Methanolysis of Styrene Oxide over Iron Pillared Clay

Wimonrat Trakarnpruk* Tanawat Tittabut
Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University,
Bangkok 10330
Tel: 0-2218-7672. E-mail: wimonrat.t@chula.ac.th

Abstract

Iron pillared bentonite clay (12.0% Fe_2O_3) was synthesized and characterized by XRD, nitrogen adsorption, chemical composition and thermogravimetric analysis. The Fe pillared bentonite clay was an active catalyst in the methanolysis of styrene oxide due to its Lewis acidity. Under the reaction conditions: 50.0 mg of catalyst; 1 mmol of styrene oxide; 2 mmol of methanol and 5 ml of CH_2Cl_2 (solvent), 2-methoxy-2-phenylethanol (95%) was produced after 30 min reaction time at 55°C. The relative activity in alcoholysis of styrene oxide dropped significantly with increasing steric bulkiness of the alcohol. The catalyst was found to be recyclable four times with no loss of activity.

Keywords : Iron, pillared, Bentonite clay, styrene oxide

1. Introduction

The demand for environmentally clean reactions has attracted considerable attention by replacing homogeneous, polluting and corrosive acid catalysts by heterogeneous systems. In recent years, clays have been widely used in organic transformations [1]. The main reason is the large variety of clays and the ease with which these materials can be modified. Besides, clays are cheap, non-corrosive and recyclable.

Bentonites constitute one of the most abundant smectitic clays in nature which possess a sandwich structure of tetrahedral–octahedral–tetrahedral aluminosilicate lamellas formed by condensation of an octahedral Al_2O_3 (or MgO) between two tetrahedral (SiO_2) layers [2]. The interlayer cations are exchangeable, thus, allowing modifications of the acidic nature of the material. Careful calcination of the exchanged clay leads to interesting materials with permanent microporosity across a range of molecular sizes. They are reported as Pillared Inter-Layered Clays (PILCs) [3]. By heating temperature greater than 300°C, the intercalated metal hydroxy cations undergo dehydration and dehydroxylation and are converted to metal oxide (e.g. Al_2O_3, TiO_2, and Fe_2O_3) clusters acting as pillars to prop the clay layers apart, thus creating a stable microporous system in the interlamellar space of clay particle. Many reactions involving unmodified, ion-exchanged as catalyst have been described: ring-opening of epoxidized methyl oleate [4], Mukaiyama aldolysis of aldehydes [5] formation of acetoamido ketones [6]. Iron-exchanged montmorillonite was reported in the acylation of sulphamides with anhydrous carboxylic acids [7], tertbutylation of phenols [8] and oxidation of alcohols [9]. Iron-pillared clay was used in heterogeneous photo-Fenton process [10], nucleophilic ring opening of oxiranes [11] and acylation [12] of aromatic hydrocarbons.

Epoxides are versatile intermediates in organic synthesis, the ring opening of epoxides can be performed using homogeneous or heterogeneous catalysis. The products are important in pharmaceutical and other chemical fields. Epoxides can be opened under a variety of conditions, although the most practical and widely employed

strategy for the synthesis of 1,2-bifunctional compounds is via nucleophilic ring-opening using a Lewis acid or a strong base. In most of the epoxide ring opening reactions under acidic conditions, the formation of a mixture of regio-isomers and polymerization is observed. Some of the reported catalysts suffer from disadvantages such as high acidity, the non-catalytic nature of the reagents, long reaction times and inconvenient handling procedures.

The opening of epoxides with alcohols is an important transformation in the synthesis of β-alkoxy alcohols, which are valuable organic solvents and intermediates. Ring opening of styrene oxide was reported over many catalysts. Kumar et al. [13] have shown that with a titanium TS-1 catalyst, styrene oxide in methanol as solvent and reactant, produced 2-methoxy-2-phenylethanol in 33% yield. Mirkhani et al. have used decatungstocerate to promote many reactions of epoxides with alcohols. For the methanolysis of styrene oxide using the decatungstocerate catalyst, a yield of 2-methoxy-2-phenylethanol of 97% was reported at the room temperature [14]. Moghadam et al. studied methanolysis reaction of styrene oxide with tin tetraphenylporphyrinato trifluoro- methanesulfonate, $Sn(tpp)(OTf)_2$ and obtained 99% yield of 2-methoxy-2-phenylethanol [15]. Besides, the reactions catalyzed by ionic liquid [16] and zeolite catalyst [17] were also reported.

