

Alkylation of naphthalene with isopropanol over a novel catalyst UDCaT-4: Insight into selectivity to 2,6-diisopropylnaphthalene and its kinetics

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Abstract

Numerous routes to 2,6-naphthalenedicarboxylic acid, a feedstock for high performance polyester polyethylene naphthalate, exist starting with the alkylation of an aromatic ring. However, the route beginning with naphthalenic compounds has an economic advantage because of reduction in the number of reaction steps to build the naphthalene ring. This has spurred a lot of interest in the shape selective dialkylation of naphthalene. Mono alkylation of naphthalene is simple, but its further shape selective dialkylation to 2,6-dialkylnaphthalene (2-DAN), is challenging. A variety of solid acid catalysts especially zeolites have been reported in studies to investigate the effect of acidity, pore geometry and shape selectivity in this reaction. However, the activity of most catalysts is susceptible to coke formation within a few hours of time on stream. It is in this perspective that we report the novelties of UDCaT-4, a synergistic combination of persulfated alumina and zirconia with hexagonal mesoporous silica, which exhibits tremendous stability, activity and selectivity in the vapour-phase isopropylation of naphthalene with isopropanol to 2,6-diisopropylnaphthalene (DIPN). It leads to better yields and selectivity in comparison with other catalysts reported in literature. A systematic investigation of the effects of various operating parameters was accomplished. Furthermore, a mathematical model was developed to describe the reaction pathway and the model validated with experimental results.

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Keywords: Alkylation; Naphthalene; Monoisopropylnaphthalene; Isopropanol; Heterogeneous catalysis; 2,6-Diisopropylnaphthalene; UDCaT-4; Persulfated alumina; Zirconia; Hexagonal mesoporous silica; Selectivity

1. Introduction

Alkylation of naphthalene with propylene or IPA has been successfully demonstrated by numerous research groups by using a variety of catalysts. H-mordenite, for instance, results in high selectivity but it suffers from severe deactivation and thus leads to low activity [1]. Proper dealumination of H-mordenite catalysts [1,2], increases the mesoporosity and also results in low acid density. Thus, selectivity of 2,6-DIPN is enhanced and its isomerisation and further polyalkylation are minimized. At 250 °C, H-mordenite resulted in 10% conversion and 6% DIPN selectivity, while its dealumination enhanced the conversion and selectivity to 27% and 11%, respectively [2]. Under similar conditions, 90% conversion and 40% DIPN selectivity were

obtained with USY [2]. Moreau et al. [3] investigated the influence of pore structure on the selectivity patterns at 473 K and concluded that HY zeolites exhibit high 2,6- and 2,7-DIPN selectivity of 41% at 95% conversion, compared to H-mordenite and H β which gave 6% and 3% selectivity at 19% and 28% conversion, respectively. Kamalakar et al. [4] concluded that lanthanum and potassium modified Y zeolite is a good catalyst with 81% conversion and 28% yield of 2,6-DIPN, since lanthanum promotes alkylation while potassium optimizes acidity and reduces coking. Anand et al. [5] adopted a multi-step temperature programmed steaming procedure to control the rate of dealumination of HY and they report an optimum acid site density and strength at 700 °C, wherein a conversion of 93% with 30% selectivity towards 2,6-DIPN was obtained. Maheshwari et al. [6] compared the isopropylation of naphthalene with the alkylation and selectivity behavior of HM, H β , HY and HZSM-5 with MCM-41 and reported that the

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Nomenclature

$[A_s]$	catalyst surface concentration of IPA (mol cm^{-3})
$[B_0]$	initial concentration of benzene (mol cm^{-3})
C_{Si}	concentration of vacant sites of type 'i'
C_{T-i}	total concentration of sites of type 'i'
D_e	effective diffusivity ($\text{cm}^2 \text{s}^{-1}$)
F_{A_0}	flow rate of IPA (mol h^{-1})
k_N	rate constant ($\text{cm}^3 \text{g}^{-1} \text{s}^{-1}$)
k_{SR_1}	second order reaction rate constant
K_{i-j}	adsorption constant for species 'j' on site of type 'i'
P_i	partial pressure of species 'i' (bar)
$-r_{\text{obs}}$	observed rate of reaction ($\text{mol g}^{-1} \text{s}^{-1}$)
R_p	radius of catalyst particle (cm)
W	weight of catalyst (g)
X_N	conversion of naphthalene

Greek letter

ρ_p	catalyst density (g cm^{-3})
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conversion follows the following trend: HY (max) > H β > HM \gg HZSM-5 > MCM-41 (min). Zhao et al. [7] investigated the immobilization of AlCl_3 on MCM-41 by selective silylation of the external surface of MCM-41. This process removes the external surface silanol groups, enhances surface hydrophobicity and significantly improves the stability of the catalyst compared to immobilization without surface modification. The selectivity towards 2,6-DIPN was enhanced by 10% at 200 °C with the surface modification compared to a simple incorporation of AlCl_3 over MCM-41. Kamalakar et al. [4] tested modified HMCM-41, HY and SAPO-5 catalysts and reported that HMCM-41 is best for the synthesis of 2,6-DIPN with a yield of 35 at 75% conversion.

