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Effects of temperature and feed composition on catalytic dehydration of methanol to dimethyl ether over γ-alumina

Freshteh Raoof [a], Majid Taghizadeh [a], Ali Eliassi [b,*], Fereydoon Yaripour [c]

[a] Chemical Engineering Department, Babol University of Technology, Babol, Iran
[b] Chemical Industries Research Department, Iranian Research Organization for Science and Technology (IROST), No. 71, Forsat Street, Enghelab Avenue, Tehran, Iran
[c] Catalysis Research Group, Petrochemical Research & Technology Company NPC, Tehran, Iran

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ABSTRACT

Catalytic dehydration of methanol to dimethyl ether (DME) is performed in an adiabatic fixed bed heterogeneous reactor by using acidic γ-alumina. By changing the mean average temperature of the catalyst bed (or operating temperature of the reactor) from 233 up to 303 °C, changes in methanol conversion were monitored. The results showed that the conversion of methanol strongly depended on the reactor operating temperature. Also, conversion of pure methanol and mixture of methanol and water versus time were studied and the effect of water on deactivation of the catalyst was investigated. The results revealed that when pure methanol was used as the process feed, the catalyst deactivation occurred very slowly. But, by adding water to the feed methanol, the deactivation of the γ-alumina was increased very rapidly; so much that, by increasing water content to 20 weight percent by weight, the catalyst lost its activity by about 12.5 folds more than in the process with pure methanol. Finally, a temperature dependent model developed to predict pure methanol conversion to DME correlates reasonably well with experimental data.

1. Introduction

Dimethyl ether (DME) with the chemical formula of CH_3–O–CH_3 is the simplest ether for preparation of some chemicals such as dimethyl sulfate and high-value oxygenated compounds. In addition, it has been used as an aerosol propellant to replace chlorofluoro carbons which can destroy the ozone layer of the upper atmosphere. It is a colorless gaseous with an ethereal smell. Unlike methane, DME does not require an odorant because it has a sweet ether-like odor. Dimethyl ether is also a clean fuel alternative to liquified petroleum gas (LPG), liquified natural gas (LNG), diesel and gasoline [1,2].

DME can be made from natural gas, coal, or biomass. This fuel burns with a visible blue flame and is non-peroxide forming in the pure state or in aerosol formulations. DME is a volatile organic compound, but is non-carcinogenic, non-teratogenic, non-mutagenic, and non-toxic [1]. Its physical and chemical properties in comparison with diesel can be summarized as follows:

- The low heat value of DME is only 64.7% of that of diesel, therefore a larger amount of fuel supply is needed to deliver the same power output for the engine.
- Cetane number of DME is higher and its auto ignition temperature is lower than that of diesel.
- DME has only got C–H and C–O bonds, but no C–C bond and it contains about 34.8% oxygen, therefore the combustion products such as carbon monoxide and unburned hydrocarbon emissions are lower than those of natural gas.
- The latent heat of evaporation of DME is much higher than that of diesel, so it will be beneficial to the NO_x reduction due to the larger temperature drop of the mixture in the cylinder.
- DME's boiling point is −24.9 °C and it must be pressurized to keep it in liquid state under ambient conditions.

Two processes are used for DME production, indirect [3–8] and direct processes [9–11]. In indirect process, methanol is converted to DME in a catalytic dehydration reactor over a solid-acid catalyst by the following reaction

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad (1)$$

In the second process (direct process), a synthesis gas (a mixture of H_2 and CO gases) is used as the feed of the process. In this process, the synthesis gas is primarily converted to methanol and then it is followed by methanol dehydration to DME. The net reaction is as follows:

$$3CO + 3H_2 \leftrightarrow CH_3OCH_3 + CO_2 \quad (2)$$

* Corresponding author. Tel./fax: +98 21 88838324.
E-mail address: alieliassi@yahoo.com (A. Eliassi).

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In this work, we have considered the conversion of methanol to DME by dehydrating process. This process is moderately exothermic and usually is conducted in an adiabatic fixed bed reactor. One of the most important problems related to the operation of heterogeneous catalysts is the loss of catalyst activity with time-on-stream. In the indirect process to produce DME using acidic γ-alumina, water has the most important effect on catalyst deactivation [11].

In this work, acidic γ-alumina has been used as the catalyst for the dehydration of methanol to DME. Methanol conversion to DME and the deactivation of the catalyst have been studied in a laboratory-scale system at various operating temperatures. A temperature dependent model has been developed to predict methanol conversion to DME at various temperatures.