In view of searching for an improved catalyst for the activation of epoxides, which renders them to be more susceptible to nucleophilic attack under milder condition, we report on methanolysis of styrene oxide to produce 2-methoxy-2-phenylethanol using iron pillared bentonite clay. This catalyst was also found to be effective when higher molecular weight alcohols were used. This catalyst has advantages such as environmentally friendly, inexpensive, easy product separation and catalyst reuse.

2. Experimental

Bentonite was obtained from source in Thailand (Cernic International Co. Ltd). The chemical composition (wt%) was: SiO_2 63.6%, $A1_2O_3$ 17.6%, CaO 3.0%, Fe_2O_3 3.1%, Na_2O 3.4%, K_2O 0.5%, loss on ignition 5.8%, surface area measured by nitrogen adsorption method (BET) is 59 m^2/g and its cation exchange capacity determined by the copper bis(ethylenediamine) method [1] is 79 meq/100 g. Styrene oxide, methanol, other reagents and solvents were supplied from Fluka.

2.1 Pillaring process

The intercalating solution was prepared by adding 0.2 M NaOH solution (200 mL) to a stirred solution of $FeCl_3$ (0.2 M, 200 mL) with OH/metal ratio of 2. Then, the intercalating solution was added very slowly at room temperature to the previously prepared aqueous suspension of the bentonite (5 g). The ratio of Fe:bentonite is 10 mmol/g. After ageing for 24 h in the presence of the mother liquor, the solid was recovered by filtration. It was then washed for a long time with distilled water until no more chloride ions were detected in the washings (tested with $AgNO_3$). The solid was then dried at 110°C for 16 h and calcined at 300°C for 4 h. (2°C/min).

2.2 Catalyst characterization

2.2.1 Chemical composition

The Fe composition of the sample was determined using a SISONS X-ray fluorescence spectrometer ARL 8410 and Varian Spectra-AA300 atomic absorption spectrometer with air/acetylene flame.

2.2.2 X-ray diffraction

Powder X-ray diffraction (XRD) spectra were recorded on a Rigaku, RINT 2200 spectrometer

using filtered CuKα radiation (λ = 0.154 nm), at 40 kV, 300 mA. and a scan rate of 3°/min.

2.2.3 Area and pore size distribution

N_2 adsorption–desorption isotherms were measured at liquid nitrogen temperature with a gas sorption analyzer (Quantachrome Autosorb-IC-VP Analyzer). Prior to the measurements, the samples were degassed at 200ºC for 2 h. The specific surface area was calculated by the BET equation [18].

2.2.4 Thermal study

Thermal analysis of samples was carried out at a heating rate of 10°C/min under a flow of nitrogen using a thermogravimetric analyzer (SDT 2960). A 150 mg sample was placed on the dish and heated from 25 to 850°C at 10°C/min with a nitrogen flow of 30 ml/min.

2.2.5 Scanning electron microscopy

Scanning electron microscopy (SEM) was performed with a JEOL JEM-6400 scanning microscope operating at an accelerating voltage in the 30–35 kV range.

2.3 Typical procedure for methanolysis of styrene oxide

The catalytic experiments were carried out in the liquid phase. A two-necked, round bottomed flask was charged by the catalyst (50 mg) which was thermally activated prior to use (120°C, 2 h) in air. After activation, the catalyst was allowed to cool at room temperature. A solution of styrene oxide in methanol (1 mmol of styrene oxide and 2 mmol of methanol) was added to the catalyst and the suspension was magnetically stirred at room temperature (33°C) or 55°C. Different solvents (5 mL) were used. Aliquots of the reaction mixture were taken at different reaction times and analyzed using gas chromatography (GC). Average value of three reactions was reported.

