



Improving the DME steam reforming catalyst by alkaline treatment of the HZSM-5 zeolite

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ABSTRACT

Dimethyl ether (DME) steam reforming for hydrogen production has been studied on a bifunctional catalyst prepared by the (wet) physical mixing (at 50 wt%) of a metallic function of CuO–ZnO–Al₂O₃ (Cu/Zn/Al atomic ratio = 4.5:4.5:1.0, prepared by co-precipitation) and an acidic function of HZSM-5 zeolite modified by alkaline treatments of different severity. The runs have been carried out in a fluidized bed reactor. The results obtained by using treated HZSM-5 zeolites and γ -Al₂O₃ as acid functions have been compared. The alkaline treatment affects both the acid properties of the zeolite (attenuating total acidity and acid strength) and its porous structure (increasing the mesoporous surface and decreasing the microporous volume and BET surface area). The attenuation in acidity hinders the formation of undesired hydrocarbons from oxygenates (methanol + DME). Consequently, alkaline treatment (with 0.2–0.4 M NaOH solutions for 300 min) is suitable for improving the kinetic performance of the bifunctional catalyst, as it provides high selectivity and a high yield of H₂ at 300 °C without hydrocarbon formation, as well as minimizing CO formation and avoiding deactivation by Cu sintering. The catalyst is stable, and its kinetic performance remains constant throughout long runs.

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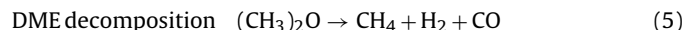
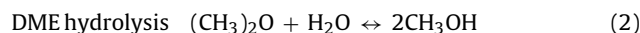
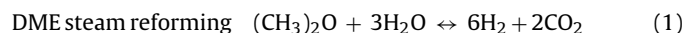
1. Introduction

Hydrogen is considered a suitable fuel to meet ever-increasing energy demand because it may be produced from renewable sources [1]. Hydrogen fuel cells are presented as an efficient and environmentally friendly power generator applicable to both mobile and stationary use [2]. Although hydrogen has a high fuel density, it is difficult to handle and, therefore, a hydrogen vector (e.g., methanol, ethanol, gasoline, diesel and methane) needs to be used for H₂ production for fuel cell processors by means of reforming processes.

Methanol can be easily and selectively converted into an H₂-rich gas at low temperature (150–300 °C) by steam reforming [3] and, therefore, it is an excellent raw material for on-board H₂ production for PEM fuel cells. However, the infrastructure for processing methanol is not well developed and methanol toxicity is high. The reforming of dimethyl ether (DME) is an alternative of growing interest [4–11], given that DME is relatively inert, non-corrosive, non-carcinogenic and can be stored and handled as LPG, which means it is more readily used as a fuel and in fuel cells [12]. DME synthesis from syngas in a single step on bifunctional catalysts is thermodynamically more favoured than methanol synthesis and,

moreover, CO₂ can be co-fed together with the syngas [13–15]. Accordingly, Olah et al. [16] consider DME synthesis in a single step as a key process for large-scale CO₂ valorization. Furthermore, DME has also attracted increased attention as a clean fuel.

The main reactions in the process of DME steam catalytic reforming are:



Steam reforming of DME (SRD) (Eq. (1)) consists of two steps in series: DME hydrolysis (Eq. (2)) on an acid function and methanol steam reforming (Eq. (3)) on a metallic function. Apart from SRD, a reverse water-gas shift reaction (r-WGS) (Eq. (4)) usually takes place on the metallic function, and methane is also formed via DME decomposition (Eq. (5)) when a strong acidic function or high temperatures are used [7]. Consequently, suitable metallic and acid functions are required for attaining high DME conversion and high H₂ selectivity by avoiding the formation of CO (poison for the anodic catalyst in PEM fuel cells) and CH₄ as byproducts.

Cu-based catalysts are well known for their high activity for methanol steam reforming and selectivity towards H₂ [17].

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Nomenclature

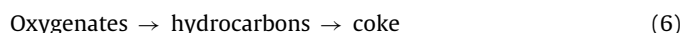
A0.2-10, A0.2-300, A0.4-300	HZ30 zeolites treated with 0.2 M NaOH for 10 min, 0.2 M NaOH for 300 min and 0.4 M NaOH for 300 min, respectively
ALU	γ -Al ₂ O ₃ acid function
Br	Brønsted acid sites
CZA	CuO–ZnO–Al ₂ O ₃ metallic function
CZA/ALU, CZA/HZ30, CZA/A0.2-10, CZA/A0.2-300, CZA/A0.4-300	bifunctional catalysts made up of CuO–ZnO–Al ₂ O ₃ and different acid functions: ALU, HZ30 zeolite or zeolites treated with alkali (A0.2-10, A0.2-300, A0.4-300), respectively
\bar{d}_{Cu}	average particle size of Cu (Å)
DME	dimethyl ether
d_{pore}	pore diameter (Å)
DSC	digital scanning calorimetry
$F_i, F_{i,0}$	molar flow rate of <i>i</i> component at the reactor outlet and in the feed, respectively
GHSV	gas hourly space velocity
HC	hydrocarbons
HZ30	parent (untreated) HZSM-5 zeolite
Lw	Lewis acid sites
MeOH	methanol
MTG, MTH, MTO	methanol to gasoline, methanol to hydrocarbons and methanol to olefins, respectively
PEM	polymer electrolyte membrane
P_i	partial pressure of <i>i</i> component (bar)
r-WGS	reverse water-gas shift reaction
S_{BET}	BET surface area of the solid (m ² /g)
S_{external}	external surface area of the solid (m ² /g)
S_{metallic}	specific metal surface area (m ² Cu/g Cu)
$S_{\text{micropore}}$	micropore surface area (m ² /g)
SRD	steam reforming of dimethyl ether
TPD	temperature programmed desorption
TPR	temperature programmed reduction
$V_{\text{mesopore}}, V_{\text{micropore}}$	mesopore and micropore volume (cm ³ /g)
X_{DME}	DME conversion
x_i	<i>i</i> component molar fraction
X_{MeOH}	methanol effective conversion in the second step of the SRD process
XRD	X-ray diffraction analysis
XRF	X-ray fluorescence spectroscopy
Y_i	yield of <i>i</i> component
ν_i	stoichiometric coefficient of <i>i</i> component

