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Preparation, characterization and catalytic activity of titania pillared montmorillonite clays

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Abstract

Titania pillared clays are prepared through a novel method using titania sol via colloidal route as the pillaring agent. Formation of pillared clay (PILC) is proved from the physico-chemical characterization using X-ray diffraction (XRD), surface area–pore volume measurements, thermogravimetric analysis (TGA), infrared (FTIR) spectroscopy and elemental analysis (ICP-AES). The acidity of the catalysts is measured from temperature-programmed desorption (TPD) of ammonia. Ethylation of benzene with ethanol is carried out in gas phase to test the catalytic activity. Good correlation is obtained with alkylation activity and acidity. Enhanced porosity upon pillaring allows shape selective catalysis within the pores to get ethylbenzene as the only product.

Keywords: Montmorillonite clays; Ti-pillaring; Benzene ethylation; Ethylbenzene

1. Introduction

Pillared clays (PILCs) are two-dimensional zeolite-like materials prepared by exchanging charge compensating cations between the clay layers with large inorganic metal hydroxycations, which are oligomeric and are formed by hydrolysis of metal oxides or salts [1]. After calcination, the metal hydroxy cations are decomposed into oxide pillars that keep the clay layers apart and create interlayer and interpillar spaces, thereby exposing the internal surfaces of the clay layers. Baes and Meisner, Burch, etc. had reported that, in principle, any metal oxide or salt that forms polynuclear species upon hydrolysis can be inserted as a pillar [1–5].

Compared to other porous solids, pillared clays demonstrate their advantage in several aspects. First, clays are abundant material and pillared clays are generally synthesized under moderate conditions with much simple procedures compared to zeolite synthesis [6,7]. Another feature is that some pillared clays have pore openings of about 1 nm or even larger [6], being much larger than those in zeolites (0.3–0.7 nm) [7]. So PILCs have a potential to serve as molecular sieves and shape selective catalysts for a wide range of molecular sizes. Furthermore, multiple components like transition metals and rare earth elements can be readily introduced into PILCs by intercalating clays with mixed pillars of oxides [5,8,9].

Ti-PILC has a considerably larger interlayer spacing in comparison with other metal oxide PILCs and shows high adsorption ability [10–17]. Thus, titania pillars are very useful in designing shape selective catalysts. In general, two different methods to create Ti complexes suitable for pillaring processes were reported in the literature. The first method to form Ti complexes in solution is the addition of $TiCl_4$ to 5 or 6 M HCl followed by dilution with distilled water and ageing from 3 h up to as long as 20 days prior to their use as pillaring agents [12,18,19]. Drawbacks of this preparation route are the highly acidic conditions one has to work in, resulting in leaching of Al and Si from the clay structure [13,19] and the requirement of careful handling of the $TiCl_4$. The second route is based on the hydrolysis of various Ti alkoxides under much milder acidic conditions [20–25]. Both these precursors should be carefully treated

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during sol preparation to avoid prior hydrolysis by moisture that lead to the hydroxide formation. XRD patterns of some Ti-PILCs [26,25] show a relatively large amount of unexpanded clay. This portion may consist of either unreacted clay or clay exchanged with some types of monomeric Ti species. Valverde et al. [27] reported that there are two 2θ values corresponding to the (1 0 0) plane due to different pillar species present. Another drawback of titania pillaring precursors is their high cost and difficulty in laboratory preparation from raw titania. Other metal PILCs mainly use inorganic salt precursors for pillaring agent preparation [28–33] and up to now there are no reports on Ti-PILCs that use inorganic salt precursors other than $TiCl_4$. Thus, the use of other inorganic precursors in pillaring agent preparation is promising.

The main aim of the present work is to prepare Ti-PILC via a cheap route, compared to the existing methods; using a cheap precursor and mild conditions. The precursor used for the preparation of the pillaring solution is the cheaply available titanyl sulphate, $TiOSO_4$. This precursor is found to be stable in air and moisture which allows rough handling. PILCs with different physico-chemical properties have been prepared by using ultrasonic techniques [34] and microwave conditions [35]. Here we report a simple, easy methodology for Ti-PILCs, suitable for shape selective organic transformations.