2. Experimental

2.1. Apparatus

A schematic diagram of the laboratory-scaled system employed in this study is shown in Fig. 1. Pure methanol was pumped from methanol storage tank at a rate of 0.121 L/h to an evaporator and then to a supperheater before entering the reactor. The superheated methanol was sent to an adiabatic fixed bed reactor. The length of catalyst bed could be adjusted for a given experiment. The axial reactor temperature at any point of the catalyst bed was measurable via a thermo-well using a thermocouple. The reactor outlet products were passed through an air cooler and a double pipe heat exchanger to cool down to the ambient temperature. Cooled products were sent to a gas–liquid separator. A back pressure regulator (BP-LF690, pressure Tech2000, England) was placed on this separator to regulate the system pressure. Before any experiments all of set up was swept by using nitrogen gas. Reaction products were analyzed by a gas chromatograph (Varian CP-3800) equipped with TCD and FID detectors. Also, the remaining methanol in the exit reactor products was measured and with comparison to the entrance methanol, the methanol conversion was estimated. BET surface area, pore volume and pore radius of the catalysts were measured by N_2 adsorption–desorption isotherm at liquid nitrogen temperature using Autosorb-3B (Quantachrome, USA). Experiments were carried out at average reactor bed temperature (operating temperatures) ranging from 233 to 303 °C at constant atmospheric pressure. The operating conditions as well as some of the characteristic of the system are reported in Table 1.

For study of the adiabatic status of the applied reactor, an experiment was performed as a blank run (without any reaction) and the temperature profile of the bed was measured by using thermocouple and thermowell. The result of this experiment is shown in Fig. 2. According to this figure, the performance of the reactor as an adiabatic reactor is reasonable. Therefore, the adiabatic assumption for the used reactor is reasonable. This experiment was performed by passing air through to the catalyst bed.

2.2. Chemicals

Acidic γ-alumina, 1–2 mm in particle size, was obtained from BASF (Kat.D10-10 S4). Physical and chemical properties of the catalyst are reported in Table 2. Methanol was obtained from Iran

Table 1
Operating conditions and some characteristics of the laboratory-scale apparatus and the catalyst used in this study

Set up characteristics	
Absolute pressure (atm)	1
Average temperature of the catalyst bed (°C)	233–303
Liquid methanol flow rate (L/h)	0.121
Reactor inside diameter (mm)	18
Thermowell outside diameter (mm)	6.35
Catalyst	
Catalyst weight (g)	8.2
Catalyst volume (cm^3)	14.2
Liquid hourly space velocity (h^{-1})	8.5

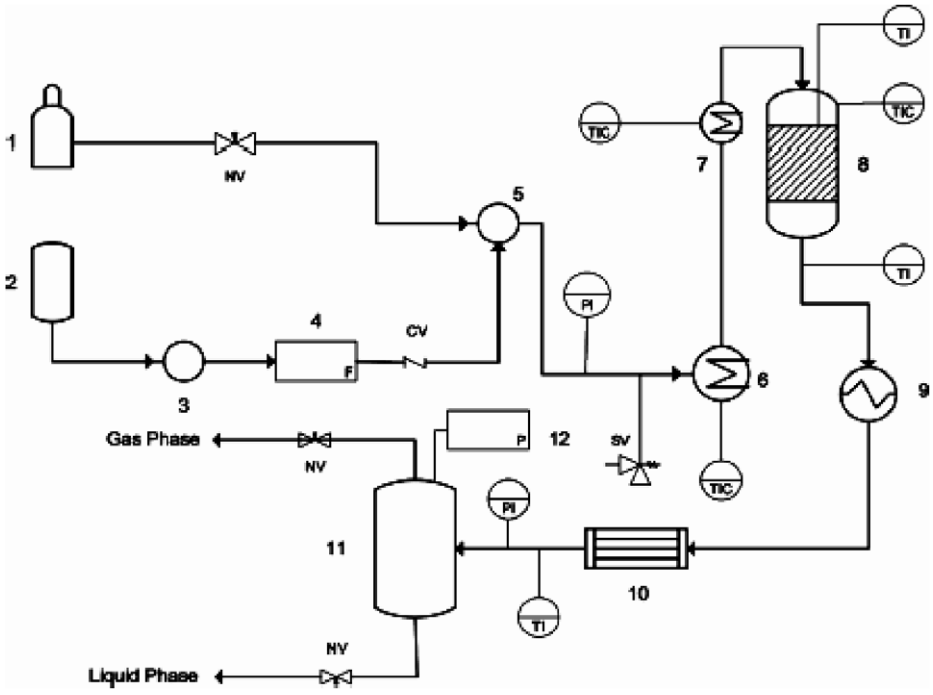

Fig. 1. A schematic diagram of the experimental apparatus for catalytic production of DME from methanol: (1) nitrogen cylinder, (2) methanol feed tank, (3) dosing pump, (4) flow meter (5) mixer, (6) evaporator, (7) preheater, (8) adiabatic fixed bed reactor, (9) air cooler, (10) condenser, (11) liquid–gas separator, (12) back pressure regulator.