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p-Cymene preparation over modified montmorillonite clays

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Abstract

Toluene isopropylation is carried out over modified montmorillonite clays. Effect of ion exchange and pillaring on the catalytic activity and selectivity is noted. Elemental analysis results give the extent of metal incorporated. Enhanced porosity is evident from X-ray diffraction as well as surface area – pore volume measurements. ^{29}Si NMR shows the resonance for T (3Si, 1Al) units which shifts proportional to the amount of pillar metal present. Among the different modifications mixed metal oxide pillaring is found to be most effective in catalytic activity, *p*-cymene selectivity and lowering deactivation.

Keywords: Montmorillonite clays; Modifications; Toluene isopropylation; *p*-Cymene

1. Introduction

Catalyst reforming process produces toluene as a major product and is thus very abundant and of low price, thus the conversion of toluene to valuable products is of current interest [1]. Isopropylation of toluene produces *p*-cymene, which is an important intermediate used in pharmaceutical industries and for the production of fungicides, pesticides, as flavoring agent and as a heat transfer medium [2]. In many petrochemical plants, *p*-cymene is produced by alkylation of toluene with propene or 2-propanol over the Friedel – Craft's catalysts such as hydrochloric acid containing $AlCl_3$, BF_3 or H_2SO_4. However the use of these homogeneous acids gives rise to many problems regarding handling, safety, corrosion and treatment of the disposed catalyst. In addition, because the reagents are mixed with acids, separation of the products from the catalyst is often a difficult and energy consuming process. Solid acid catalysts solve this problem and are considered to be candidates for the alkylation catalysts [3–5]. The common heterogeneous catalysts used for *p*-cymene preparation are zeolites, mesoporous molecular sieves and mixed metal oxides.

Present study uses clays as catalysts. Clays are now widely used as catalysts due to its eco-friendly nature. Montmorillonite is a smectite type clay mineral that posses some unique properties such as cation exchange capacity, swelling and intercalation, which allow modifications to its structural as well as textural properties for efficient catalysis. The commonly used modification methods in clays are acid activation, cation exchange, intercalation and pillaring. Intercalation of organic moiety restricts the use of clays in high temperature reactions due to its thermal decomposition.

Here we are using acid activated montmorillonite KSF for gas phase toluene isopropylation reaction. The effect of ion exchange and single as well as mixed pillaring on the catalytic activity is studied. The cations of interlamellar space have no fixed sites in the lattice, when the mineral is immersed in an electrolyte; exchange readily takes place according to the principle of equivalence between the external and internal cations [6]. It has been realized that metal exchanged clay minerals possess catalytic potentialities in their own right as an acid and redox catalyst without any additional treatment [7]. In the present work cation exchange is done using Na^+ ions. Pillared clays are smectite clay minerals that have been modified through the introduction of large inorganic polyoxocations into their interlayer regions. The resultant materials, after calcination,

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contain oxide pillars capable of preventing the collapse of the interlayer spaces. This generates a micro porous structure, a high specific surface area and the presence of acid centers both on the surface of the layers and on their pillars, which makes these materials suitable for use as adsorbents and catalysts [8–11]. Thus pillaring transforms the clays to thermally stable structure suitable for high temperature reactions.

The enhanced porosity upon pillaring allows shape selective catalysis inside the pores that avoids higher substitution, which leads to bulkier products. Among the ortho, meta and para products, in the present work at optimized conditions, pillared clays result only in ortho and para where para is the major product. The high para selectivity may be due to lower steric hindrance and kinetic diameter. Present study evaluates the influence of different modifications on montmorillonite clays for high temperature reaction. We are using acid activated montmorillonite clay as the parent clay on which ion exchange is done with Na^+ ions. Alumina and chromia single as well as mixed pillaring is also done. The influence of different parameters such as WHSV, temperature and reactant molar ratio on the activity is studied in detail. The effect of different clays on the conversion and selectivity is noted.

