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Synthesis of dimethyl ether from methanol over aluminium phosphate and silica–titania catalysts

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Abstract

A series of solid–acid catalysts with different content of components were prepared by co-precipitation (sol–gel) method. These samples comprised silica–titania and modified γ-Al_2O_3 with phosphorus. To determination of optimum ones, the effects of various contents of phosphorus have been investigated. Dehydration of methanol to dimethyl ether (DME) on solid–acid catalysts was studied in a fixed-bed reactor at a temperature of 300 °C under atmospheric pressure and a GHSV of 15,600 h^{-1}. The catalysts have been characterized using BET, XRD, FT-IR, NH_3–TPD and elemental analysis techniques and also the results were reported. According to the experimental results, silica–titania catalysts have exhibited low activity for DME synthesis. Phosphorus-modified catalysts have shown better performance compared to the untreated γ-Al_2O_3. It was found that surface areas increase with increasing in the molar ratio of aluminium-to-phosphorus at aluminium phosphate catalysts. Also, by modifying alumina with phosphorus, it was observed that the surface acidity of aluminium phosphate catalysts decrease with increasing in the molar ratio of Al/P at aluminium phosphate catalysts. The sample of non-stoichiometric aluminium phosphate (molar ratio of Al/P = 2) have exhibited the best conversion without any by-product.

Keywords: Methanol; Dehydration; Dimethyl ether; Solid–acid catalysts

1. Introduction

Catalytic dehydration of methanol is commercially important for the production of dimethyl ether (DME). During the last few years, with increasingly stringent environmental regulations, DME has received global attention due to its potential use as a clean alternative fuel for diesel engines [1]. It is also used as an intermediate for producing many valuable chemicals such as lower olefins, methyl acetate, dimethyl sulfate, LPG alternative and power generation [2–6].

Several solid–acid catalysts have been studied for this reaction [2,7–11]. Although γ-Al_2O_3 is an excellent catalyst for the methanol dehydration, but this sample undergo a fairly rapid, irreversible deactivation. The deactivation of solid–acid catalysts used in hydrocarbon transformation is mainly due to the deposite of heavy secondary products (HCs) inside the pores generally known as coke [12,13]. It is known that HCs are formed on the strong acid-sites on the surface of the catalyst. In order to avoid the formation of coke and to increase the DME selectivity to 100%, the strength of the acid-sites must be reduced. It has been found that if the reaction of methanol dehydration take place on the modified-alumina catalysts with phosphorus, can be caused to reduce the amounts of coking and by-products [1,14].

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In the present work, the catalytic dehydration of methanol to DME has been studied over γ-Al_2O_3, silica–titania and modified-alumina with phosphorus catalysts. The effects of phosphorus on the catalytic activity of γ-Al_2O_3 have been investigated. In addition, we have investigated the correlation of the activity results with surface acid properties of these catalysts. The properties of catalysts were characterized by using BET, NH_3–TPD, etc. Finally, the catalysts were tested for the dehydration reaction in a vertical fixed-bed reactor under normal atmospheric pressure. This work is part of a long-range effort to develop a new know-how to produce DME from methanol at Haldor Topsøe A/S.

2. Experimental

2.1. Material

The starting materials were aluminium nitrate nanohydrate [ANN; $Al(NO_3)_3 \cdot 9H_2O$], tetraethyl orthosilicate [TEOS; $Si(OC_2H_5)_4$], tetraisopropyl orthotitanate [IZPT; $Ti(OC_3H_7)_4$], *ortho*-phosphoric acid [H_3PO_4, 85 wt%], oxalic acid dihydrate [$C_2H_2O_4 \cdot 2H_2O$] and ammonia solution [maximum 33% NH_3].

2.2. Catalysts preparation

2.2.1. γ-Al_2O_3

γ-Al_2O_3 (DME–SCAT2) was obtained by the thermal decomposition of the boehmite (γ-AlOOH, DME–SCAT1) precursor at 550 °C for 6 h at heating rate of 2 °C/min. A commercially available catalyst (it has been developed by Haldor Topsøe A/S, DME–FCAT) was used as a reference solid–acid catalyst for the methanol dehydration reaction.

2.2.2. Silica–titania

Acidic medium. A series of SiO_2–TiO_2 samples were prepared by varying the amount of silica loading (25, 50, 75 wt%) by co-precipitation (sol–gel) method as follows. An appropriate amount of TEOS and IZPT separately were dissolved in ethanol (the TEOS:EtOH and IZPT:EtOH molar ratios are 1:2). Then, two solutions were mixed in a glass beaker (1000 cm^3) at the room temperature and subsequently, DM water that its pH has adjusted at 1 by addition of oxalic acid, was added to the mixture with vigorous stirring. Since, the used precursors don't have the hydrate water, the H_2O/(TEOS + IZPT) ratio was adjusted to 1:1 by addition of the calculated amount of H_2O. After precipitation, the mixture was filtered and was then dried at 110 °C overnight and calcined in air at 500 °C for 6 h at heating rate of 2 °C/min. In more detail silica–titania catalysts with 50, 75 and 25 wt% silica loading, were applied DME–TS1, DME–TS2 and DME–TS3, respectively.

Basic medium. An addition of an excess aqueous ammonia (33%) in room temperature after addition of TEOS solution to that of IZPT, results fast hydrolysis and condensation of TEOS and IZPT in the basic medium (pH 7.6). The precipitate was filtered and then, as for the prepared catalysts in an acidic medium, dried at 110 °C overnight and calcined at 500 °C for 6 h at heating rate of 2 °C/min.

2.2.3. Aluminium phosphates

A series of aluminium phosphate catalysts were prepared by varying the molar ratio of Al/P (1, 2 and 3) by co-precipitation method as follows. Aluminium phosphate was precipitated by adding aqueous ammonia to the solution of ANN and 85% H_3PO_4 with constant stirring at about 700 rpm till the pH of the final solution reached 9. The precipitate was filtered, washed with distilled water to be free from anion. Then the final solid was dried at 110 °C overnight and calcined in air at 650 °C for 3 h at heating rate of 2 °C/min. In more detail, aluminium phosphate catalysts with molar ratio of aluminium-to-phosphorus 1, 2 and 3 were applied on DME–AlP1, DME–AlP2 and DME–AlP3, respectively.

2.2.4. Characterization of the catalysts

BET surface area, pore volume and pore diameter was measured by N_2 adsorption–desorption isotherm at liquid nitrogen temperature using Autosorb-3B (Quantachrome, USA). Prior to the adsorption–desorption measurements, all the samples were degassed at 300 °C in N_2 flow for 16 h.

The XRD pattern of all the calcined samples were recorded on an X-ray diffractometer (X'Pert PRO, Model PW3040/60 console) using Cu Kα monochromatized radiation source and Ni filter in the range $2\theta = 5$–$90°$.

The acidity of the samples was measured by temperature programmed desorption of ammonia (NH_3–TPD). In a typical experiments, the TPD of NH_3 was performed using 0.2 g of the catalyst in the temperature range 90–850 °C after pretreatment at 500 °C in a flow of helium. The sample was saturated with 2% NH_3/He gas mixture stream (100 N ml/min) for 1 h at 150 °C. After saturation, the sample was flushed in a He flow (65 N ml/min) for 2 h to remove any loosely bound ammonia on the sample. The temperature of the sample was then raised at heating rate of 10 °C/min to 850 °C. The amount of NH_3 desorbed from the sample was monitored by a Quadrupole Mass Spectrometer (In-Process Instruments, IPI, Model GAM 400).

The FT-IR spectra of catalysts were carried out on Bio-Rad Laboratories FT-IR spectrophotometer