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The interaction effects of dehydration function on catalytic performance and properties of hybrid catalysts upon LPDME process

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ABSTRACT

Three bi-functional catalysts have been prepared by physical mixing of a commercial methanol synthesis catalyst (CuO–ZnO–Al₂O₃) with three different methanol dehydration catalysts including: H-MFI90, γ -Al₂O₃ and H-Mordenite in order to investigate the role of interaction effects of dehydration component on characteristic properties and performance of these admixed catalysts. The bi-functional catalysts have been characterized by XRD, N₂ adsorption, H₂-TPR, NH₃-TPD and XRF techniques and tested in a mixed slurry bed reactor at the same operating conditions (T=240 °C, P=50 bar, H₂/CO=2, SV=1100 ml g-cat⁻¹ h⁻¹) for 60 h time on stream. Among the examined bi-functional catalysts, the physical mixture of KMT+HMFI-90, which had lower reducing peak temperature (T=200 °C), higher S_{Cu} (39.1 m² g-cat⁻¹) and Cu Dispersion (11.6%), showed higher X_{CO} (84 mol%), yield of DME (Y_{DME}=55.5 mol%), DME selectivity (Select_{DME}=66.7 mol%) and also good stability over 60 h time on stream as compared to the other catalysts. This could be assigned, from NH₃-TPD results, to more middle strength acidic sites of H-MFI90 zeolite (SiO₂/Al₂O₃=90, total acid site density=476 μ mol/g-cat) which inhibits detrimental interactions with methanol synthesis catalyst and deep dehydration of methanol.

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1. Introduction

Today, due to air pollution and limited crude oil reserves, a clean alternative fuel is desired. Dimethyl ether (DME) is expected to be a high performance alternative fuel for diesel fuel due to its high cetane number and zero content of sulfur. Also it can be used as a high-quality household fuel in place of liquefied petroleum gas (LPG). As a household fuel, DME posses better combustion performance than LPG. DME can also be used as a hydrogen carrier for fuel cells, as aerosol propellants and as refrigerants [1–3]. DME can be prepared from various energy sources including biomass or coal, as well as natural gas. At present, DME is produced in small quantities by methanol dehydration since methanol itself is an expensive chemical feedstock. Recently, direct synthesis of

DME from synthesis gas (syngas) which called STD (syngas to DME) as a new route has attracted many researchers and industrial attention due to possible lower production cost of DME [4,5]. The main reactions included in the STD process can be depicted as follows.

Methanol synthesis reactions:



Methanol dehydration reaction:



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Water gas shift reaction:



By choosing reactions (1) and (4) as independent reactions in methanol synthesis reactions and combination with reaction (3) as dehydration reaction the overall reaction for STD process is as follows:



In the STD process, these reactions occur on a bi-functional catalyst in a reactor. These reactions form a synergistic system that allows higher per pass syngas conversion in comparison with methanol synthesis reaction alone and removes thermodynamic restrictions in the following manner: methanol produced by reactions (1) and (2) is consumed in reaction (3) for the formation DME and water and the water generated in reaction (3) which can limit the rate of reaction (3), is shifted by reaction (4), forming carbon dioxide and hydrogen which in turn are the reactants for methanol synthesis reaction, therefore the products of each step are reactants of the another step [6,7]. Methanol synthesis reactions and water gas shift reaction are catalyzed by standard methanol synthesis catalysts which are mainly a copper–zinc based catalyst. Dehydration reaction (3) is catalyzed over solid-acid catalysts such as zeolite or γ -alumina [8]. The effects of the composition of metallic and acidic functions and also the effects of reaction conditions on the yield and selectivity of DME for STD process have been studied in the literatures [9–12]. In general, there are some problems associated with the acidic function of a bi-functional catalyst in STD process, which mainly related to the number of acidic sites, kind of these sites (Brønsted and Lewis), strength of the acid sites and detrimental interaction between the MeOH synthesis and MeOH dehydration catalysts.