2. Experimental

2.1. Catalyst preparation

Montmorillonite KSF (Aldrich) is used for modifications. Na^+ ion exchange is done by treatment with 0.5 M sodium nitrate (Merck) solution at 343 K for 24 h, then filtered, made nitrate free by washing and is dried at 383 K. Pillaring is done on the Na^+ exchanged clay. 0.2 M solution of Chromium nitrate (CDH) was partially hydrolyzed by drop wise addition of 0.3 M sodium carbonate (Sd Fine Chemicals Ltd.) solution with a base to metal ratio of 2 under vigorous stirring for 2 h at 368 K and is again stirred at the same temperature for 6 h. This pillaring solution is then added to the previously swelled sodium exchanged montmorillonite clay with a metal to clay ratio of 10 mmol/g clay. The solution is stirred at 343 K for 24 h, kept overnight, filtered and is washed free of nitrate ions. Drying at 383 K and calcination at 773 K for 5 h leads to chromia pillared montmorillonite. Alumina pillaring adopts the same method as above using aluminium nitrate (Sd Fine Chemicals Ltd.) solution, but here the pillaring solution is prepared at 343 K.

For mixed pillared system 5 mmol of each pillaring solution is mixed to give total of 10 mmol metal/g clay. Further treatments are the same as that for single pillared clays. All the systems are calcined at 773 K for 5 h. Montmorillonite KSF is designated as M, sodium exchanged one as NM, chromia pillared clay as CM and alumina pillared system as AM. The mixed pillared systems are designated as ACM, where as C stands for chromia and A for alumina pillars to give the corresponding mixed pillared clay.

2.2. Characterization of the catalysts

The as-synthesized ion exchanged and pillared clays are characterized using various techniques to know the structural modifications of montmorillonite.

The X-ray diffraction pattern of the catalysts is obtained using a Rigaku D MAX III VC Ni-filtered Cu Kα radiation ($\lambda = 1.5404$ Å at a scan rate of 4°/min). A Micromeritics Gemini 2360 surface area analyzer is used to get the BET surface area with N_2 adsorption at liquid N_2 temperature (77 K). Elemental analysis of prepared catalysts was done using inductively coupled plasma – atomic emission spectrometer after the separation of silica using HF ('GBC' Plasmalab 8440 M instrument). Solid-state ^{29}Si NMR experiments were carried out over a *Brucker DSX-300* spectrometer at resonance frequency of 59.63 MHz.

2.3. Catalytic activity

Toluene (Qualigens) and isopropanol (Qualigens) are used as received. The catalyst was activated at 773 K for 2 h before subjecting to the reaction. Toluene alkylation is carried out at atmospheric pressure in a fixed bed, vertical, down- flow glass reactor placed inside a double-zone furnace under a continuous flow of nitrogen. Exactly 0.5 g of the sample is sandwiched between the layers of inert silica beads. A thermocouple detector monitors the temperature of the catalyst. The reactants are fed into the reactor by means of a syringe pump (Cole Palmer®) at required WHSV, molar ratio and temperature. The products and the unreacted reactant were condensed by means of a water condenser and are trapped in an ice bath. The liquid samples are collected and subjected to Gas Chromatographic analysis using Chemito GC 1000 gas chromatograph with BP1 capillary column connected to a FID detector. The isopropanol conversion and product selectivity (weight percentage) are noted.

3. Results and discussion

3.1. Catalyst characterization

XRD patterns of different systems in Fig. 1 clearly shows that an appreciable shift to 2θ values of the (1 0 0) plane from ~9° towards left is there on pillared clays and is found to be absent upon ion exchange. The increased d-spacing, i.e. the enhanced interlayer distance is obtained using Bragg equation. Kloprogge [12] reported that pillared smectites are clays with high permanent porosity obtained by separating the clay sheets by a molecular prop or pillaring agent. Pillaring and thus the increased porosity are evident from the shift of 2θ values towards left and the corresponding drastic increase in d-spacing. Mixed pillaring shows maximum d-spacing, surface area and pore volume. The data is given in Table 1. Mixed pillaring is thus more efficient in propping apart the clay layers [13]. Fig. 1 shows the presence of very small amount of unex-