List of Figures

Figure 1.1: Various applications of TiO₂
Figure 1.2: Crystal structure of (A) Anatase titania, (B) Rutile titania and (C) Brookite titania
Figure 1.2a: Structure of rutile and anatase TiO₂
Figure 1.3: The multiple plots of powder XRD patterns of the titania sample scanned in air at various temperatures
Figure 1.4: TiO₂ pigment manufactured by the sulphate process
Figure 1.5: TiO₂ pigment manufactured by the chloride process
Figure 1.6: Schematic representation of sol-gel process
Figure 1.7: A typical autoclave used in hydrothermal synthesis
Figure 1.8: Schematic diagram of low pressure CVD
Figure 1.9: XRD spectra of (A) anatase titania (B) rutile titania
Figure 1.10: UV-Vis absorption spectra of anatase (A) and rutile (R) titania
Figure 1.11: TG-DTA curves of the TiO₂ precursor solution
Figure 1.12: N₂ adsorption-desorption isotherm and pore size distribution of synthesized TiO₂ sample
Figure 1.13: FTIR spectra of TiO₂ samples S1, S2 and S3
Figure 1.14: SEM images of synthesized TiO₂ samples (a) S1, (b) S2, (c) S3
Figure 1.15: HRTEM images of S1 (a) nanocubes and (b) corresponding lattice; (c) nanospheres and (d) corresponding lattice
Figure 1.16a: TPD CO₂ spectra of TiO₂ A2-pure anatase; R2-pure rutile
Figure 1.16b: TPD NH₃ spectra of TiO₂ A2-pure anatase; R2-pure rutile
Figure 1.17: High resolution XPS spectra of the Ti 2p region
(A = Anatase; R = rutile) 43
Figure 1.18: Raman spectra of (a) Degussa TiO2 and (b) anatase TiO2 45
Figure 1.19: Determination of point of zero charge by potentiometric
mass titration technique 47
Figure 1.20: Photoluminescence spectra of various TiO2 samples 51
Figure 1.21: TiO2 as a photocatalyst 54
Figure 1.22: Mechanism of TiO2 photocatalysis 56
Figure 2.1: X-ray diffraction profiles of synthesized TiO2 samples R2
(rutile + anatase mixed phase) and R3 (anatase) 83
Figure 2.2a: Raman spectra of R3a [TiCl3 (HNO3):Tu:Oa (1:4:1)] 86
Figure 2.2b: Raman spectra of R2a [TiCl3 (HNO3):Tu (1:4)] 86
Figure 2.3: TGA-DTA curves of the precursor for
R2 [TiCl3 (HNO3):Tu (1:2)] 88
Figure 2.4: SEM images of the TiO2 samples 89
R2 [TiCl3 (HNO3):Tu (1:2)], R2a [TiCl3 (HNO3):Tu (1:4)],
R3 [TiCl3 (HNO3):Tu:Oa (1:2:1)] and R3a
[TiCl3 (HNO3):Tu:Oa (1:4:1)]
Figure 2.5 (a): N2 adsorption-desorption isotherm of R2 90
Figure 2.5 (b): Pore size distribution of R2 90
Figure 2.6 (a): N2 adsorption-desorption isotherm of R2a 91
Figure 2.6 (b): Pore size distribution of R2a 91
Figure 2.7 (a): N2 adsorption-desorption isotherm of R3 91
Figure 2.7 (b): Pore size distribution of R3 91
Figure 2.8 (a): N2 adsorption-desorption isotherm of R3a 92
Figure 2.8 (b): Pore size distribution of R3a 92
Figure 2.9: IR spectra of R1[TiCl3 (HNO3)]; R2[TiCl3 (HNO3):Tu (1:2)]
and R3 [TiCl3 (HNO3):Tu:Oa (1:2:1)] 94
Figure 2.10: PZC plots of R1, R2 and R3

Figure 2.11: XPS spectra of Ti 2p, O 1s, N 1s and S 2p peaks of sample R2

Figure 2.12a: TPD profiles R2 and R2a

Figure 2.12b: TPD profiles R3 and R3a

Figure 2.13: IR spectra of adsorbed pyridine on R2 [TiCl\(_3\) (HNO\(_3\)):Tu (1:2)]

Figure 2.14: Absorption spectra of Titanium (III) solution (a) before hydrolysis (b) during hydrolysis (c) after hydrolysis

Figure 2.15: X-ray diffraction profiles of TiO\(_2\) samples synthesized by hydrolysis method.

