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Relationship between surface acidity and activity of solid-acid catalysts in vapour phase dehydration of methanol

M. Mollavali [a],*, F. Yaripour [b],*, Sh. Mohammadi-Jam [b], H. Atashi [a]

[a] *Department of Chemical Engineering, Faculty of Engineering, University of Sistan and Baluchestan, P.O. Box 98164-161, Zahedan, Iran*
[b] *Catalyst Research Group, Petrochemical Research and Technology Company, National Petrochemical Company, 14358, Tehran, Iran*

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ABSTRACT

A series of solid-acid catalysts comprised of γ-alumina and modified γ-alumina with different of silica were prepared by co-precipitation method. The catalysts were characterized using XRD, TGA, NH_3-TPD and BET techniques. Dehydration of methanol to dimethyl ether (DME) on solid-acid catalysts was studied in a fixed-bed reactor at the same operating conditions ($T = 300$ °C, $P = 16$ bar, WHSV = 26.07 h^{-1}). According to the experimental results, silica-modified catalysts have shown better performance compared to the pure γ-alumina. It was found that surface areas increase with increasing silica loading. The results of NH_3-TPD analysis showed that the surface acidity of aluminosilicate catalysts increases with increase in SiO_2/Al_2O_3 molar ratio. Also, it was found that the catalysts with highest portion of weak and/or moderate acid sites exhibit the best catalytic performance and stability. The sample with 3 wt.% silica loading has exhibited the best activity for methanol conversion.

1. Introduction

During the past few years, DME has received global attention as a clean-burning alternative fuel for diesel engines due to the increasingly stringent environmental regulations [1]. DME can also be used as an aerosol propellant in the cosmetic industry to replace CFC and LPG. Aerosol-based household products include hair sprays, and dyes, personal care mousses, antiperspirants, and room air fresheners. Then there would be a growing requirement to produce large scale of DME to meet the future market.

Nowadays, DME is made by the catalytic dehydration of methanol, a method which is industrially important for the production of dimethyl ether. Conventionally, the preparation is performed over a solid-acid catalyst at a reaction around 300 °C under high pressure [2,3].

The solid-acid catalysts used for dehydration of methanol are HZSM-5, H-Y zeolite, γ-Al_2O_3, and modified γ-alumina with silica, phosphorus, etc. [4–7]. It has recently been found that if the reaction of methanol dehydration takes place on the modified-alumina catalysts with silica, it can reduce the amounts of coking and by-product [8,9].

In the present study, to elucidate the role of solid-acid catalysts and to develop a high performance catalyst, (from both an activity and a yield point of view) a series of catalysts comprising pure γ-Al_2O_3 and modified-alumina with silica were prepared by co-precipitation method, tested and screened for methanol dehydration to DME under the same operating conditions. The solid-acid catalysts were also characterized by XRD, TGA, NH_3-TPD and BET methods. In addition, the effects of different SiO_2 loading on the activity, selectivity and yield have been investigated.

2. Experimental

2.1. Catalyst preparation

2.1.1. γ-Al_2O_3

γ-Al_2O_3 was obtained by the thermal decomposition of the boehmite (γ-AlOOH) precursor at 550 °C for 6 h at heating rate of 2 °C/min.

2.1.2. Aluminosilicates

A series of modified γ-alumina catalysts with different silica loading were prepared by co-precipitation method as follows. Aluminum nitrate nanohydrate (ANN) and tetraethyl orthosilicate (TEOS), as starting materials for Al_2O_3 and SiO_2 respectively, were dissolved in ethanol separately. Then TEOS solution was added to ANN solution. de-minirized (DM) water (H_2O/TEOS = 10)

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* Corresponding authors. Tel: +98 2188043037; fax: +98 2188064161.
E-mail addresses: M.Mollavali@yahoo.com (M. Mollavali), f.yaripour@npc-rt.ir, Fereydoon_Yaripour@yahoo.com (F. Yaripour).

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was added to the mixture. Then an appropriate amount of NH_4OH solution (32%) was added to the precursor solution containing ANN and TEOS in ratio $NH_4OH/EtOH = 1/3$ in about 20 min with vigorous stirring. A white, gelatinous precipitate forms during the addition. The resulting mixture was aged for 24 h at 50 °C under 400–450 rpm agitation. The solid product was dried at 110 °C for 24 h and calcined in air at 650 °C for 6 h at a heating rate of 2 °C/min to obtain the final catalysts. The samples modified by 0.5, 1, 3, 4, 6, 9, 11, 15, 20 and 30 wt.% silica were named as AS0.5, AS1, AS3, AS4, AS6, AS9, AS11, AS15, AS20 and AS30, respectively.

2.2. Characterization techniques

BET surface area (S_{BET}), total pore volume (V_p) and mean pore diameter (‹d_p›) were measured by N_2 adsorption–desorption isotherm at liquid nitrogen temperature (77 K) using NOVA 2200 instrument (Quantachrome, USA). Prior to the adsorption–desorption measurements, all the samples were degassed at 200 °C in N_2 flow for 16 h.

The XRD patterns of all the calcined samples were recorded on a Philips X, Pert (40 kV, 30 mA) X-ray diffractometer using Cu-K_α radiation source ($I = 1.542$ Å) and Ni filter in the range of $2\theta = 2°$ to $100°$.