2.4 Recycling of the catalyst

Catalyst recycling experiments were carried out with repeated use of the catalyst. After each reaction, the catalyst was removed by filtration, washed with water, acetone, dried at 120°C and reused.

3. Results and discussion

3.1 Catalyst characterization

The content of iron in the bentonite and Fe pillared bentonite clays determined by XRF together with its specific surface area and pore volume determined by BET are reported in Table 1.

Table 1 Iron content and surface area

Catalyst	Fe_2O_3 (%)	Surface area (m^2/g)	Pore volume (cm^3/g)
Bentonite	3.1	85	0.16
Iron pillared bentonite	12.0	220	0.28

The specific surface area and pore volume of the iron pillared bentonite (220 m^2/g and 0.28 cm^3/g, respectively) were higher than those of the bentonite. Figure 1 represents the nitrogen adsorption–desorption isotherms of the Fe-pillared bentonite which is type IV, corresponding to mesoporous adsorbent.

The X-ray patterns of bentonite and iron pillared bentonite are shown in Figure 2. The XRD pattern of bentonite exhibits main peaks around 2θ = 6°, 20° and 24°. There is also some quartz impurity, d_{101} was observed at 2θ = 26° [19]. The peak at 2θ = 6° is assigned to the basal (001) reflection (d_{001} = 11.8 Å). The XRD pattern of iron pillared bentonite showed a peak shift to lower angle, 2θ = 5.0° (d_{001} = 18.4 Å), indicating

intercalation of the iron complexes into the clay interlayers.

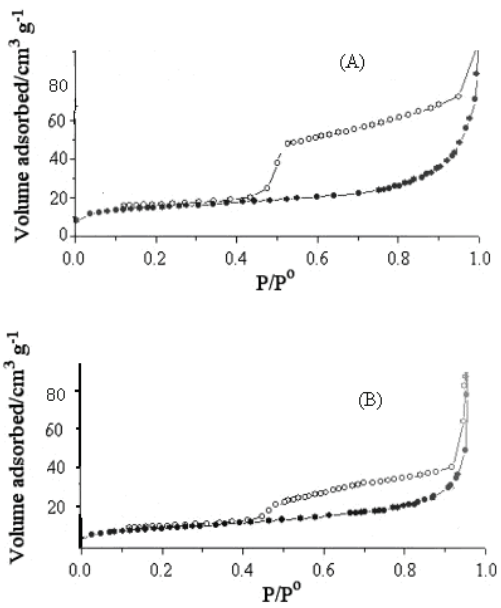


Figure 1 N_2 adsorption–desorption isotherms of (A) bentonite (B) Fe-pillared bentonite

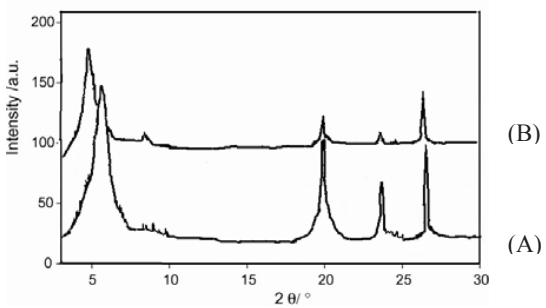


Figure 2 XRD patterns of (A) bentonite and (B) Fe-pillared bentonite

Figure 3 shows TGA/DTG diagrams of the bentonite and Fe-pillared bentonite. Two stages of mass losses were observed. The first weight loss around 100°C was attributed to desorption of physisorbed water. The second weight loss around 600-700°C was attributed to the dehydroxylation of OH groups on the internal and/or external surface of the sample. This peak in the Fe-pillared bentonite appeared at higher temperature than that of the bentonite.

