_1} C_{AS}\right) \quad \text{(eqn 3)}
\]

Similarly,

\[
\left(-r_B\right)_{Ad} = k_2 \left(C_B C_s - \frac{1}{K_2} C_{BS}\right) \quad \text{(eqn 4)}
\]

\[
\left(-r_C\right)_{Ad} = k_3 \left(C_C C_s - K_3 C_{CS}\right) \quad \text{(eqn 5)}
\]

\[
\left(-r_D\right)_{Ad} = k_6 \left(C_D C_s - K_6 C_{DS}\right) \quad \text{(eqn 6)}
\]

\[
\left(-r_W\right)_{Ad} = k_7 \left(C_W C_s - K_7 C_{WS}\right) \quad \text{(eqn 7)}
\]

Let \(K_C = \frac{1}{K_5}\), \(K_D = \frac{1}{K_6}\), \(K_W = \frac{1}{K_7}\)

The eqn 5 to 7 becomes

\[
\left(-r_C\right)_{Ad} = k_3 \left(C_C C_s - \frac{1}{K_C} C_{CS}\right) \quad \text{(eqn 8)}
\]
\[
\left(-r_D\right)_{Ad} = k_6(C_D C_S - \frac{1}{K_D} C_{DS}) \quad \text{(eqn 9)}
\]

\[
\left(-r_W\right)_{Ad} = k_7(C_W C_S - \frac{1}{K_W} C_{WS}) \quad \text{(eqn 10)}
\]

The rate for the surface reaction can be written as follows:

The rate of alkylation (-\(r_{AS}\)) is given as,

\[
-r_{AS} = k_3 C_{AS} C_{BS} - k'_3 C_{CS} C_{WS} \quad \text{(eqn 11)}
\]

If reversible natures of reactive step are neglected, then equations (11) can be reduced to,

\[
-r_{AS} = k_3 C_{AS} C_{BS} \quad \text{(eqn 12)}
\]

The adsorbed phase concentrations can be related to the bulk phase concentrations if adsorption is rapid as compared to chemical reaction rates,

\[
C_{AS} = K_1 C_A C_S, \quad C_{BS} = K_2 C_B C_S, \quad C_{CS} = K_C C_C C_S, \quad C_{DS} = K_D C_D C_S, \quad C_{WS} = K_W C_W C_S
\]

\[
\text{(eqn 13)}
\]

Balancing the total no of catalytic sites,

\[
C_T = C_S + C_{AS} + C_{BS} + C_{CS} + C_{DS} + C_{WS}
\]

\[
\text{(eqn 14)}
\]

Substituting eqn 13 in 14

\[
C_T = C_S (1 + K_1 C_A + K_2 C_B + K_C C_C + K_D C_D + K_W C_W)
\]

\[
\text{(eqn 15)}
\]

One can get the vacant sites as,

\[
C_S = \frac{C_T}{1 + K_1 C_A + K_2 C_B + K_C C_C + K_D C_D + K_W C_W}
\]

\[
\text{(eqn 16)}
\]
The adsorption of dialkylated compound is assumed to be lesser as compared to others species as it is the largest \([40-42]\) i.e.

\[
1 + K_1 C_A + K_2 C_B + K_C C_C + K_W C_W \gg K_D C_D
\]  
(eqn 17)

\[
C_S = \frac{C_T}{1 + K_1 C_A + K_2 C_B + K_C C_C + K_W C_W}
\]  
(eqn 18)

The rate of disappearance of Catechol is reduced to,

\[-r_{AS} = k_3 K_1 C_A C_S K_2 C_B C_S \]  
(eqn 19)

\[-r_{AS} = \frac{k_3 C_A^2 K_1 K_2 C_A C_B}{(1 + K_1 C_A + K_2 C_B + K_C C_C + K_W C_W)^2} \]  
(eqn 20)

Let \(k_3 C_T^2 = k_r\)

\[-r_{AS} = \frac{K_1 K_2 C_A C_B}{(1 + K_1 C_A + K_2 C_B + K_C C_C + K_W C_W)^2} \]  
(eqn 21)

At \(t=0\), \(C_C, C_D, \) & \(C_W = 0\)

Thus the initial rate for the disappearance of catechol is given as,

\[-r_{AS} = \frac{K_1 K_2 C_A C_B}{(1 + K_1 C_A + K_2 C_B)^2} \]  
(eqn 22)