The acidity of the samples was measured by temperature-programmed desorption of ammonia (NH_3-TPD) using TPR/TPD 2900 instrument (Micromeritics, USA) with a conventional flow apparatus which included an on-line thermal conductivity detector (TCD). In a typical analysis, 0.25 g of the sample was degassed at 500 °C under He flow rate of 30 ml/min for 60 min at a heating rate of 10 °C/min. Next, the sample was cooled down to 150 °C and then saturated with 2%NH_3/He for 40 min. The sample was then purged with He flow for 30 min to remove weakly and physically adsorbed NH_3 on the surface of the catalyst. After these operations, the sample was cooled down to 90 °C and then was heated at 10 °C/min under the flow of He carrier gas (40 ml/min) from 90 °C to 850 °C and the amount of ammonia in effluent was measured via TCD and recorded as a function of temperature.

The proper temperature for the calcination process and phase transformation conditions of the dried samples was determined by thermo-gravimetric analyzer (TGA) using TGA 50 instrument (Shimadzu, Japan). Samples were heated from 25 °C to 1000 °C at 10 °C/min until no weight loss occurred.

2.3. Catalytic performance

A schematic representation of the experimental set-up is shown in Fig. 1. In the feed section, nitrogen as the internal standard, was fed through a set of mass flow controllers (Bronkhorst HI-TECH, EL-FLOW®) and methanol was pumped from a feed tank through a set of mini-metering pumps (ILSHIN Autoclave Co., LTD, Korea). Methanol and N_2 were subsequently introduced into a pre-heater that was set at a temperature of 250 °C. The down stream effluent was constantly kept at temperatures above 150 °C, to avoid possible condensation of water, methanol or DME.

The dehydration reaction was carried out in a fixed-bed micro-reactor made of stainless steel with an inner diameter of 9 mm. Prior to the catalytic activity measurements, the samples were crushed, sieved (mesh size: 25–40 or 90–125 μm) and then were in-situ heated-treated, at a heating rate of 5 °C/min under N_2 flow (50 ml/min) at 220 °C for 2 h under atmospheric pressure. Activity tests were carried out at 300 °C and 16 bar. In each test, 1 g catalyst was loaded, and the methanol flow rate and weight hourly space velocity (WHSV) was 0.55 ml/min and 26.07 h^{-1}, respectively. A small portion of the reactor effluent was sent to a gas chromatograph (GC) for on-line analysis. The Agilent Technologies (HP) 6890 N gas chromatograph was equipped with a thermal conductivity detector (TCD) and a capillary column (HP-PlotQ, 25 m × 320 μm × 10 μm, SS) for separating CH_4, MeOH, DME and C_2–C_4 olefin/paraffin compounds. The reaction performance results including methanol

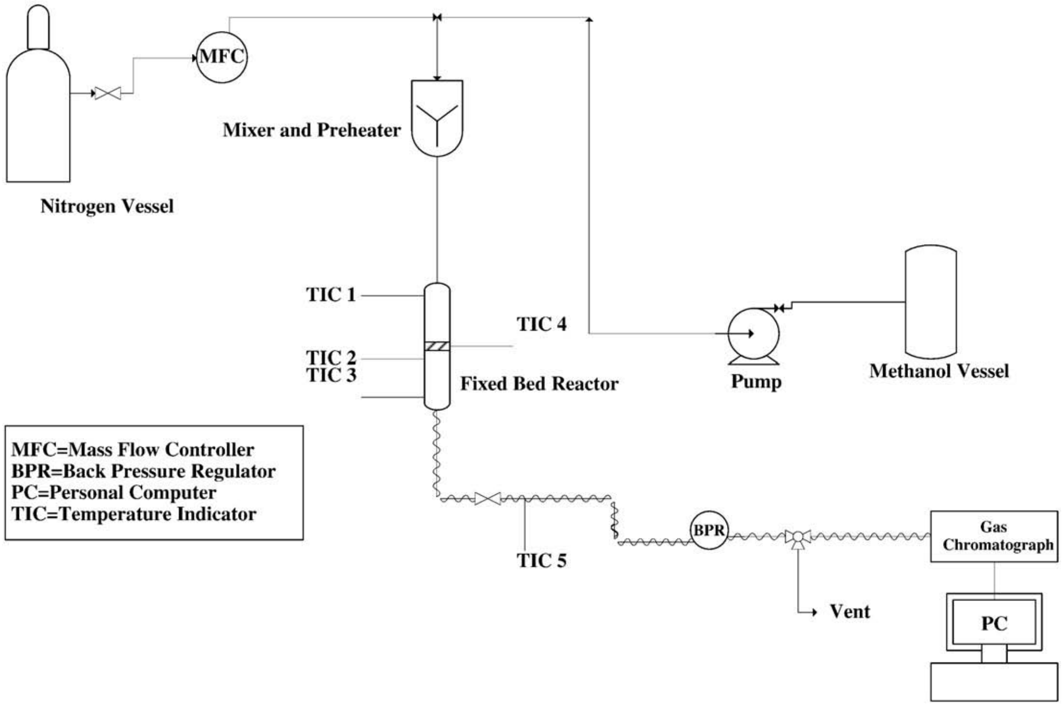

Fig. 1. Schematic representation of experimental set-up.