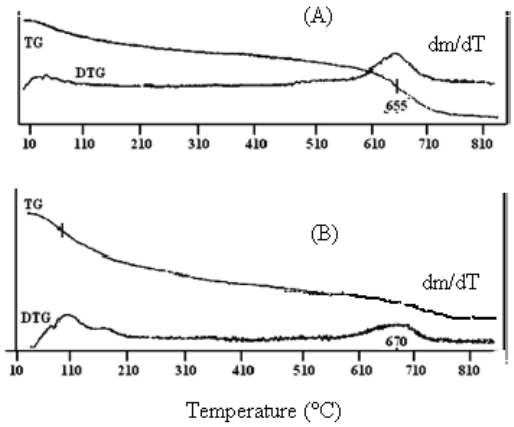


Figure 3 TGA/DTG curves for (A) bentonite and (B) Fe-pillared bentonite

The scanning electron microscopy (SEM) analysis of the bentonite and Fe-pillared bentonite is presented in Figure 4. It shows particle size for bentonite and Fe-pillared bentonite around 5–10 μm and 15 μm, respectively.

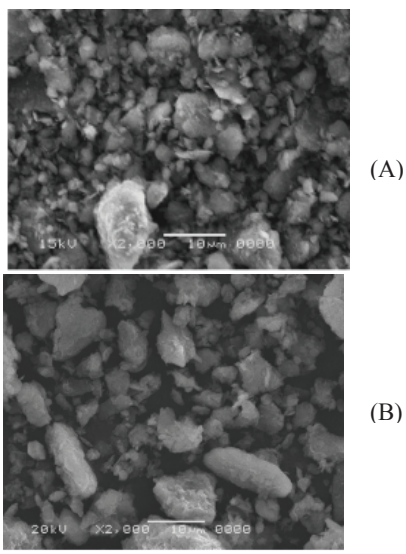
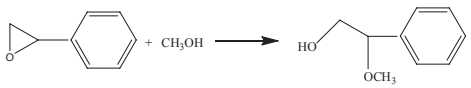


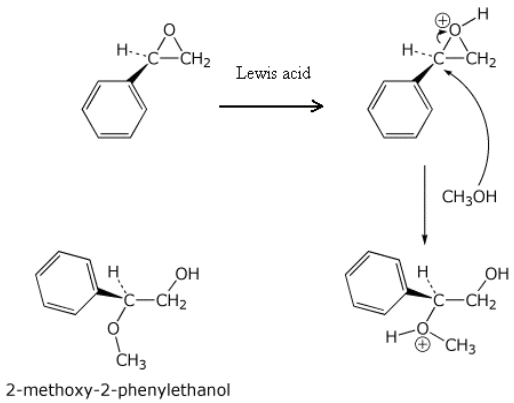
Figure 4 SEM images of (A) bentonite and (B) Fe-pillared bentonite

3.2 Catalytic activity

The result of methanolysis of styrene oxide was shown in Table 2. In the absence of catalyst, no reaction occurred. The reaction product is 2-methoxy-2-phenylethanol (equation 1) revealed by NMR spectrum (shown in Figure 5). Epoxide ring opening reaction proceeds along Lewis-acid catalyzed pathways [20] (Equation 2).



(1)



(2)

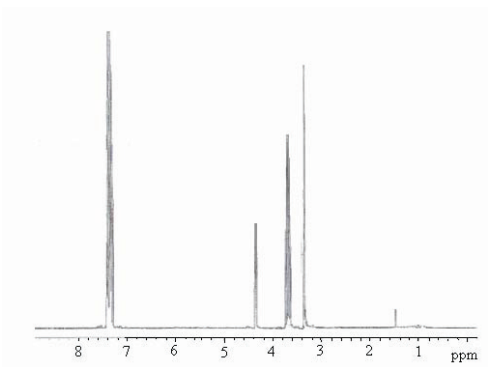


Figure 5 NMR spectrum of 2-methoxy-2-phenylethanol

Conversion of styrene oxide obtained from the iron pillared bentonite (12.0% Fe_2O_3) is higher than that of the bentonite (3.1%Fe_2O_3). The higher Lewis acidity of iron pillared clay is believed to primarily catalyze the ring opening reaction of styrene oxide by nucleophilic attack with methanol. Conversion achieved at 55°C is higher than that at room temperature (33°C). Both the bentonite and iron pillared bentonite gave nearly 100% selectivity to 2-methoxy-2-phenylethanol. In this work no other products (e.g. phenylacetaldehyde or phenyl acetaldehyde dimethyl acetal) were detected, contrary to that reported in the literature [21].

