Egyptian Journal of Petroleum (2014) **23**, 247–254

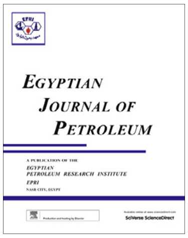
HOSTED BY

ELSEVIER

Egyptian Petroleum Research Institute

Egyptian Journal of Petroleum

www.elsevier.com/locate/egyjp
www.sciencedirect.com



FULL LENGTH ARTICLE

The performance of chemically and physically modified local kaolinite in methanol dehydration to dimethyl ether

Sanaa M. Solyman [a,*], **Mohamed A. Betiha** [b]

[a] *Petrochemical Department, Egyptian Petroleum Research Institute, Nasr City, 11727 Cairo, Egypt*
[b] *Refining Department, Egyptian Petroleum Research Institute, Cairo, Egypt*

Received 21 April 2013; accepted 1 September 2013
Available online 13 October 2014

KEYWORDS

Kaolinite modification;
Characterization;
Dimethyl ether preparation

Abstract The catalytic activity of modified natural kaolinite as a solid acid catalyst for dimethyl ether (DME) preparation was investigated by following up the conversion% of methanol and the yield% of DME. Natural kaolinite (KN) was treated chemically with H_2O_2 (KT) followed by thermal treatment at 500 °C (KC) and then mechano-chemically by ball milling with and without $CaSO_4$ (KB-Ca and KB, respectively). These samples were characterized by XRD, FTIR, SEM, HRTEM, TGA and NH_3-TPD techniques. The different techniques showed that the chemical treatment of kaolinite with H_2O_2 resulted in partial exfoliation/delamination of kaolinite, decreased the amount of acidic sites which is accompanied by increasing their strength. Calcination only decreased the acidic strength and slightly enlarged the particle size mostly due to heat effect. Ball milling resulted in multitude randomly-oriented crystals and increased the amount of acidic sites with the same strength of KT sample. $CaSO_4$ mostly produced ordered monocrystalline kaolinite and created new acidic sites with slightly lower strength relative to KB. The catalytic activity and selectivity depend on the reaction temperature, the space velocity and the strength of acid sites. The most active sample is KB-Ca, which gives 84% DME due to its high amount and strength of acidic sites. The different modification methods resulted in 100% selectivity for DME.

1. Introduction

Dimethyl ether (DME) is of interest in the production of clean fuel, as a chemical intermediate for the preparation of many important chemicals, such as dimethyl sulfate and high-value oxygenated compounds [1–5]. Its physical properties are similar to those of liquefied petroleum gas (LPG), so it is used as a replace or a blend-stock with LPG for home heating and cooking [6,7] and also considered as an alternative for diesel fuel. Recently, the conversion of methanol/DME to triptane (2, 2, 3-trimethylbutane) has spurred particular research interest by Hazari et al. [8]. Practically, triptane is a high-octane and high-value fuel component. DME has been produced by

---

[*] Corresponding author. Tel.: +20 2 22747917; fax: +20 2 22747433.
E-mail address: sanaa8763@hotmail.com (S.M. Solyman).

Peer review under responsibility of Egyptian Petroleum Research Institute.

http://dx.doi.org/10.1016/j.ejpe.2014.08.001
1110-0621

catalytic dehydration of methanol over a solid-acid catalyst [6,9–14]. As an alternating process, the direct synthesis of DME from syngas was proposed over bifunctional catalysts, which had two kinds of active sites: one is for methanol formation and the other for methanol dehydration [5,15].

On the other hand, the grinding of kaolinite (either wet or dry) has been the subject of research for a long time which resulted in various effects on the structure and properties often accompanied by structural transformations and chemical reactions [16,17]. Miller and Oulton [18] indicated a prototropy effect on kaolinite during percussive grinding i.e., a transfer of protons from one phase to another that takes place within the structure. Also, Juhasz reviewed the processes involved in grinding kaolinite, and developed tests to study processes during intensive grinding (super grinding), as the mechanical activation of kaolins, including kaolinite and dickite [19]. Also, mechano-chemical activation caused significant changes in the kaolinite structure by increasing the number of lattice defects, surface energy, dehydroxylation temperature and chemical reactivity [19–22].