Amongst solid acids other than zeolites, sulfated zirconia is the most extensively studied catalyst due to its superacidity [8]. However, some of the major problems associated with sulfated zirconia in its bulk form are its low efficiency due to low surface area ($\sim 100 \text{ m}^2/\text{g}$), rapid deactivation and relatively poor stability in reactions where water is generated as a co-product. The activity and stability of sulfated zirconia are improved by incorporating alumina and further treatment with ammonium persulfate (e.g. isomerization of *n*-butane) [9]. Supporting this mixed oxide (persulfated alumina zirconia) on hexagonal mesoporous silica (HMS) resulted in a new catalyst, UDCaT-4, a perfect blend of superacidic centers, high surface area and ordered mesoporosity. We have already tested the activity of UDCaT-4 in the benzylation of toluene with benzyl chloride [10] and in vapour-phase isopropylation of mesitylene with isopropanol [11]. Moreover, the stability and robustness of the catalyst have also been ascertained in presence of HCl and water respectively, formed as co-products in these reactions.

The current paper brings out the novelties of UDCaT-4 in the isopropylation of naphthalene with IPA, including development of a kinetic model.

2. Experimental

2.1. Chemicals

Isopropyl alcohol and cyclohexane (both HPLC grade) and naphthalene (AR grade) were procured from E. Merck (India) Ltd., Mumbai.

2.2. Catalyst preparation and characterisation

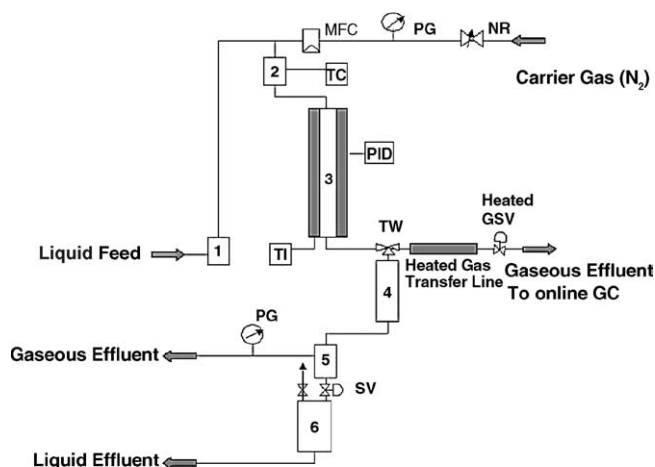
UDCaT-4 was synthesised by an established procedure developed in our laboratory and its full characterisation has been reported [10,11].

2.3. Experimental setup and reaction procedure

A downflow fixed bed hastelloy HC-276 reactor with 25.4 mm ID and 300 mm length at atmospheric pressure, equipped with an upstream vaporiser and downstream condenser, supplied by Chemito Instruments Pvt. Ltd., Mumbai, India was used for all experimental investigations (Fig. 1).

The liquid feed containing the desired proportion of naphthalene, IPA and cyclohexane as solvent was fed by a double piston pump (Well Chrom HPLC-pump K-120) to the vaporiser. The gaseous feed was transported to the reactor by using N_2 as a carrier gas at a known flow rate. In a typical run, 2 g of catalyst was charged to the reactor, packed in a layer of ceramic wool and supported by glass beads. The reactor was maintained under isothermal conditions during the isopropylation of naphthalene. The effects of various parameters, like mole ratio, WHSV, reaction temperatures and W/F_{A_0} were studied. A steady state was typically achieved within 30–45 min and the samples were collected typically after 1 h. Samples were condensed after the steady state and analysed by GC.

The samples were analyzed on a GC (GC1000 Chemito) equipped with capillary column of 0.22 mm \times 25 m and FID detector and confirmed by GC-MS.



1. Pump 2. Vaporiser 3. Reactor 4. Condenser 5. Phase Separator 6. Receiver

Fig. 1. Schematic flow diagram of fixed bed catalytic reactor.

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