Figure 2.16: TGA-DTA curves of the precursor for A5 synthesized by hydrolysis of TiCl\(_3\) in nitric acid medium at 60 °C

Figure 2.17: SEM images of the TiO\(_2\) samples A1, A2, A3 synthesized by hydrolysis method and Ald, commercial sample from Aldrich

Figure 2.18: TEM image of A8 synthesized by hydrolysis of TiCl\(_3\) in presence of HNO\(_3\) at room temperature

Figure 2.19a: N\(_2\) adsorption-desorption isotherm of A8

Figure 2.19b: Pore size distribution of A8

Figure 3.1: Diffuse reflectance spectra of synthesized titania samples R1 [TiCl\(_3\) (HNO\(_3\))], R2 [TiCl\(_3\) (HNO\(_3\))]:Tu (1:2)], R3 [TiCl\(_3\) (HNO\(_3\))]:Tu (1:2:1)], and Degussa P-25

Figure 3.2: EDAX elemental analysis of sample R2a [TiCl\(_3\) (HNO\(_3\))]:Tu (1:4)]

Figure 3.3: EDAX elemental analysis of sample R3a [TiCl\(_3\) (HNO\(_3\))]:Tu:Oa (1:4:1)]

Figure 3.4: TEM image of sample R3

Figure 3.5: TEM image of sample R3a

Figure 3.6: Particle size distribution of R3

Figure 3.7: Particle size distribution of R3a
Figure 3.8: PL emission spectra of titania samples R1, R2 and R3 128
Figure 3.9: Photocatalytic degradation profiles of the TiO₂ catalysts R1, R2 and R3 131
Figure 3.10: Time dependant UV-Vis spectra of MB in presence of sample R3 132
Figure 3.11: Comparative photocatalytic degradation profiles of hydrolysis synthesized sample A8, Degussa and Aldrich 134
Figure 3.12: UV-Vis spectra of congo red dye solution 136
Figure 3.13: UV-Vis absorption spectra of congo red dye in presence of catalyst R3 [TiCl₃ (HNO₃):Tu:Oa (1:2:1)] 137
Figure 3.14a: CR degradation profiles of various TiO₂ catalysts synthesized by hydrolysis of TiCl₃ 140
Figure 3.14b: Time dependant UV-Vis spectra of CR in presence of catalyst A8 140
Figure 4.1: XRD patterns of R1 [TiCl₃ (HNO₃)], R2a [TiCl₃ (HNO₃):Tu (1:4)], and R3a [TiCl₃ (HNO₃):Tu:Oa (1:4:1)] 149
Figure 4.2: N₂ adsorption-desorption isotherm and mesopore size distribution (inset) of the synthesized TiO₂ catalyst R3a [TiCl₃ (HNO₃):Tu:Oa (1:4:1)] 149
Figure 4.3: Epoxidation of cyclohexene catalyzed by synthesized TiO₂ samples and Degussa P-25 catalyst 152
Figure 4.4: Product distribution of catalytic epoxidation of cyclohexene 154
Figure 4.5: Product distribution of catalytic epoxidation of cis-cyclooctene 158
Figure 4.6: IR spectra of pyridine adsorbed on R3a 159
Figure 4.7: IR spectra of pyridine adsorbed on R1 161
Figure 5.1: XRD patterns of the ZnO-TiO₂ nanocomposites Z1 (10% ZnO), Z2 (20% ZnO), Z3 (40% ZnO), Z4 (70% ZnO) used for the benzylation reactions 171
Figure 5.2a: N₂ adsorption desorption isotherm of Z1 173
Figure 5.2b: Pore size distribution of Z1 173
Figure 5.3a: N₂ adsorption desorption isotherm of Z2
Figure 5.3b: Pore size distribution of Z2
Figure 5.4a: N₂ adsorption desorption isotherm of Z3
Figure 5.4b: Pore size distribution of Z3
Figure 5.5a: N₂ adsorption desorption isotherm of Z4
Figure 5.5b: Pore size distribution of Z4
Figure 5.6: Overlays of porosity profiles of various ZnO-TiO₂ composites
Figure 5.7: TEM image of sample Z4 70 % ZnO(TiO₂)
Figure 5.8: TPD profiles of various ZnO-TiO₂ catalysts (A - region of weak acid sites, B - region of medium strength acid sites, C – region of strong acid sites).
Figure 5.9: IR spectra of Z4, 70 % ZnO(TiO₂) with adsorbed pyridine
Figure 5.10: Conversion of toluene (wt%) vs reaction time over various catalysts
Figure 5.11: Selectivity patterns of the various catalysts toward the yield
Figure 5.12: X-ray diffraction pattern of Z4a
Figure 5.13: IR spectra of Z4a with pyridine adsorbed and heated at different temperatures and also without adsorbed pyridine
Figure 5.14: ¹³C NMR spectra of 4-methyl-4′-methoxy benzophenone (4,4′-MMBP)
List of Tables