Modifications of kaolinite surfaces have been studied using a combination of intercalation and thermal treatment [23,24]. New additional phases of kaolinite were found and modification of the hydroxyl surfaces was extensive even with mild heating or due to intense local heating. Schrader observed that the crystal structure was deformed mainly along the *c* axis during mechanical treatment and proved to be more resistant along the *b* axis [25]. The structural changes of kaolinite, especially with respect to its hydroxyl groups (contain outer and inner hydroxyl groups which were designated as OuOH and InOH, respectively), were mainly investigated by means of infrared spectroscopy [21,26].

The request for needed fuels and different chemical feedstocks fluctuates, and as a result, logistical mismatches can occur in furnishing of their raw materials such as coal, biomass, crude oil, and methane. To overcome these challenges, industry requires a versatile, robust suite and economic process of conversion technologies, many of which are mediated by the synthesis of dimethyl ether (DME) as valuable intermediates.

In this paper, natural kaolinite was chemically, thermally, mechanically and mechano-chemically treated and, characterized through XRD, FTIR, HRTEM, SEM, NH_3-TPD and TGA techniques. The catalytic activity of different modified kaolinite samples was investigated in the preparation of DME by methanol dehydration, seriously lacking in the literature as a cheap source for DME. The textural and structural changes in all samples were correlated with conversion% of methanol and selectivity to DME.

2. Experimental

2.1. Kaolinite modification

Firstly, Egyptian natural kaolinite (KN) was treated with hydrogen peroxide (p.a., 30%) to eliminate organic matter. This treatment was conducted by magnetic stirring for 6 h at 60 °C, filtrated off, dried at 110 °C, and denoted as KT. A portion of KT sample is calcined at 500 °C for 8 h, and denoted as KC. A portion of KC sample is ball milled (Planetary Ball Mill PM 400, Tungsten Carbide Balls, 250 rpm) for 8 h with and without 2.5% w/w $CaSO_4$ (denoted as KB-Ca and KB, respectively).

2.2. Characterization

The crystallographic structures of the materials were determined by a powder X-ray diffraction system (XRD, BRUKER axs–D8 ADVANCE) equipped with Cu-Kα radiation (λ = 0.15406 nm).

Fourier transform infrared spectroscopy (FTIR) measurements were performed using Nicolet IS-10 FTIR over the wave number 4000–400 cm^{-1}. High-resolution transmission electron microscopy (HRTEM) image was conducted on a JEOL 2011 (Japan) electron microscope at 200 k V.

Scanning electron microscopy (SEM) images were taken using a JEOL JSM-5300 instrument working at 30 kV.

Temperature programed desorption (NH_3-TPD) of ammonia was measured using a CHEMBET 3000 chemical absorber (Quantachrome). Samples were activated at 500 °C for 1 h in a flow of helium; subsequently ammonia was introduced for 1.5 h at 100 °C. The physically adsorbed ammonia molecules were removed by purging with helium flow until the baseline was flat. The reactor temperature was then increased to 700 °C with a ramping rate of 10 °C/min.

Thermal stability was carried out in a TA Instruments SDTQ 600 simultaneous TGA thermogravimetric analyzer. The analyses were conducted for a total sample mass of 10.0 ± 0.2 mg. The samples were heated under nitrogen flow (100 ml min^{-1}) from 50 to 750 °C, at 20 °C min^{-1}.

2.3. Dehydration method

The vapor phase dehydration of methanol was carried out in a conventional flow type reactor as described in detail in previous work [14]. The reaction temperature ranged from 200 to 500 °C and the catalyst weight is 2.5 g. The reaction products were analyzed on a gas liquid chromatograph (Hewlett Packard-5890) equipped with FID detector and connected with Carbowax backed column.

3. Results and discussion

3.1. Characterization of kaolinite samples

3.1.1. X-ray diffraction analysis

The XRD analysis of (KN), (KT), (KC), (KB) and (KB-Ca) samples indicated the structural formula of $Al_2Si_2O_5(OH)_4$ and is shown in Fig. 1. The XRD pattern of KT shows rapid changes in the kaolinite structure after chemical treatment with H_2O_2. Mostly, H_2O_2 diffused into the interlayer spaces of kaolinite, eliminated the organic contaminants in-between layers, exchanged with water and some alkali earth metal oxides such as MgO and CaO and catalytically decomposed into O_2 and H_2O at 60 °C by Mn oxides located in mineral interlayer. The gas evolved can disrupt individual silicate layers which reflected a slight increase in d-spacing of 001 plane [27,28]. Also, the relative reflection intensity values (I/I_o) which are simply the ratio between the peak height of modified samples (I) and the corresponding peak in parent kaolinite (I_o) for all