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Friedel–Crafts green alkylation of xylenes with *tert*-butanol over mesoporous superacid UDCaT-5

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ABSTRACT

Friedel–Crafts green alkylation of xylenes with *tert*-butanol was investigated in the presence of mesoporous superacidic catalysts named as UDCaT-4, UDCaT-5 and UDCaT-6. The catalysts are modified versions of zirconia showing high catalytic activity, stability and reusability. The catalytic activity is in the order: UDCaT-5 (most active) > UDCaT-6 > UDCaT-4 > sulfated zirconia (least active). Synergistic effect of very high sulfur content present (9% (w/w) S) and preservation of tetragonal phase in UDCaT-5, in comparison with sulfated zirconia (4% (w/w) S), were responsible for higher catalytic activity. The performance of UDCaT-5 in alkylation of xylenes was studied with *tert*-butanol with reference to selectivity and stability. Alkylation of *m*-xylene over UDCaT-5 gives 96% conversion of *tert*-butanol with 82% selectivity towards 5-*tert*-butyl-*m*-xylene (5-TBMX) under optimum reaction conditions. The formation of products is correlated with the acidity of the catalyst. The reactions were conducted in liquid phase at relatively low reaction temperatures (130–160 °C). A systematic investigation of the effects of various operating parameters was done to describe the reaction pathway. The reaction was carried out without any solvent in order to make the process cleaner and greener. An overall second order kinetic equation was used to fit the experimental data, under the assumption that both xylene and *tert*-butanol are weakly adsorbed. An independent study of dehydration of *tert*-butanol (TBA) was also done. Alkylation of *o*-xylene and *p*-xylene with *tert*-butanol was also studied. The overall process is green and clean.

Keywords: Friedel–Crafts green alkylation; *tert*-Butyl xylenes; UDCaT-5; Sulfated zirconia; Green chemistry

1. Introduction

Aromatic alkylation processes normally require Friedel–Crafts acid catalysts such as $AlCl_3$, BF_3, $TiCl_4$, liquid HF, and $AlCl_3$ with elemental iodine (Olah, 1963; Olah et al., 1991). Several problems are associated with these catalysts such as toxicity, corrosiveness, low selectivity, and disposal of effluents (Clark and Macquarrie, 1997; Corma, 1995; Corma and Garcia, 2003). Relatively high concentration of catalyst is needed; often the amounts are more than stoichiometric making the reactions inherently polluting (Lorenc et al., 1992). Due to ever increasing societal, environmental, and economic pressure, efforts have been devoted to the development of environmentally friendly catalysts for the production of industrially important chemicals and intermediates (Sheldon and Downing, 1999; Sheldon and van Bekkum, 2001; van Bekkum et al., 1994; Wilson et al., 2000; Clark et al., 2000; Gracia et al., 2008; Yadav, 2005).

Alkylation of xylenes with *tert*-butanol (TBA) is an important reaction both in organic synthesis and chemical manufacturing. Some dimethyl alkylbenzenes have assumed practical significance. In particular, 1,2-dimethyl-4-*tert*-butylbenzene or 4-*tert*-butyl-*o*-xylene (4-TBOX) was proposed as the starting substance for the production of novel phthalocyanine pigments, plasticizers, photographic materials and other valuable products (Derfer and Derfer, 1978; Franck and Stadelhofer, 1988; Fiege et al., 1991; Isakov et al., 1996). *tert*-Butylated xylenes are usually manufactured by reacting xylenes in the presence of liquid acid catalysts, with pure isobutylene or C_4 fraction from naphtha crackers containing isobutylene, giving wide product distribution. These processes suffer from problems associated with the use of highly corrosive liquid acids and also the source of isobutylene. The development of a technologically efficient, highly productive and environmentally safe method for the synthesis of dimethyl-*tert*-butylbenzene

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