The catalytic activity of the pillared clay is evaluated for ethylation of benzene to give ethylbenzene, the important raw material in the petrochemical industry for the manufacture of styrene, which is a widely used industrial monomer. Worldwide capacity of ethylbenzene production is about 23 million metric tons per year [36]. Conventionally ethylbenzene is produced by benzene alkylation with ethylene using homogeneous mineral acids such as aluminium chloride or phosphoric acid as catalysts that cause a number of problems concerning handling, safety, corrosion and waste disposal. Society now demands alternative eco-friendly catalysts, which make clays, zeolites, and other solid acid catalysts important. Clay-based catalysts have been extensively studied for alkylation of hydrocarbons [34,35,37–40]. The present work makes use of ethanol and benzene for the selective formation of ethylbenzene on titania pillared montmorillonite.

2. Experimental

2.1. Materials

Pillaring is done on montmorillonite KSF (Aldrich). Prior to pillaring, KSF is treated with 0.5 M sodium nitrate (Merck) solution at 70 °C for 24 h, then filtered, made nitrate free by washing and is dried at 110 °C to get the sodium-exchanged montmorillonite. Treatment with sodium nitrate replaces the exchangeable cations Ca^{2+}, K^{+}, Fe^{3+}, H^{+}, etc. present between the layers i.e. when the mineral is immersed in an electrolyte, exchanges governed by the principle of equivalence will take place between the external and internal cations. Titania pillaring agent is prepared using the method reported by Sivakumar et al. [41]. Titanyl sulphate (M/s Travancore Titanium Products, Trivandrum, India, 99% purity) is used as a precursor for the synthesis of titania sol. In a typical experiment, titanyl sulphate is dissolved in 500 ml of distilled water (0.2 M) and is hydrolyzed by slow addition of ammonium hydroxide (10%, S.D Fine Chemicals Ltd.) solution under constant stirring at room temperature, until the reaction mixture attained a pH of 7.5. The precipitate obtained is separated by filtration and is washed free of sulphate ions with distilled water. The precipitate is further dispersed in 1 l of hot distilled water and is peptized by the addition of 10% HNO_3 (Merck) solution to get titania sol at around a pH of 1.6. This pillaring solution is then added to the previously swelled 1% suspension of sodium-exchanged montmorillonite clay in distilled water, with a metal to clay ratio of 10 mmol/g. The solution is stirred at 70 °C for 24 h, kept overnight, filtered, washed free of nitrate ions, dried at 110 °C and calcined at 500 °C for 5 h to get titania pillared montmorillonite. Montmorillonite KSF is designated as M; sodium exchanged one as NM and titania pillared clay as TM. For comparison of physico-chemical properties and catalytic activity studies, both M and NM are also calcined at 500 °C for 5 h.

The pillaring solution precursor can be prepared by dissolving partially hydrated titania or metatitanic acid $TiO(OH)_2$ (M/s Travancore Titanium Products, Trivandrum, India, 98% purity) in hot concentrated H_2SO_4 (Merck). It is then diluted and filtered to get the yellowish titanyl sulphate, $TiOSO_4$ (0.2 M).

2.2. Characterization techniques

The X-ray diffraction pattern of the catalysts is obtained using a Rigaku D MAX III VC Ni-filtered Cu K alpha 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_2adsorption at liquid N_2 temperature (77 K). The catalysts are heated at 400 °C for 3 h under a flow of nitrogen before running the analysis. The *t*-method of de Boer et al. [42] is used to calculate the micropore volume and external surface area of the catalysts. The difference between the BET surface area and the external surface area gives internal surface area, i.e., the surface area from pores. Mesopore volume is obtained by subtracting micropore volume from the total pore volume. The mean pore width is obtained from the relation $d_m = 2V/A$, where V is the pore volume and A is the internal surface area [43]. Elemental analysis of prepared catalysts is done with inductively coupled plasma-atomic emission spectrometer after the quantitative separation of silica using HF. Analysis is done using 'GBC' Plasmalab 8440M instrument. TG analysis of the dried samples is performed in a Perkin–Elmer Pyris Diamond thermogravimetric/differential thermal analyzer by heating the sample at a rate of 20 °C min^{-1} from room temperature