Table 2 Methanolysis of styrene oxide

Catalyst	Reaction time	Reaction temperature (°C)	Conversion (%)
none	36 h	33	0
bentonite	36 h	33	39
Iron pillared bentonite	30 min	33	77
	30 min	55	95

Reaction conditions: 50.0 mg of catalyst; 1 mmol (0.12 mL) of styrene oxide; 2 mmol of methanol and 5 ml of CH_2Cl_2 (solvent)

3.3 Effect of solvents

For heterogeneous catalysis in the liquid phase, the solvent can influence the rates of reaction by the solvation of reactants and intermediates in solution. On the other hand, the solvent can also affect the rate by competing with reactant molecules for active sites on the surface of a heterogeneous catalyst [22]. Solvents may stabilize or destabilize transition states and intermediates formed on the catalyst surface.

The influence of solvents in the catalytic ring opening of styrene oxide was investigated at 33°C for the comparison of activity. The results of the effect of polar and non-polar solvents are given in Table 3. CH_2Cl_2 showed the highest conversion

(77%) followed by hexane (70%) and THF (56%). For CH_3CN a lowering of the conversion (35%) was observed, this might be due to competitive binding of solvent molecules to the active sites (Lewis acid sites) of the catalysts, preventing the reaction process.

Table 3 Methanolysis of styrene oxide in various solvents over iron pillared bentonite

Solvent	Dipole moment	Dielectric constant	Conversion (%)
CH_2Cl_2	1.8	9.1	77
CH_3CN	3.2	37.5	35
hexane	0	1.9	70
THF	1.7	7.6	56

Reaction conditions: 50.0 mg of catalyst; 1 mmol (0.12 mL) of styrene oxide; 2 mmol of methanol; 5 ml of solvent; time 30 min; temperature 33°C

3.4 Effect of alcohols

Using the optimized reaction conditions, we investigated the scope of ring-opening reaction with different alcohols and the results are summarized in Table 4. When the bulkier alcohols, such as *i*-propanol, *t*-butanol, and benzyl alcohol, were used, lower conversions were observed. Among the alcohols tested for this reaction, methanol gave the highest conversion. As the alkyl group of alcohol becomes bulkier, the yield of the ring-opening reaction gradually decreases. This indicated the steric hindrance of nucleophile in access to the location of active sites in micropores of the catalyst. A similar result was previously reported over $Cu(bpy)(H_2O)_2$-$(BF_4)_2$(bpy) catalyst [23].

3.5 Recycling of catalyst

After use, the catalyst was washed with water and acetone and dried at 120°C. The reusability of the catalyst was investigated in the same reaction. As shown in Figure 5, the good performance of the iron pillared bentonite was maintained for at least up to four recyclings.

Table 4 Methanolysis of styrene oxide with different alcohols over iron pillared bentonite

Alcohol	Time	Conversion (%)
Methanol	30 min	95
i-Propanol	10 h	54
t-Butanol	10 h	50
Benzyl alcohol	10 h	36

Reaction conditions: 50.0 mg of catalyst; 1 mmol (0.12 mL) of styrene oxide; 2 mmol of alcohol; 5 ml of CH_2Cl_2 (solvent), time 30 min; temperature 55°C

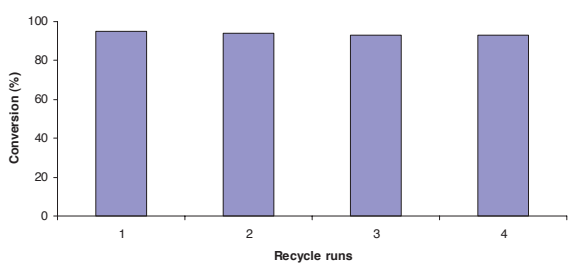


Figure 5 Recycling tests on iron pillared bentonite in the methanolysis of styrene oxide

4. Conclusions

Iron pillared bentonite clay was synthesized and characterized. The interlayer distance of the Iron pillared bentonite was increased. The catalyst showed high activity for methanolysis of styrene oxide in a very short time under mild condition. The advantages of this catalyst are stability, reusability and cheap.

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