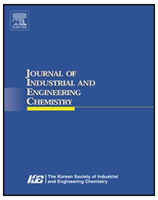
Journal of Industrial and Engineering Chemistry 36 (2016) 169–179

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec



Development of a bifunctional catalyst for dimethyl ether steam reforming with $CuFe_2O_4$ spinel as the metallic function

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ARTICLE INFO

Article history:
Received 26 November 2015
Received in revised form 19 January 2016
Accepted 25 January 2016
Available online 11 February 2016

Keywords:
DME steam reforming
DME hydrolysis
Boehmite
Acid function
Bifunctional catalyst

ABSTRACT

This study aims at optimizing the composition of the bifunctional catalyst with $CuFe_2O_4$ spinel metallic function for the steam reforming of DME (SRD). The γ-Al_2O_3 obtained by calcination of boehmite at 550 °C proves to be the most suitable acid function, given that it provides high activity for DME hydrolysis and avoids hydrocarbon formation in the 300–400 °C range. Furthermore, the optimum mass ratio between $CuFe_2O_4$ and γ-Al_2O_3 functions is 1/1 at 350 °C, since it allows obtaining the highest DME conversion and H_2 yield with suitable catalyst stability and mechanical resistance.

Introduction

The depletion of fossil fuels linked to the increasing global demand of energy has boosted the search of alternative energy sources. Among them, H_2 appears as a clean raw material and energy carrier that can be used in transport and stationary energy generation [1–4]. Over the past decade, dimethyl ether (DME) received considerable attention as a hydrogenated intermediate for producing H_2 by reforming due to its advantages, such as high hydrogen to carbon ratio, high energy density and storage and handling as LPG, and therefore is suitable to be used in fuel cells. Furthermore, it is non-toxic, non-carcinogenic and non-corrosive [5]. Moreover, the single-step synthesis of DME from syngas over a bifunctional catalyst is considered a suitable process for the large-scale valorization of CO_2, given that it is thermodynamically more favored than the synthesis of methanol, and it allows co-feeding CO_2 together with the syngas [6–10]. Another reason for approaching the technological development and industrial implementation of DME synthesis is the increasing availability of methane derived from the exploitation of shale gas resources [11].

The steam reforming of DME (SRD) proceeds over bifunctional catalysts (with metallic and acid functions) and consists of two steps in series:

DME hydrolysis (over the acid function)

$$(CH_3)_2O + H_2O \Leftrightarrow 2CH_3OH \tag{1}$$

MeOH steam reforming (over the metallic function)

$$CH_3OH + H_2O \Leftrightarrow 2H_2 + CO_2 \tag{2}$$

Consequently, the SRD reaction is:

$$(CH_3)_2O + 2H_2O \Leftrightarrow 6H_2 + 2CO_2 \tag{3}$$

Nevertheless, both the metallic and the acid function of the bifunctional catalyst can promote other undesired reactions in parallel, such as: (i) reverse water-gas shift reaction (r-WGS), Eq. (4), which usually takes place on the metallic function; (ii) methane formation, *via* DME decomposition, Eq. (5); (iii) C_{2+} hydrocarbon formation, by means of methanol to hydrocarbons (MTH) reaction, Eq. (6), when a strong acidic function or high temperatures are used [12,13].

r-WGS

$$CO_2 + H_2 \Leftrightarrow H_2O + CO \tag{4}$$

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http://dx.doi.org/10.1016/j.jiec.2016.01.030
1226-086X/

Nomenclature

Abbreviations

d_{pore}	pore diameter (Å)
F_{HC}	molar flow rate of hydrocarbons at the reactor outlet (mol/min)
F_{DME}, $F_{DME,0}$	molar flow rate of dimethyl ether at the reactor outlet and inlet, respectively (mol/min)
F_{MeOH}, $F_{MeOH,0}$	molar flow rate of methanol at the reactor outlet and inlet, respectively (mol/min)
P, P_{DME}	total pressure and DME partial pressure in the feed, respectively (bar)
S_{BET}	BET surface area (m^2/g)
T_C	calcination temperature of boehmite (°C)
V_{pore}	pore volume (cm^3/g)
X_{DME}, X_{MeOH}	conversion of dimethyl ether and methanol, respectively
Y_{H_2}, Y_{HC}	yield of hydrogen and hydrocarbons, respectively

DME decomposition

$$(CH_3)_2O \rightarrow CH_4 + H_2 + CO \qquad (5)$$

MTH

$$MeOH/DME \rightarrow (CH_2)_n + H_2O \qquad (6)$$

Consequently, in order to attain high DME conversion with high H_2 selectivity in the SRD process, the bifunctional catalyst must combine suitable metallic and acid functions, which minimize the formation of CO (a poison for the anode catalyst in PEM fuel cells) and CH_4, and avoid formation of C_{2+} hydrocarbons.

