

# **An efficient ring opening reaction of methyl epoxystearate promoted by synthetic acid saponite clays**

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## **Supplementary Information**

### **Contents:**

- 1. Materials**
- 2. Characterization techniques**
- 3. Tests on methyl epoxystearate from Prileshajew process**

## 1. Materials

### *Synthesis of H-SAP (A), (B) and (C)*

Synthetic saponite sample with a gel composition of  $1\text{SiO}_2$ :  $0.835\text{MgO}$ :  $0.056\text{Al}_2\text{O}_3$ :  $0.056\text{Na}_2\text{O}$ :  $20\text{H}_2\text{O}$  and a nominal cationic exchange capacity (CEC) of 104.9 meq/100 mg was prepared and optimized in our lab., as reported in literature [C. Bisio, G. Gatti, E. Boccaleri, L. Marchese, L. Bertinetti, S. Coluccia, Langmuir, 2008, 24, 2808-2819].

Amorphous silica (11.9 g,  $\text{SiO}_2$  99,8%, by Sigma-Aldrich) and aluminium isopropoxide (4.7 g,  $\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$  98%, by Sigma-Aldrich) were dispersed in a solution prepared by dissolving 0.92 g of NaOH (Sigma-Aldrich) in few ml of water. The obtained dense gel was accurately mixed with a Teflon rod and a mechanical stirrer. After 1 h, 35.8 g of magnesium acetate tetrahydrate ( $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (99%, Sigma-Aldrich) were added. After 1h, the gel (with pH about 8-9) was introduced in a Teflon cup of an autoclave (Anton PAAR 4748) and heated in a oven for 72 h at 513 K. After the hydrothermal crystallization, the pH of the mother liquor was 4-5. Finally, the product was filtered, washed with deionised water up to neutrality, and dried at 393 K. The so-produced material was submitted to a classical ion exchange procedure in a saturated NaCl solution for 36 h at room temperature in order to remove completely other cations inside the interlayer space. The solid was then filtered and washed with deionised water until complete elimination of chloride (tested by  $\text{AgNO}_3$  solution). This material will be hereafter named as Na-SAP.

Part of Na-SAP material was submitted to ion exchange process in acid solution to activate the surface acidity through the replacement of interlamellar  $\text{Na}^+$  ions with protons. The exchange procedure was realized in three HCl solutions with different concentration (0.01, 0.1 and 1N), at room temperature, stirring the solid in the three acid solutions for 36 h. H-exchanged saponite samples were obtained after filtration and washing of the solid materials until the disappearance of chlorides. These samples prepared in different acid solutions will be named as H-SAP (A) (prepared in 0.01N HCl solution), H-SAP (B) (in 0.1N HCl solution) and H-SAP (C) (in 1N HCl solution).

### *Synthesis of Al-SBA-15*

The aluminium-containing SBA mesoporous solid was prepared following the procedure reported in literature [Y. Yue, A. Gédéon, J. L. Bonardet, N. Melosh, J. B. D'Espinoze and J. Fraissard Chem. Commun., 1999, 1967–1968]: 9 mL of tetraethyl orthosilicate (TEOS) and a calculated amount of aluminium isopropoxide, to obtain a given Si/Al ratio of 20, were added to 10 mL of

aqueous HCl at pH 1.5. This solution was stirred for 5 h and then added to a second solution containing 4 g triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (P123, Aldrich) in 150 mL of aqueous HCl at pH 1.5 at 313 K. The mixture was stirred for 48 h at 313 K. Finally, the solid obtained was filtered, washed several times by water dried at 373 K, and finally calcined in air flow.

## 2. Characterization techniques

Infrared spectra were collected on a Thermo Electron Corporation FT Nicolet 5700 Spectrometer with resolution of  $4\text{ cm}^{-1}$ . Self-supporting pellets were placed into an IR cell equipped with KBr windows permanently attached to a vacuum line, allowing all treatments and adsorption-desorption experiments to be carried out in situ.

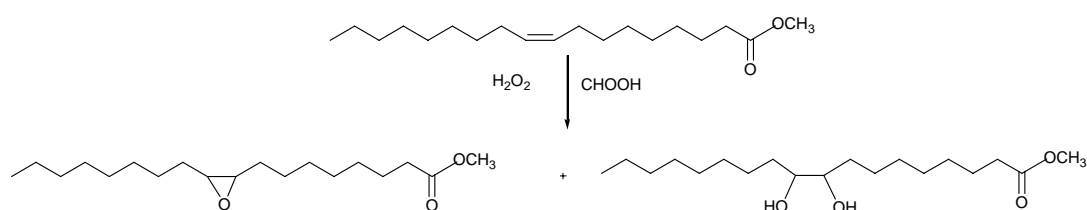
Before gas adsorption experiments, saponite samples were outgassed at 573 K at a heating rate of  $10\text{ K min}^{-1}$ , for 3 h.

After the thermal treatment, samples were then cooled down to room temperature for the collection of IR spectra upon  $\text{NH}_3$  adsorption. CO adsorption experiments were run at low temperature around 100 K.

### 3. Tests on methyl epoxystearate from Prileshajew process

In the present work, the two-step conversion of methyl oleate into keto- and hydroxyether derivatives may occur very efficiently over two non-conventional solid catalysts. Nevertheless, methyl epoxystearate is typically synthesized according to a classical peroxyacid route (Prileshajew process), using, for instance, concentrated formic acid and 50% hydrogen peroxide (Scheme 2).

Scheme 1-SI: Synthesis of methyl 9,10-epoxystearate via peroxyacid route



Therefore, a second batch of epoxystearate was obtained by this method and used as substrate for ring opening in the presence of methanol with H-SAP (A). It is worth noting that the synthesis of epoxystearate over Ti-MCM-41 needs less post-synthesis work-up and purification than after the Prileshajew method (due to lower amount of acidic side products and contaminants). Epoxide conversion of the reactant synthesized by the ‘classical’ Prileshajew method and the one obtained by alternative heterogeneous epoxidation after 60 min are fully comparable (96% vs. 98% respectively). Reaction products are methyl methoxyhydroxystearate with a selectivity of 72% and oxostearate with a selectivity of 28%. However, at the initial stage, the reaction on the epoxystearate synthesized following the peroxyacid route proceeds more slowly (30% vs. 90% after 5 min of reaction). This result, obtained at laboratory scale, shows that an acid layered catalyst, H-SAP (A), can be effectively used also on epoxystearate samples obtained by the conventional peroxyacid route. Nevertheless, by carrying out both synthetic steps (epoxidation and ring opening) over heterogeneous catalysts (Ti-MCM-41 and H-SAP (A)), the desired ring-opening products can be obtained even in a more efficient and less time-consuming way.