The rate constant for the surface reaction should follow an Arrhenius type temperature dependency. The temperature dependence of the kinetic and adsorption parameters can be expressed mathematically as:

\[K = K^0 \exp \left( \frac{-E_a}{RT} \right) \]  
(eqn 23)
\[ K_1 = K_1^0 \exp\left(\frac{-\Delta H_{ad}}{RT}\right) \]  

(eqn 24)

The parameters \( K_r, K_1 \) and \( K_2 \) were determined by fitting the LHHW models with experimental initial rate data in equation 22 and the remaining parameters \( K_C, K_D \) and \( K_W \) were determined by fitting the LHHW model with experimental rate data over the entire reaction time (equation 21). The optimum values of these parameters are obtained by minimising the square of relative difference between the experimental rates and the theoretical rates. The experimental rate was calculated from the concentration profiles of CAT with respect to time as follows,

\[ -r = \frac{1}{w} \left( \frac{dC_A}{dt} \right) \]  

(eqn 25)

The experimental rate calculated by the above formula is plotted against the predicted rate in Fig. 2.11 and it shows that the experimental rate matches well with predicted rate.
Fig. 2.11 Comparison of experimental versus predicted rates at different temperatures.

The Arrhenius plot shown in the Fig. 2.12 for the temperature dependency of surface reaction rate is used to calculate the energy of activation for the butylation of catechol. Table 2.2 and Table 2.3 summarize the rate constants, adsorption equilibrium constants, activation energy and the pre-exponential factor characterizing the system. It can be seen that the adsorption constant of the reactants are comparatively higher as compared to the product, indicating that the reactants would have more affinity to come to the surface and form the products. Once the product is formed, it would be desorbed more easily. Also, it can be observed from the Table 2.2 that as the temperature increases the adsorption constant decreases and hence it indicates that adsorption of the reactants and
products on the catalysts is an exothermic process. The rate constant for the alkylation reaction increases with increase in the temperature. The rate constant increases by about 1.5 times when temperature is increased from 80 °C to 90 °C further increase by 10 °C increases the rate constant by 1.2 times. The rate constant for the reaction increases by further 1.2 when the temperature is increased from 100 °C to 110 °C. Fig. 2.13 to 2.16 shows the van’t-Hoff’s plot for temperature dependence of the compounds adsorbed on the surface of the catalyst. It can be seen from the Table 2.3 that the pre-exponential factor for the reaction is higher than the adsorption indicating that the adsorbed reactants can easily undergo surface reaction leading to products. The energy of activation for butylation of catechol is found to be 33.53 kJ/mol.

![Arrhenius plot showing temperature dependency of surface reaction rate.](image)

**Fig. 2.12** Arrhenius plot showing temperature dependency of surface reaction rate.
Fig. 2.13 van’t Hoff plot showing temperature dependency of adsorption parameter, for catechol.

Fig. 2.14 van’t Hoff plot showing temperature dependency of adsorption parameter, for tert-butyl catechol.
Fig. 2.15 van’t Hoff plot showing temperature dependency of adsorption parameter for \textit{p-}tert\textit{-}butyl catechol.

Fig. 2.16 van’t Hoff Plot showing temperature dependency of adsorption parameter for water.
### Table 2.3 Adsorption and kinetic constants for butylation of CAT.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$K_r$</th>
<th>$K_1$</th>
<th>$K_2$</th>
<th>$K_c$</th>
<th>$K_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kg/(kg mmol min))</td>
<td>(dm³/g)</td>
<td>(dm³/g)</td>
<td>(dm³/g)</td>
<td>(dm³/g)</td>
</tr>
<tr>
<td>80</td>
<td>6.508</td>
<td>2.456</td>
<td>2.123</td>
<td>0.890</td>
<td>0.968</td>
</tr>
<tr>
<td>90</td>
<td>10.045</td>
<td>2.019</td>
<td>1.490</td>
<td>0.806</td>
<td>0.806</td>
</tr>
<tr>
<td>100</td>
<td>12.841</td>
<td>1.873</td>
<td>1.184</td>
<td>0.725</td>
<td>0.735</td>
</tr>
<tr>
<td>110</td>
<td>16.155</td>
<td>1.653</td>
<td>1.033</td>
<td>0.683</td>
<td>0.659</td>
</tr>
</tbody>
</table>