CuO–ZnO–Al_2O_3 (CZA) is the standard catalyst for methanol synthesis and is the most widely studied metallic function for the bifunctional catalysts in SRD due to its high activity and H_2 selectivity in the methanol steam reforming step [14–20]. Nevertheless, its low thermal resistance due to copper sintering above 300 °C [15,18,21] has boosted the development of alternative metallic functions prepared by incorporating different metallic oxides (Fe_2O_4, ZrO_2) [22,23]. Among the new catalysts, $CuFe_2O_4$ spinel appears as a promising metallic function for the SRD process [21,24–26] since it avoids sintering problems of the CZA conventional metallic function, is cheap and gives way to higher selectivity to H_2 in the methanol steam reforming compared to noble metal catalysts [27,28]. Furthermore, $CuFe_2O_4$ spinel has proven to be active in the WGS reaction, which contributes to increasing H_2 yield, Eq. (3) [29].

Nevertheless, $CuFe_2O_4$ spinel has low mechanical resistance, so that a binder is needed to minimize the solid loss by attrition when the catalyst is used in a fluidized bed reactor [21]. Accordingly, boehmite (or aluminum oxyhydroxide, AlO(OH)) appears as a proper choice, since it confers high mechanical resistance upon the $CuFe_2O_4$ spinel [30]. Moreover, after calcination in the 300–700 °C temperature range, the boehmite adopts γ-Al_2O_3 form [31] of moderate acidity. Therefore, the boehmite plays the role of spinel binder and, once it has been calcined, the role of the acid function required in the bifunctional catalyst for DME hydrolysis (the first step of the SRD reaction) [26,32,33]. Nevertheless, due to its moderate acidity, γ-Al_2O_3 requires relatively high temperatures (above 350 °C) [13] for attaining high conversion in DME hydrolysis. Consequently, it is worth considering the addition of different acid solids of higher acid strength to the boehmite in order to improve the kinetic behavior of the acid function in the bifunctional catalyst for the SRD reaction. The mixture of acid functions should enhance the catalytic activity of pure boehmite and avoid hydrocarbon formation, with stability being suitable.

This work deals with the selection of the most suitable acid function, as well as the optimum mass ratio between the metallic and acid functions for the bifunctional catalyst, with $CuFe_2O_4$ spinel metallic function being used in the SRD reaction. The selection of the acid function has been approached by analyzing separately the kinetic behavior (activity/selectivity and stability) of different acid functions for DME hydrolysis reaction, Eq. (1). First, the effect thermal treatment of boehmite has on its porous structure and acidity has been determined, and the kinetic behavior in the DME hydrolysis of boehmite calcined at the optimum temperature (γ-Al_2O_3) has been studied and compared with that of a commercial γ-Al_2O_3. Secondly, an analysis has been carried out on the possible enhancement of the kinetic behavior for DME hydrolysis of γ-Al_2O_3 prepared from boehmite by adding stronger acid solids. The acid solids studied as additives include HZSM-5 zeolites of different SiO_2/Al_2O_3 ratios (30, 80 and 280), both pure and modified by alkali treatments of different severity. For the selection of the optimum mass ratio between the metallic and acid functions, the kinetic performance is analyzed in the SRD reaction for five bifunctional catalysts prepared using different proportions of $CuFe_2O_4$ spinel and the previously selected acid function.

Experimental

Catalysts

Acid functions

Boehmite (AlO(OH)) was provided by Sasol (DISPERAL®) and was calcined in air at different temperatures in a muffle oven (*Thermicon P Heraeous S.A.*) following a heating ramp of 5 °C/min to the established temperature (200, 400, 550, 750 and 900 °C), which was kept constant for 2 h. The commercial γ-Al_2O_3, studied for comparison, was provided by Merck. The ZSM-5 zeolites (SiO_2/Al_2O_3 = 30, 80 and 280, denoted Z30, Z80 and Z280, respectively) were supplied in their ammonium form by Zeolyst International. The modified ZSM-5 zeolites (denoted A2Z30 and A4Z30) were prepared by alkaline treatment of the commercial Z30 zeolite (at 80 °C for 300 min with 0.2 and 0.4 M NaOH solutions, respectively), by following the method described elsewhere [13,34]. The acid form of the parent zeolites and the alkali treated zeolites were obtained by calcination in a muffle oven (*Thermicon P Heraeus, S.A.*) at 550 °C for 3 h, following a previously described heating sequence [13].

The hybrid acid functions were prepared by mixing boehmite with the other acid solids (Z30, Z80, Z280, A2Z30 and A4Z30), with boehmite/acid solid mass ratio being 80/20. The resulting catalyst particles were prepared by wet extrusion and sieved to a 90–250 μm particle size. The solid was finally dried at 110 °C for 40 h and subsequently calcined at 550 °C for 2 h, so that boehmite adopted γ-Al_2O_3 form. These hybrid acid functions are denoted with letter B followed by the symbol of the corresponding acid solid.

Bifunctional catalysts

The $CuFe_2O_4$ spinel metallic function was prepared by sol-gel method, with $Cu(NO_3)_2{\cdot}3H_2O$ (*Panreac*), $Fe(NO_3)_3{\cdot}9H_2O$ (*Panreac*) and citric acid ($C_6H_8O_7$) as reactants [21]. The resulting spinel was calcined at 900 °C for 10 h, agglomerated by wet extrusion with the binder boehmite in different mass proportions and calcined for 2 h at 550 °C in order to obtain the γ-Al_2O_3 form of boehmite, which acts as the acid function in the bifunctional catalyst. The selection