



Research paper

Acid activation effect on the catalytic performance of Al-pillared bentonite in alkylation of benzene with olefins



Hossein Faghihian ^{a,*}, Mohammad Hadi Mohammadi ^b

^a Department of Chemistry, Shahreza Branch, Islamic Azad University, P.O. Box 311–86145, Shahreza, Isfahan, Iran

^b Department of Basic Science, Zawul Institute of Higher Education, Post Box 21258, Kabul, Afghanistan

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ABSTRACT

In this research pillared catalysts were prepared by pillaring of bentonite and acid-treated bentonite with aluminum. The synthesized samples were characterized by X-ray diffraction, FT-IR spectroscopy, N₂ adsorption isotherms, NH₃ temperature programmed desorption, scanning electron microscopy (SEM) and elemental and thermal analysis techniques. Acid-treated sample contained lower Al content compared to the untreated sample, but its total pore volumes (TPV) and BET surface area was higher. Alkylation of benzene with linear olefins (1-decene and 1-dodecene) was studied with the prepared catalysts. Acid-activated pillared catalyst, due to its higher surface acidity showed enhanced catalytic activity compared to the untreated sample. The catalysts activity was also enhanced by increasing benzene to olefin molar ratios and reaction temperature. The catalysts showed higher activity when shorter chain hydrocarbon olefin was used. In acid-activated pillared catalysts higher selectivity for 2-phenyl isomer was obtained with 1-dodecene.

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1. Introduction

Alkylation of aromatic hydrocarbons with olefins is an important industrial process for production of linear alkyl benzenes which is the key essential reagent for preparation of synthetic detergents. Alkylation reaction traditionally is catalyzed by aluminum trichloride or hydrofluoric acid. Because of the hazardous nature of the system, there is a need to develop solid acid catalysts to replace the existing production catalyst. Solid acids such as zeolites (Craciun et al., 2007; De Almeida et al., 1994; Yuan et al., 2002), clays (Awate et al., 2004; Borutskii et al., 2007; Guerra et al., 2008), have been studied as alkylation catalysts. By use of acid catalysts, generally high conversions are obtained but the product range is wide. Depending on the properties of catalyst, even with 1-olefins, by branching and double bond isomerization of olefins all mono-alkylated isomers are formed. Other by-products may be formed by poly-alkylation, isomerization and oligomerization of olefins (Craciun et al., 2007). Knowledge of the influence of different experimental parameters on the products range offers an important tool for development of more efficient catalytic processes.

Over the past decade, considerable attentions have been focused on clays as catalyst and catalyst supports because of their porosity, reactivity and thermal stability. Acid-treated montmorillonite was the catalyst

commonly used for initial cracking reactions in the 1930s (Thomas and Thomas 1997). Pillared interlayered clays (PILC) were used to optimize the catalytic cracking of crude oil. Catalysts with larger pore size and good hydrothermal stability were suggested to increase the yield of lighter fractions from heavy crude oil (Ding et al., 2001; Frost et al., 1998; Klopogge, 1998). Katikaneni et al. (1995) used Al-PILC to convert canola oil to fuel using a fixed bed reactor.

Although the clays have shown considerable activity in their raw form, but to improve their activity some chemical and thermal activation steps are needed (Lagaly et al., 2013). PILC prepared with inorganic polycations have high thermal stability, good rigidity, uniform micropores and excellent acidity and provide wide opportunities to be used as solid acid catalysts for variety of organic transformations (Gopal Mishra and Ranga Rao, 2004). The number of ionic precursors and thus the number of pillars introduced in clay depend on the cation exchange capacity (CEC) of the parent clay. Montmorillonite is currently used as a catalyst material because of its relatively high CEC and its potential to modify the interlayer distance by replacing of initial cations. Metals commonly used as ionic precursors are Al, Zr and Ti (Vicente et al., 2013). Aluminum is commonly used as Keggin ion $[(Al_3O_4(OH)_{24}(H_2O)_{12}]^{7+}$ but other mono and polynuclear species may be present depending on the pH of the solution (Benito et al., 1999).

Acid activation of montmorillonite before the pillaring step strongly influences the performance and activity of the clay and produces new material with physicochemical properties intermediate between those of conventional pillared clays and acid-activated clays (Komadel and Madejova, 2013; Vicente et al., 2013). The aim of this work is to

* Corresponding author. Tel.: +98 321 3292515, +98 3117932700; fax: +98 321 3291018, +98 3117932700.

E-mail address: Faghihian@iaush.ac.ir (H. Faghihian).

investigate the effect of acid-activation process on the performance of aluminum-pillared bentonite (AIPBent) in alkylation of benzene with long chain [C₁₀, C₁₂] olefins.

2. Experimental

2.1. Techniques

Chemical composition of the samples was determined by XRF method using Bruker S4 PIONEER (Germany) equipment. The CEC of the samples was measured with 0.01 M copper ethylenetetramine solution (Ammann et al., 2005). The crystallinity and structural changes of the samples were examined by X-Ray Diffraction (XRD) technique by a Bruker D8 ADVANCE, P4 PIONEER diffractometer (Germany). FT-IR spectra were prepared by JASCO, FT-IR-6300 spectrometer (Japan) with standard mid-IR DTGS detector. FT-IR spectra were recorded in the range of 400–4000 cm⁻¹ with KBr pellets technique. The BET surface area and total pore volume of the catalysts were determined by N₂ adsorption isotherms prepared by BELsorp max 113, Japan, Inc. system.

