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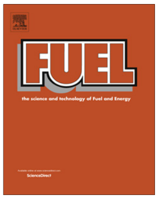

Two practical equations for methanol dehydration reaction over HZSM-5 catalyst – Part I: Second order rate equation

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HIGHLIGHTS

- Methanol to dimethyl ether reaction was performed over commercial sample of HZSM-5.
- A simple reversible second order equation was developed for the reaction rate over HZSM-5 catalyst.
- One dimensional plug flow reactor was modeled based on the derived rate equation of HZSM-5.

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ABSTRACT

In present contribution, a suitable rate of reaction for pure methanol with no water as feed over commercial catalyst of HZSM-5 at industrial conditions in methanol dehydration process is found. This second order rate of reaction shows good agreement with experimental data with R^2 of more than 90%. Modeling results are also revealed that the proposed rate of reaction predicts the behavior of process, properly and therefore, this rate equation is reliable and accurate for simulation.

1. Introduction

It is well known that dimethyl ether (DME) has many advantages and DME could be used as a proper substitute for diesel or liquefied petroleum gas (LPG) in coming decades. DME is produced from the variety of feed-stocks such as natural gas, crude oil, residual oil, coal, waste products and bio-mass [1]. Usually, DME is produced directly from syngas and indirectly via methanol dehydration. In the direct method, methanol is produced in the middle of reaction and consumed in dehydration reaction, so methanol does not appear in the final step. Furthermore, direct DME production is a highly exothermic reaction as well as a complicated process. The indirect method is a simple reaction process that uses solid acid catalysts and DME is commercially produced by this method (Eq. (1))

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O, \Delta H_{rxn} = -21.225\ \text{kJ/mol} \qquad (1)$$

Different researchers are shown that the dehydration reaction can take place on the solid–acid catalysts such as γ-alumina, alumina modified with silica and phosphorus, Al_2O_3–B_2O_3 and zeolites materials such as chabazite, mordenite, SAPOs, H-ZSM-5and H-Y in the temperature range of 250–400 °C and pressure up to 18 bar [2–4]. Among these catalysts, γ-alumina and HZSM-5 are extensively studied and they have attracted a great deal of attention as potential catalysts because of their high activity and proper stability [5–9].

Importance of DME has motivated numerous researches to focus on investigation of various catalysts for methanol dehydration reaction. Based on our previous paper [10], the reaction mechanism and kinetic rate equation for methanol dehydration to produce dimethyl ether have been studied, extensively. Except from our recent paper [10], almost the entire rate equations are obtained from the experiments conducted in conditions far away from industrial reactors. Besides, in industrial reactors pure methanol with no water and nitrogen is fed to the reactor in order to meet the highest conversion in presence of commercial catalysts. Therefore, in our previous paper [10], two rate equations for

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Nomenclature

A	vertical surface area (m^2)
C_{ave}	average heat capacity of fluid (J/mol K)
F_{a0}	molar flow rate (mol/s)
k	reaction rate constant (mol/kg-cat s)
K_{eq}	thermodynamic equilibrium constant
K_{cat}	heat conduction coefficient (J/m K s)
P	pressure (bar)
r	reaction rate (mol/kg-cat s)
R^2	mean square error in regression
T	reactor temperature (K)
V	reactor volume (m^3)
WHSV	weight hourly space velocity (g MeOH/g-cat h or h^{-1})
X	methanol conversion
W	catalyst weight (g)

industrial conditions of methanol dehydration process (pure methanol with no water and nitrogen as feed) over industrial γ-alumina (Engelhard Company) and HZSM-5 (SiO_2/Al_2O_3 = 67.6, Zeochem AG Company) catalysts are proposed. In order to extend our earlier results, it is tried to present a simple and new reaction rate equation for methanol dehydration reaction over HZSM-5 catalyst, based on experimental data. The reliability of the derived rate equation is also examined by means of mathematical models. It is worth mentioning that almost all previous papers failed to present a rate equation based on catalyst properties (acidity) and operating parameters (temperature and space velocity). Therefore, part II of this paper attempts to propose such equation as a novel study, in future.

