



# Novel mesoporous solid superacids for selective C-alkylation of *m*-cresol with *tert*-butanol

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## Abstract

*tert*-Butylated phenols, which are important precursors in a variety of industries, are usually manufactured by reacting phenol in the presence of liquid acid catalysts, with pure isobutylene or C<sub>4</sub> fraction from naphtha crackers containing isobutylene. These processes suffer from problems associated with the use of highly corrosive liquid acids and also the source of isobutylene. In the current study, alkylation of *m*-cresol was studied with *tert*-butyl alcohol (TBA) using sulphated zirconia and three novel superacidic catalysts, namely, UDCaT-4, 5 and 6. The new catalysts UDCaT-4, UDCaT-5 and UDCaT-6 are modified versions of zirconia. Amongst these, UDCaT-5, with 9% w/w sulphate content, was found to be the most active. Effects of different parameters such as, speed of agitation, catalyst loading, reactant ratio (mole ratio of *m*-cresol to that of TBA), effect of temperature and the recycle of catalyst are discussed. The conversion of *m*-cresol and the selectivity for mono C-alkylated product at a *m*-cresol to TBA mole ratio of 3:1, using 0.03 g/cm<sup>3</sup> UDCaT-5 at 120 °C under autogenous pressure, were 89% and 90%, respectively. The reaction was carried out without using a solvent to make the process greener and cleaner. The selectivity for the 2-*tert*-butyl-5-methylphenol was 93%. The reaction mechanism is discussed. A second order rate equation fits the data well. The apparent activation energy was determined as 9.04 kcal/mol.

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**Keywords:** Alkylation; *m*-Cresol; Mesoporic superacidic catalysts; UDCaT-4; UDCaT-5; UDCaT-6; Chlorosulphonic acid; Green process; Selectivity; 1-Cyclohexyloxybenzene

## 1. Introduction

Friedel–Crafts reactions, in general, are carried out using highly corrosive liquid acids, which pose loss of yield, corrosion of equipment and post-treatment pollution problems. Alkylation reaction of *m*-cresol with *tert*-butyl alcohol is an important reaction both in organic synthesis and chemical manufacturing. The alkylated *m*-cresols are used as raw materials for the manufacturing of a variety of resins, durable sur-

face coatings, varnishes, wire enamels, printing inks, surface-active agents, rubber chemicals, antioxidants, fungicides, petroleum additives, ultraviolet absorbers, and heat stabilizers for polymeric materials [1–3]. *tert*-Butylated phenols are generally prepared by reacting phenol with pure isobutylene gas or C<sub>4</sub> fraction of naphtha by using a liquid acid catalyst, giving wide product distribution. The use of highly corrosive and polluting liquid acids is a major environmental problem and therefore solid acids are much sought after. Both the formation of O- and C-alkylated products is possible depending on reaction conditions such as reaction temperature and type of catalyst used. Catalysts with strong acidic sites or reaction at high reaction temperature, typically over 80 °C, lead to the formation

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**Nomenclature**

A	TBA	$M$	mole ratio
$a_p$	surface area of catalyst (cm)	$r_i$	rate of reaction of species ' $i$ ' (mol/cm <sup>3</sup> s)
B	<i>m</i> -cresol	$R_p$	radius of catalyst particle (cm)
P	isobutene	$S$	vacant catalyst sites
$C_i$	concentration of species ' $i$ ' (mol/cm <sup>3</sup> )	$Sh_i$	Sherwood number of species $i$
$C_{V-Si}$	concentration of vacant sites of type ' $i$ '	$t$	time (min)
D	<i>tert</i> -butylated <i>m</i> -cresol	W	water
$D_e$	effectivity diffusivity (cm <sup>2</sup> /s)	$X_i$	conversion of species $i$
$D_{ij}$	diffusivity of ' $i$ ' in ' $j$ ' (cm <sup>2</sup> /s)		
$d_p$	diameter of catalyst particle (cm)		
E	di- <i>tert</i> butyl ether	<i>Subscripts</i>	
K	adsorption/mass transfer/reaction rate constant	SR	surface reaction
		T	total catalyst sites
		0	initial concentration

of C-alkylated products [4] while catalysts with weak acidic sites or reaction at low temperature lead to the formation of O-alkylated products [5,6]. 2-*tert*-Butyl-5-methylphenol is a precursor for a number of commercially important antioxidants and a light protection agent of the bisphenol and thiobisphenol type. 2-*tert*-Butyl-5-methylphenol is also used to prepare important UV absorber, and musk ambrette which is a perfume fixation agent [2]. Stevens [7] prepared *tert*-butylated *m*-cresol from isobutene as an alkylating agent with cresol:isobutene mole ratio of 0.7:1, whereas Gehlawat and Sharma [8] reported the same reaction by using H<sub>2</sub>SO<sub>4</sub> with a mole ratio of 1 where maximum yield of 80% was obtained. 2-*tert*-Butyl-5-methylphenol was also prepared by transbutylation of *m*-cresol with 4,6-di-*tert*-butyl-3-methylphenol at 80–100 °C in the presence of an acid treated clay with difficulty [9]. This isomer was also synthesized by controlled debutylation of 4,6-di-*tert*-butyl-3-methylphenol by heating with the phenolates of aluminium [10] and zirconia [11,12] (Table 1). There is a tremendous scope for devising a new catalytic process for the synthesis of *tert*-butylated cresols to replace conventional homogeneously catalyzed, highly polluting processes. Besides, due to the problems associated with unavailability, transportation and handling of isobutylene, particularly for usage in low-tonnage fine and speciality chemical industry (typically 10–100 TPA production), it is advantageous

to generate isobutylene in situ. Dehydration of *tert*-butanol is an attractive source for the same. Further, *tert*-butanol is available as a by-product in the ARCO process for propylene oxide which could be used effectively for this purpose. We have successfully carried out *tert*-butylation of several aromatic compounds by using *tert*-butanol, methyl-*tert*-butyl ether (MTBE) and isobutene as alkylating agents using ecofriendly solid acid catalysts [13–17]. The only problem which needs to be considered was activity and stability of solid catalysts in the presence of water. Our laboratory has been engaged in preparing several solid acid catalysts to make the processes environmental friendly by using them in industrially important reactions. In particular, sulphated zirconia has been extensively studied in a number of reactions [18–31] and it was believed that this solid superacid should be modified to bring in shape selectivity, mesoporosity and better acidity. Recently, we prepared novel solid superacids named as UDCaT-4, UDCaT-5 and UDCaT-6 which have found a great potential for industrially important reactions [29,32,33]. The acronym UDCaT symbolizes the University Department of Chemical Technology (UDCT), which is now renamed as University Institute of Chemical Technology (UICT), Mumbai. The work summarizes the investigation of activity and selectivity of these novel materials in alkylation of *m*-cresol with *tert*-butanol, including kinetics and mechanism.

Table 1  
Published literature on preparation of 2-*tert*-butyl-5-methylphenol

Reactants	Temperature, °C	Catalyst	Mole ratio	Conversion, %	Ref.
Cresol:isobutene	80	H <sub>2</sub> SO <sub>4</sub>	0.7:1	–	[7]
Cresol:isobutene	80	H <sub>2</sub> SO <sub>4</sub>	1:1	80	[8]
<i>m</i> -Cresol and 4,6-di- <i>tert</i> -butyl-3-methylphenol	80–100	Acid treated clay	–	–	[9]
4,6-Di- <i>tert</i> -butyl-3-methylphenol	280	Phenolates of aluminium and zirconia	–	–	[10–12]

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