The micropore volumes (V_μ) of the samples were obtained from the *t*-plot method (Lippens and de Boer, 1965). Temperature programmed desorption (TPD) profile of ammonia was used to evaluate the surface acidity of the samples by a Micromeritics TPD/TPR 2900 instrument equipped with a thermal conductivity detector (TCD). Approximately 0.25 g of the sample was activated under helium flow at 300 °C for 1 h and then ammonia was passed over the sample at 100 °C for 30 min. To remove the adsorbed ammonia, helium was purged to the samples at the same temperature for 1 h. The TPD profiles were obtained from 100 to 550 °C with heating rate of 10 °C min⁻¹. Loss on ignition of the samples was calculated by the thermal curves taken by a Mettler, TG50 Thermal Analyzer from 25 to 900 °C under nitrogen atmosphere. Scanning electron microscopy (SEM) images were prepared by Philips XL SERIES, XL30 (Germany) system to examine the morphology of the samples.

2.2. Chemicals

Bentonite was purchased from Sigma-Aldrich (CAS-No. of 1302-78-9). H₂SO₄ (95–98%), KBr, CuCl₂, ethylenediamine, NaOH, aluminum chloride (AlCl₃, 6H₂O, 99%), 1-decene and 1-dodecene were prepared from Merck Company. Benzene (99%) was obtained from Bandar Imam Petrochemical Company (B.I.P.Co.), Iran. All chemicals were research grade and used as received without further purification.

2.3. Synthesis of acid-activated pillared samples

The starting material was sodium bentonite (particle size ≤ 2 μm, CEC of 74 meq/100 g). Two acid-activated samples were prepared by treating bentonite with 2 M and 4 M H₂SO₄ according to the procedure described by Falaras et al. (2000). The samples were designated as A2Bent and A4Bent respectively. Pillared samples were prepared by the method reported by Chae et al. (2001). Appropriate amount of pillaring solutions (aluminum hydroxyl-oligomeric solution, OH/Al molar ratios of 2), required for the Al/clay ratio of 25 (mmol Al/g clay) was added slowly to 1.0 liter of distilled water containing 10 g of the sample (parent and acid-activated bentonite). The final product was dried at 110 °C and calcined at 300 °C. Pillared bentonite was designated as AIPBent and the pillared samples prepared by acid-activated bentonite (A2Bent and A4Bent) were designated as A2-AIPBent and A4-AIPBent respectively.

2.4. Catalytic activity of the samples

The catalytic activity of the synthesized samples was tested in a 100 ml stainless still reactor containing 0.3 g of calcined catalysts. The molar ratios of the reactant and the temperature were adjusted and the mixture was stirred for 270 min. Alkylation products were analyzed by FISIONS GC 8000 series gas chromatograph with a DB-17 capillary column coupled to a flame ionization detector.

3. Results and discussion

3.1. Catalyst characterization

Bentonite has many industrial applications and montmorillonite is its principal constituent. It has interlayered cations with weak bonds. These cations are easily exchangeable, causing swelling of the structure. As a result, the opening of the layer permits exchange of the existing cations with bigger cations, such as polyhydroxocations (Sapag and Mendioroz, 2001). The chemical composition of the bentonite obtained by XRF method revealed that the framework cations were mainly Al³⁺, Fe³⁺ and Mg²⁺ and Na⁺, K⁺ and Ca²⁺ were exchangeable interlayer cations (Table 1). The effect of acid-activation on the structural and textural modification was studied by different techniques including chemical analysis, XRD, FT-IR, SEM, CEC and surface area measurements.

By acid-treatment, the interlayer cations were replaced by H⁺ ions followed by dissolution of octahedral aluminum and subsequent dissolution of the structural cations. Tetrahedral silica of the structure was not dissolved at low acid concentration, while the octahedral layer

Table 1
Physicochemical properties of samples.

Catalyst	Concentration (mass%)					
	Bentonite	AIPBent	A2Bent	A4Bent	A2-AIPBent	A4-AIPBent
SiO ₂	58.27	54.32	60.3	61.67	56.98	56.12
Al ₂ O ₃	20.53	25.12	18.66	18.23	23.24	24.09
Fe ₂ O ₃	3.75	3.45	3.34	3.26	3.03	3.12
MgO	2.24	1.78	1.67	1.65	1.45	1.55
Na ₂ O	2.10	0.22	0.23	0.28	0.20	0.20
CaO	1.37	0.18	0.47	0.23	0.08	0.08
K ₂ O	0.38	0.26	0.32	0.33	0.29	0.29
LOI ^a	10.24	14.51	14.48	13.97	14.36	14.13
CEC ^b (meq/100 g)	74.73	21.18	68.21	67.47	23.01	20.15
S _{BET} (m ² /g)	34	265	129	127	296	278
TPV ^c (cm ³ /g)	0.123	0.198	0.270	0.269	0.298	0.299
V _μ ^d (cm ³ /g)	–	0.112	–	–	0.155	0.135
d ^e (001) (Å)	11.86	18.69	12.27	11.78	18.21	18.31
Acidity (meq NH ₃ /g)	0.04	0.68	0.78	0.87	0.96	1.42

^aLoss on Ignition determined by DTG method, ^bMeasured by adsorption of copper ethylenetetramine, ^cTotal pore volume at a relative pressure of 0.99, ^dMicropore volume obtained from the *t*-plot method, ^eBasal spacing obtained by XRD.

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