### Table 2.4 Activation and pre-exponential factors for reactants and products.

<table>
<thead>
<tr>
<th></th>
<th>$E_a$</th>
<th>$\Delta H_{ad}$</th>
<th>Pre-exponential factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butylation of CAT</td>
<td>33.53</td>
<td>_</td>
<td>6.27x10⁵</td>
</tr>
<tr>
<td>Adsorption (CAT)</td>
<td>_</td>
<td>-14.23</td>
<td>1.88x10⁻²</td>
</tr>
<tr>
<td>Adsorption (TBA)</td>
<td>_</td>
<td>-26.99</td>
<td>2.05x10⁻⁴</td>
</tr>
<tr>
<td>Adsorption (4-TBC)</td>
<td>_</td>
<td>-10.13</td>
<td>2.81x10⁻⁵</td>
</tr>
<tr>
<td>Adsorption (water)</td>
<td>_</td>
<td>-14.03</td>
<td>7.98x10⁻¹</td>
</tr>
</tbody>
</table>

### 2.5 Regeneration of catalyst

In order to study the recyclability of the catalyst, the 15WZ- catalyst used in the first cycle was separated by filtration, washed with methanol and dried at 150 °C for 3 h and rerun with fresh reaction mixture. The methanol washed catalyst showed 38 % catechol conversion in 120 min and about 10% decrease in selectivity towards 4-TBC. The lower activity of the washed catalyst could be attributed to the presence...
of very strongly bound organic species on the surface of the catalyst. Further, we tried
to regenerate the catalyst by calcination at 500 °C for 4 h. There is a marginal
decrease in selectivity as compared to the fresh catalyst however the catechol
conversion decreased to 54 % in 120 min. The activity loss observed with the
regenerated catalyst can be attributed to partial loss of acid sites of the catalyst during
reaction/ regeneration [24].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Conversion of CAT</th>
<th>% Selectivity of 4-TBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>Recycled</td>
<td>38</td>
<td>89</td>
</tr>
<tr>
<td>Regenerated</td>
<td>54</td>
<td>96</td>
</tr>
</tbody>
</table>

**Table 2.5** Conversion and selectivity data for recycled and regenerated 15WZ catalyst.

### 2.6 Conclusions

By performing the catalytic activity evaluation and detailed physicochemical
studies using multiple analytical techniques, we have investigated the influences of
various loadings of WO$_3$ on ZrO$_2$ support for the catalytic activity and product
selectivity in catechol alkylation with t-butyl alcohol. From this reaction, 4-TBC is
obtained as the major product, and DTBC is obtained as a minor product. Both
compounds were verified by comparison with Aldrich standard 4-TBC, GC/MS and
$^{1}\text{H}$-NMR. The conclusions from the present results can be summarized as given
below:

1. We conclude that WO$_x$/ZrO$_2$ is highly active and selective catalyst for the
   alkylation of CAT with TBA to produce 4-TBC as compared to conventional
   liquid acids, zeolites, functionalized ionic liquids or clay-based porus
montmorillonite heterostuructures (PMH) solid acid catalysts that are reported in the literature so far.

2. The 15WZ catalyst, with very high specific surface area and good balance of acid strength and pore size distribution was found to be the most efficient with conversion and selectivity of 99% for the synthesis of 4-TBC.

3. The alkylation reaction of CAT with TBA is a typical example of Friedel-Craft acid-catalyzed electrophilic substitution reaction. Dehydroxylation of tert-butyl catechol by the acid sites of the catalyst leads to the formation of tert-butyl cation species. The butyl carbocation reacts mainly at the para-position of the CAT to form 4-TBC, trace amount of DTBC compound is produced by further alkylation of 4-TBC.

4. The LHHW surface reaction controlled kinetic model was developed based on the product distribution. The model was found to fit reasonably well with the experimental data. From the estimated adsorption and kinetic parameters, the energy of activation was evaluated and found to be 33.5 kJ/mol.

5. The catalyst could not be recycled or regenerated to give the same activity as the 1st cycle; the activity loss observed with both recycled and regenerated catalyst could be due to partial loss of acid sites of the catalyst during reaction/regeneration. Detailed microscopic, spectral and XRD studies would help in understanding the root cause for the deactivation of catalyst after single use.

References cited


24. Bordoloi, A.; Mathew, N.T.; Devassy, B.M.; Mirajkar, S.P.; Halligudi, S.B.

25. Sarish, S.; Devassy, B.M.; Böhringer, W.; Fletcher, J.; Halligudi, S.B.


