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Highly active and selective C-alkylation of *p*-cresol with cyclohexanol using *p*-TSA treated clays under solvent free microwave irradiation

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ABSTRACT

The efficiency of *p*-TSA treated clays was probed in the alkylation of *p*-cresol under solvent free microwave irradiation. The different aspects of the reaction studies include variation of temperature, duration of contact between the reactants, mole ratio of cresol to cyclohexanol and the clay treated with *p*-TSA to different extent. The acid strength as well as reaction parameters such as temperature and time were found to be the main factors controlling the reactivity and selectivity. The reaction was carried out in the temperature range 413–443 K. Lower temperature range favoured O-alkylation and higher temperatures yielded C-alkylated *p*-cresol. The catalyst retained its catalytic activity even after three consecutive runs. The results obtained with clays were compared with other solid acid catalysts such as aluminium exchanged clay, hydrochloric acid treated clay and K-10.

1. Introduction

Uses of synthetic fuels, polymeric materials and lubricating oils have been increasing day by day but these compounds undergo thermal degradation in the presence of heat, light, air and ozone. To protect them against such deterioration use of antioxidants has become increasingly important [1,2]. Alkyl phenols and their derivatives are widely used as antioxidants and multifunctional stabilizers and hence their synthesis becomes important. Organic synthesis using heterogeneous catalysts without any solvents is undoubtedly the best alternative method. Friedel–Crafts alkylation has been recognized as one of the most important tools for introducing an alkyl substituent into an aromatic ring [3–5]. Green chemical process for sustainable development always involves considerations such as use of cost-effective catalysts without any additives and employing a solvent free system. The concept of green chemistry and its applications in synthetic organic chemistry has been emerging as major route for the development of clean chemical synthesis. [6].

Very few catalysts have been used for the alkylation of phenol using cyclohexanol, such as cation-exchange resin KU-2, H-zeolite and other conventional Lewis and Brønsted acid catalysts [7]. However, the procedure followed produces many side products, is time consuming, and results in large amount of solvent waste. Hence environmentally friendly catalyst with solvent free alkylation in short intervals of time is a challenging task for modern organic synthesis. However, only few reports are available on the alkylation of phenols and cresols using cyclohexanol with environmentally friendly materials like clay catalysts. Compared to homogeneous catalysts, heterogeneously catalyzed methodologies based on expensive transition metals [8–11] and more recently an unmodified commercial magnetite catalyst have been proposed as alternatives. However reported protocols with these catalysts are generally energy intensive (24 h + for completion) having poor recyclability [12,13]. These disadvantages can be minimized by using solid acid catalysts such as zeolites [14], clays [15], ion exchange resins [16] and sulphated zirconia. Zeolites are recognized as shape selective catalysts particularly in the preparation of fine chemicals and chemical intermediates [12,17,18]. Montmorillonite clays are reported to be versatile catalysts for many organic transformations [19–21]. Clays can be modified in different ways in order to obtain the desired properties. Acid activation of bentonite is an important process for modifying the physical and chemical properties of the clay. Acid treated clays are prepared conventionally by treating the clay with mineral acids for several hours at elevated temperatures. Maximum activation of the catalyst was achieved in just 10 min with microwave heating. This is attributed to intensive, localized and uniform heating of reaction mixture by microwaves. Microwave irradiation processes not only decrease reaction time from hours to minutes, but also known to reduce side reactions, enhance yield and improve reproducibility [22]. The objective of this work was to study the effect of microwaves in the

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