

Combined Catalytic Activity of Cation-Exchanged Montmorillonite and Camphorsulfonic Acid in the Preparation of Cumene from Benzene and 2-Propanol

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Introduction

Montmorillonite clay belongs to smectite family and has an expandable layer structure of aluminosilicate. The layered structure facilitates the uptake of cations such as Zn²⁺, Al³⁺ and Fe³⁺. Cation-exchanged clays show high Bronsted acidity due to protons in the interlamellar zone formed by polarization of coordinated water molecules. Such clays can function as solid acid catalysts in organic reactions (Richard, 1992).

Cumene, the starting material for the industrial preparation of phenol, has been formed in 26% yield by alkylating benzene with isopropanol in the presence of Al³⁺-montmorillonite (Wijeratne *et al.*, 2006); isopropyl carbocation formed from isopropanol undergoes an electrophilic aromatic substitution reaction. With a view to improving the yield of cumene, we envisaged facile generation of isopropyl carbocation from an intermediate sulfonate ester, and examined the reaction of isopropanol and benzene in the presence of metal-cation-exchanged montmorillonite and camphorsulfonic acid.

Materials and methods

Preparation of catalyst

Na⁺-Montmorillonite clay (5 g) was stirred overnight with a 0.5 M solution of cation chloride (pH 3.5, 200 ml) to obtain Mⁿ⁺-montmorillonite clay catalyst (Mⁿ⁺ = H⁺, Na⁺, Zn²⁺, Cd²⁺, Cu²⁺, Al³⁺, Fe³⁺, Ce⁴⁺). The clay was then centrifuged and washed with distilled water repeatedly until washings showed negative test for chloride ions. The clay sample was then dried under ambient air for a week and ground to pass through a mesh of size 100. The clay samples were characterized using their XRD patterns and FT-IR spectra. The catalyst was activated at 150 °C for 2 h prior to the study of its catalytic activity.

Isopropylation of benzene

2-Propanol (50 mmol), benzene (100 mmol) and Mⁿ⁺-montmorillonite (0.5 g), 10-camphorsulfonic acid (0.5 g) were placed in a two necked flask equipped with a Dean-Stark apparatus. The reaction was maintained at reflux temperature for 48 h. The mixture was then allowed to reach room temperature and filtered to separate the clay catalyst. The filtrate was distilled under reduced pressure to collect the fraction containing cumene. The effect of reaction time, molar ratio of reactants and amount of catalyst on the yield of cumene was investigated. The product was characterized using an authentic sample of cumene (FT-IR, ¹H-NMR, gas chromatography).

Results

Effect of different catalysts on isopropylation of benzene

As expected, camphorsulfonic acid alone did not produce cumene from the reaction of benzene with isopropanol. However, the reaction mixture of camphorsulfonic acid, benzene, isopropanol and Mⁿ⁺-montmorillonite (Mⁿ⁺ = H⁺, Al³⁺ or Fe³⁺) furnished cumene in 60% yield; with Mⁿ⁺-montmorillonite (Mⁿ⁺ = Zn²⁺, Cu²⁺ or Cd²⁺) the yield was 50%. The reaction mixtures containing Na⁺ or Ce⁴⁺-montmorillonite did not produce cumene.

Effect of amount of clay catalyst

Isopropylation of benzene in the presence of camphorsulfonic acid was carried out with varying amounts of Al³⁺-montmorillonite (0.1–1.0 g). With small amounts (0.1 or 0.2 g) of the clay, the yield of cumene was 20%; with 0.3 g the yield increased to 40%. Cumene was isolated in 60% yield when 0.5 g or more (0.8, 1.0 g) clay catalyst was used.

Effect of reaction time

The highest yield (60%) of cumene was obtained when the reaction time was 40 h or more (50 h). At 10 h, 20 h and 30 h of reaction time, the yield of cumene was 0, 20% and 30%, respectively.

Discussion

Alkylation of benzene to provide alkyl benzene is generally carried out by a Friedel-Crafts reaction using an alkyl halide and a Lewis acid such as AlCl_3 , FeCl_3 , ZnCl_2 and SnCl_4 . Alkyl halides, their precursors and Lewis acids are hazardous to the environment. Industrial preparation of isopropylbenzene (i.e., cumene) employs high temperatures and pressures (250°C, 30 atm) in addition to Lewis acids/phosphoric acid. We have prepared cumene in 26% yield from isopropanol and benzene under mild conditions (80 °C, 1 atm) using the clay catalyst, Al^{3+} -montmorillonite (Wijeratne *et al.*, 2006).

In the present study, we observed that introduction of camphorsulfonic acid in catalytic amounts to the reaction mixture considerably increased the yield from 26% to 60%. M^{n+} -montmorillonite presumably catalyzes the initial formation of isopropyl camphorsulfonate from isopropanol and camphorsulphonic acid. The sulfonate group being a good leaving group, M^{n+} -montmorillonite readily generates the carbocation for subsequent isopropylation of benzene. In the latter step, camphorsulfonic acid is released. The absence of cumene in the

reaction mixtures containing Na^+ or Ce^{4+} -montmorillonite could be accounted for by the low polarizability of Na^+ ions and the oxidation of isopropanol by Ce^{4+} .

Conclusions

Cation-exchanged montmorillonite and camphorsulfonic acid serve as catalysts in the reaction of benzene and isopropanol to give cumene under mild conditions. Camphorsulfonic acid potentiates the catalytic activity of M^{n+} -montmorillonite enhancing the yield of cumene from 26% to 60% (with $\text{M}^{n+} = \text{H}^+$, Al^{3+} or Fe^{3+}) or 50% (with $\text{M}^{n+} = \text{Zn}^{2+}$, Cu^{2+} and Cd^{2+}). The clay catalyst is cheap and reusable and does not produce hazardous by-products in the reaction. Low temperatures and low pressures make this process not only eco-friendly but also economically viable.

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References

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