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Isopropylation of 2-naphthol over mesoporous silicoaluminophosphate-37 (MESO-SAPO-37): the effect of bond dissociation energy on product distribution†

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The vapor phase isopropylation of 2-naphthol (2-NP) with isopropyl alcohol (IPA) in the presence of recently developed mesoporous silicoaluminophosphate assembled from a microporous SAPO-37 precursor (MESO-SAPO-37) was investigated. The bond dissociation energy calculation revealed that the reaction proceeds by *O*-alkylation followed by rearrangement into *C*-alkylated products. The presence of a phenolic hydroxyl group facilitates *o*- and *p*-directing (1- and 6-positions of 2-NP) and favors 1- and 6-isopropyl-2-naphthols as the major products. The moderately acidic MESO-SAPO-37 showed a maximum 2-NP conversion of 60% achieved with a selectivity of 60% for 6-isopropyl-2-naphthol (6-IP-2-NP) under optimum reaction conditions ($T = 250\text{ }^{\circ}\text{C}$, $\text{WHSV} = 9.4\text{ h}^{-1}$ and a 2-NP:IPA ratio of 1:20).

1. Introduction

Friedel–Crafts alkylation is one of the most studied and utilized reactions for C–C bond formation in organic synthesis.^{1–10} For example, the alkylated product of 2-naphthol (2-NP), namely the 2-substituted 2-naphthol derivative *viz.* 6-isopropyl-2-naphthol (6-IP-2-NP) was found to be an important intermediate in the synthesis of the anti-inflammatory drug naproxen.¹¹ Numerous studies have been reported on the Friedel–Crafts reaction, in both homogeneous and heterogeneous acid catalysis using catalysts such as sulfuric acid, *p*-toluene sulfonic acid, phosphoric acid, aluminum chloride, boric acid, and alumina-silica support, clay, zeolites, *etc.*^{1,8–10} However, the use of homogeneous catalysts results in a large number of side products, which require tedious workup to separate the products, and the disposal of the effluent, which poses severe environmental problems.^{1,9,10}

On the other hand, solid acid catalysts, mainly zeolite and zeolite-like molecular sieves, have shown immense potential for alkylation of aromatic compounds.^{12–27} For example, Sugi *et al.*¹² demonstrated that acidic sites present in the internal and external frameworks of SAPO-5 played an important role in the selectivity of 4,4'-DIPB (4,4'-diisopropylbiphenyl) for isopropylation of biphenyl.

The presence of acidic sites on external surfaces facilitates non-regioselective product distribution.¹² On the other hand, Davis *et al.* found that dealuminated Mordenite (MOR) is found to be more selective towards 4,4'-DIPB (90%).¹³ In similar reactions, the size of aromatic compounds, the alkylating agent, zeolite pore size, and strength of acidic sites determine the reaction mechanism and the deactivating nature of the catalyst system.^{14,15} In this regard different solid acid catalysts with various substrates^{12–16} have been explored, however only few reports are available on alkylation of naphthalene and their derivatives. Chu *et al.*¹⁷ studied isopropylation of naphthalene over different zeolites (USY, β -zeolite, Mordenite and ZSM-5). Among the various zeolites studied, the USY zeolite possessing a 3D-supercage is found to be ideal for better conversion and stability with less coke formation for the above-mentioned reaction. Later, Kulkarni *et al.*¹⁸ studied 1-naphthol alkylation with methanol over La and Mg modified Y zeolite and showed that alkali metals modified zeolites control the catalyst deactivation. Similarly, Yadav *et al.*¹⁹ studied the acylation of 2-methoxynaphthalene (2-MON) with acetic anhydride over ZSM-5, zeolite Y, Mordenite, aluminium pillared clay *etc.* It was observed that none of the catalysts were able to activate the 6-position of 2-MON. In 2-naphthol alkylation, Kirumakki *et al.*²² found that *O*-alkylated products are preferred in methylation over H-Beta, HY and HZSM-5 catalysts. The use of a bulky alkylating agent²³ *viz.*, tripropylene is found to be helpful in activation of the 6-position of 2-NP using various zeolites as catalysts owing to the steric hindrance generated by the alkylating agent. It was also demonstrated in the literature that aromatic compounds having a hydroxyl group (phenolic) kinetically facilitates *O*-alkylation,²⁵ which further isomerizes into a 1-alkylated

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