2. Experimental

2.1. Catalyst characterization

The crystallinity and phase purity of the sample are evaluated using X-ray powder diffraction (XRD, PW1840 device, Philips) from $2\theta = 5–90°$ at a step size of 0.02° using of Cu kα monochromatized radiation (tube anode) operated at 40 kV and 30 mA. The Brunauer–Emmett–Teller (BET) surface area is measured by N_2 adsorption–desorption at liquid nitrogen temperature (−196 °C), using a NOVA2200 instrument (Quantachrome, USA). Prior to the adsorption–desorption tests, the sample is degassed at 200 °C for 3 h in the flowing N_2 and under vacuum to remove moisture and any other adsorbates. The surface acidity of the sample is determined using temperature-programmed desorption of ammonia (TPD) using a BEL-CAT PCI 3135 with thermal conductivity detector (TCD). In a typical analysis, 0.097 g of sample is pretreated at 500 °C for 3 h to remove adsorbed water and then was saturated with ammonia at 100 °C for 1 h. The sample is then purged with helium for 50 min to remove weakly adsorbed ammonia from the catalyst surface. The temperature is raised from 96 to 610 °C at the heating rate of 10 °C/min to obtain the desorption curve of NH_3. The morphology of the HZSM-5 individual crystals is observed by scanning electron microscopy (SEM) with TESCAN-VEGA microscope. The chemical compositions of HZSM-5 (Al_2O_3, SiO_2, Na, K, Ca, Mg and Fe) are determined using inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin–Elmer, model THERMO). Fourier transform infrared (FT-IR) spectrum of the catalyst in the range of 400–4000 cm^{-1} is obtained on Verteex89 (Brucker, Germany) using KCl pellet at room temperature.

2.2. Catalytic activity test

The catalytic activity of the sample for the methanol dehydration reaction is measured in a vertical fixed-bed micro-reactor (316 stainless steel, inside diameter (ID = 0.019 m and length = 0.178 m) at atmospheric pressure. Typically, methanol (Grade AA, 99.9 wt.% purity, Fanavaran Petrochemical) is fed into pre-heater to vaporize by pump. The reaction temperature is measured using a stainless steel sheathed thermocouple placed in the core of the catalyst bed. The reaction temperature is ranged from 160 to 400 °C. All the experiments are performed using 3 g of catalyst with the weight hourly space velocity (WHSV) varying from 15 to 90 g of methanol per gram of catalyst per hour (gg^{-1} h^{-1} or h^{-1}) by varying the flow rate of methanol. All data are reported after 5 h on stream. The composition analysis is determined using the gas chromatography (Young Lin, ACME 6100) equipped with a flame ionization detector (FID). A TRB-5 capillary column (30 m × 0.53 mm × 2.65 μm) is used and analysis is conducted under an isothermal condition and temperature of 40 °C for 5 min. The temperature of the effluent line is maintained at 150 °C, to avoid possible condensation of methanol and water. The schematic of the experimental set-up is shown in Fig. 1.

3. Results and discussions

3.1. Textural and acidic properties of the catalyst

The XRD pattern for HZSM-5 is shown in Fig. 2. The XRD result shows that the HZSM-5 sample consisting in crystalline exclusively of the diffraction peaks for MFI structure. The chemical composition of H-ZSM-5 zeolite and the BET results are given in Table 1. The crystal size of HZSM-5 is derived to be 10.79 nm using the Scherrer method. The nature of N_2 adsorption–desorption isotherm for HZSM-5 is represented a type IV and type II curve using the IUPAC classification for hysteresis loops, which are characteristic of

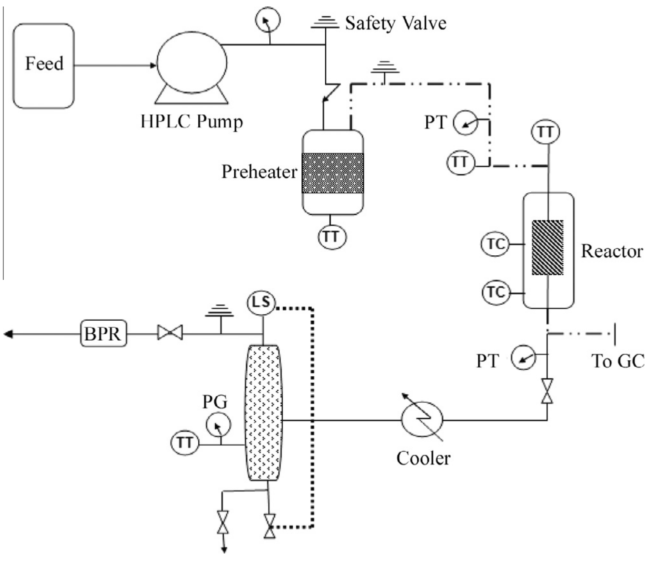

Fig. 1. The set-up of the reactor.

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