In other words, the reaction of methanol over acid catalysts can lead to the formation of hydrocarbons such as olefins in addition to DME [13]. Most of the researchers have claimed that acid sites of weak or intermediate strength are responsible for the selective DME formation, and the strong acid sites may further convert formed DME to light olefins that finally causes coke deposition and deactivation of catalyst [6,14,15]. Therefore, a dehydration catalyst with the right acidity is crucial to the performance of a dual catalyst system [4,16].

Based on these aspects, the authors tried to develop a suitable bi-functional catalyst through correlation of catalytic behavior and properties of three different hybrid catalysts with the acidity of their corresponding dehydration functions upon LPDME process. These catalysts were made from well physically mixing of three commercial solid acid catalysts, namely H-MFI90 ($\text{SiO}_2/\text{Al}_2\text{O}_3=90$), H-Mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3=45$) and γ - Al_2O_3 , with KMT as commercial methanol synthesis catalyst. Catalysts life time and the effects of different H_2/CO molar feed ratio on the carbon utilization of process were also investigated.

2. Experimental

2.1. Catalyst preparation

Three Bi-functional catalysts were prepared by well physically mixing of the commercial methanol synthesis

catalyst ($\text{CuO-ZnO-Al}_2\text{O}_3$, namely KMT) and three different commercial methanol dehydration catalysts namely H-MFI90 ($\text{SiO}_2/\text{Al}_2\text{O}_3=90$), γ - Al_2O_3 and H-Mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3=45$) powders at a weight ratio of metallic function to acidic one of 3:1 [12]. The resultant powder was molded under pressure to tablets which then were crushed and sieved to particles with size 90–120 μm in order to avoid pore diffusion limitations.

2.2. Catalyst characterization

BET surface area, pore volume and pore diameter was measured by N_2 -physisorption at 77 K using NOVA 2000 Series (Quantachrome, USA). Prior to the adsorption–desorption measurements, all the samples were degassed at 150 °C in N_2 flow for 16 h.

A PW-1800 Philips X-ray diffractometer with monochromatized CuK_α radiation ($\lambda=1.5406 \text{ \AA}$) was used for X-ray measurement. The chemical compositions of catalysts (Cu, Zn, Al, Si and etc.) were determined by X-ray fluorescence. PW-1800 Philips X-ray fluorescence has been used for elemental analyzing.

The acidity of the samples was measured on a micro-meritics 2900 by temperature-programmed desorption of ammonia (NH_3 -TPD) with a conventional flow apparatus which included an on-line thermal conductivity detector (TCD). In a typical analysis, NH_3 -TPD was performed using 0.35 g of the catalyst which was degassed at 600 °C in a helium flow, cooled to 150 °C and then saturated with NH_3 for 15 min. After saturation, the sample was purged with He for 30 min to remove weakly adsorbed NH_3 on the surface of the catalyst. During this time, a constant TCD level was attained. The temperature of the sample was then raised at a heating rate of 5 °C/min from 150 to 700 °C and the amount of ammonia in effluent was measured via TCD and recorded as a function of temperature.

A PulseChemiSorb 2705 was used for performing temperature-programmed reduction (TPR). A 50 mg sample was initially flushed with He flowing 40 cm^3/min as the temperature was increased at a ramp 10 °C/min to 120 °C where it was held for 20 min in order to remove water and effluent. Then 50 cm^3/min of the reducing gas (5.1% H_2 in Ar) was switched on, and the temperature was increased at a ramp of 10 °C/min to 700 °C. The amount of the consumed hydrogen was determined by a thermal conductivity detector (TCD).

The specific surface area of metallic copper was measured by the decomposition N_2O on the metallic copper surface as follows:



The pulse titration technique was employed in test. Ar was used as the carrier gas and the amount of the consumed N_2O was determined by a (TCD). The specific surface area of the metallic copper was calculated assuming a reaction stoichiometry of two Cu atoms per oxygen atoms a Cu surface density of $1.46 \times 10^{19} \text{ Cu atoms/m}^2$ [17].

2.3. Experimental set-up and catalytic tests

A schematic view of the set-up is shown in Fig. 1. In the feed section, the reactants CO , H_2 and nitrogen as the internal

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