Table 1.1: Comparative study of different phases of titania 6
Table 1.2: A brief literature status of TiO₂ synthesis using titanium alkoxide as precursor 22
Table 1.3: A brief literature status of TiO₂ synthesis using titanium trichloride as precursor 23
Table 1.4: A brief literature status of TiO₂ synthesis using titanium tetrachloride as precursor 24
Table 1.5: Literature status for synthesis of S-doped TiO₂ 27
Table 1.6: Literature status of epoxidation reactions on various catalysts 59
Table 1.7: Literature status of benzylation reactions on various catalysts 61
Table 2.1: TiO₂ synthesis using TiCl₃ and thiourea 79
Table 2.2: TiO₂ synthesis using TiCl₃, thiourea and oxalic acid 80
Table 2.3: Characteristic peaks of rutile and anatase TiO₂ 83
Table 2.4: Summarizes the crystal phase and Scherrer crystallite sizes of the samples as obtained from XRD 84
Table 2.5: Structural properties of the synthesized titania samples 93
Table 2.6: pH-pzc values of the synthesized samples 97
Table 2.7: Peak assignments of XPS spectra 99
Table 2.8: Total acidity of the synthesized samples 101
Table 2.9: TiO₂ synthesis by hydrolysis of TiCl₃ 106
Table 2.10: Synthesis of titania samples prepared by using aqueous solutions of TiCl₃ 109
Table 2.11: Synthesis of titania samples prepared by using aqueous solutions of TiCl$_3$ in nitric acid medium

Table 3.1: Catalysts synthesized by thiourea precursor method

Table 3.2: Catalysts synthesized by hydrolysis method

Table 3.3: The calculated band gaps of the prepared titania samples

Table 3.4: The pH-pzc values of the prepared titania samples

Table 3.5: Structural properties of synthesized TiO$_2$ samples

Table 3.6: Epoxidation of cyclohexene over various TiO$_2$ samples

Table 3.7: Epoxidation of cis-cyclooctene over various TiO$_2$ samples

Table 3.8: Activity of different catalysts for epoxidation of cyclohexene and cis-cyclooctene

Table 3.9: IR absorption frequencies following adsorption of pyridine on various catalysts

Table 4.1: Pre-optimized reaction conditions used for benzylation of different substrates

Table 4.2: Structural properties of the ZnO-TiO$_2$ composites

Table 4.3: Results of pore analysis of the synthesized ZnO-TiO$_2$ composites

Table 4.4: IR absorption frequencies following adsorption of pyridine on catalyst Z4

Table 4.5: Activity selectivity profiles of ZnO – TiO$_2$ composites for benzylation of toluene

Table 4.6: Activity selectivity profiles of ZnO – TiO$_2$ composites for benzylation of anisole
## List of Schemes

<table>
<thead>
<tr>
<th>Scheme 1.1:</th>
<th>Mechanism for the TiO$_2$/UV process</th>
<th>57</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheme 2.1:</td>
<td>A schematic diagram of the synthesis procedure</td>
<td>77</td>
</tr>
<tr>
<td>Scheme 2.2:</td>
<td>Reactor set up for temperature programmed desorption of ammonia</td>
<td>100</td>
</tr>
<tr>
<td>Scheme 3.1:</td>
<td>Chemical structure of Methylene Blue dye</td>
<td>129</td>
</tr>
<tr>
<td>Scheme 3.2:</td>
<td>Chemical structure of Congo Red dye</td>
<td>135</td>
</tr>
<tr>
<td>Scheme 4.1:</td>
<td>Epoxidation of Cyclohexene</td>
<td>150</td>
</tr>
<tr>
<td>Scheme 4.2:</td>
<td>Epoxidation of Cis-cyclooctene</td>
<td>155</td>
</tr>
<tr>
<td>Scheme 5.1:</td>
<td>Mechanism for the Friedel Crafts acylation of benzene</td>
<td>166</td>
</tr>
<tr>
<td>Scheme 5.2:</td>
<td>Reaction set up for benzoylation reactions</td>
<td>169</td>
</tr>
<tr>
<td>Scheme 5.3:</td>
<td>Reaction of toluene with $p$-toluoyl chloride</td>
<td>182</td>
</tr>
<tr>
<td>Scheme 5.4:</td>
<td>Reaction of anisole with $p$-toluoyl chloride</td>
<td>190</td>
</tr>
</tbody>
</table>