Accordingly, commercial or laboratory synthesized CuO–ZnO–Al₂O₃ metallic functions have been widely used in the bifunctional catalysts for SRD [6,18–22]. Other Cu-based metallic functions studied for SRD include Cu–CeO₂ [23–25] and Cu–Ni [26]. Noble metal based catalysts, such as Pt/Al₂O₃ or Ru/Al₂O₃, give way to a relatively high DME conversion, although a rather high production of CH₄ is obtained [11]. The formation of CH₄ (up to 25%) can be significantly reduced (to 7%) by mixing Pt/Al₂O₃ catalysts with Pd/Al₂O₃, with no loss in hydrogen production activity [27].

The choice of acid function is essential for the development of catalysts for SRD, given that hydrolysis is the process limiting step. γ -Al₂O₃ is the more commonly used catalyst [4,8–10,18,26,28], but due to its very low acidity, high temperatures (usually in the 300–400 °C range) are required for high DME conversion, with considerable sintering of the Cu metallic function at these temperatures. Spinel has been proposed for improving the stability of Cu metallic functions above 300 °C, and a spinel of CuM₂O₄

(M = Fe, Mn, Cr, Ga, Al and others) has greater stability than a commercial CuO–ZnO–Al₂O₃ metallic function [8–10,28]. It has also been proven that Ni addition attenuates Cu sintering, given that it improves surface dispersion and strengthens the interaction between Cu and γ -Al₂O₃ [26].

However, the use of γ -Al₂O₃ as an acid function for SRD has the additional inconvenience of promoting DME decomposition and the r-WGS reaction due to the high temperatures required for DME hydrolysis and, therefore, the formation of significant amounts of CH₄ and CO, which is a handicap for PEM fuel cells, given that CO concentrations lower than 50 ppm are required for avoiding anodic catalyst poisoning [29]. As an alternative to γ -Al₂O₃, acid functions of higher acidity have been proposed, such as 12-tungstosilicoheteropolyacids (H₄SiW₁₂O₄₀) deposited on γ -Al₂O₃ [30], WO₃/ZrO₂ [21,24,25], H-mordenite or HZSM-5 zeolites [5–7,20,22,23,31–33]. HZSM-5 zeolites are much more active for DME hydrolysis and allow obtaining high yields of H₂ at considerably lower temperatures (around 100 °C lower) than those required with γ -Al₂O₃ [5,6]. Nevertheless, due to their excessive acidity, they give way to hydrocarbons at temperatures close to 300 °C, which significantly reduces H₂ yield [7,31,32], and significant coking (deactivated catalyst) also occurs on the catalyst surface due to the condensation of the hydrocarbons formed [20]:



This paper studies the attenuation of HZSM-5 zeolite acidity by alkaline treatment (with NaOH) and the effect of treatment conditions on the physical–chemical properties of the zeolite. Likewise, the effect of this alkaline treatment is determined on the kinetic performance of: (i) the zeolite in DME hydrolysis (Eq. (2)) and (ii) the bifunctional catalyst (with CuO–ZnO–Al₂O₃ metallic function) prepared using different treated zeolites in the reforming of DME (Eq. (1)) and methanol (Eq. (3)), and in the formation of undesired byproducts, i.e., CO (Eq. (4)), CH₄ (Eq. (5)) and hydrocarbons (Eq. (6)). The study of coke deposition (second step in the scheme in Eq. (6)) is beyond the scope of this paper.

An alkaline treatment of the HZSM-5 zeolite is efficient for improving the kinetic behaviour and stability of the zeolite by attenuating acidity and mesopore generation. Accordingly, the condensation and coke formation reactions are attenuated in several processes, such as the transformation of methanol into olefins [34], the direct hydroxylation of benzene to phenol [35] and the selective transformation of aqueous ethanol into olefins [36,37].

2. Experimental

2.1. Catalyst synthesis

The bifunctional catalysts have been prepared by the wet physical mixing of CuO–ZnO–Al₂O₃ metallic function (called CZA, Cu/Zn/Al atomic ratio = 4.5:4.5:1.0), prepared by coprecipitating the corresponding nitrates with Na₂CO₃ at pH = 7.0 and 70 °C under conditions established in previous papers [38,39] and calcined at 325 °C for 3 h, and different acid functions, namely, γ -Al₂O₃, commercial HZSM-5 zeolite and HZSM-5 zeolites modified by different alkaline treatments. The homogeneous mixtures obtained are centrifuged to separate the solid, which is dried, firstly at ambient temperature for 24 h and then in an oven at 110 °C for another 24 h. The powder obtained is calcined at 325 °C for 3 h and subsequently pressed, ground and sieved to a particle size between 0.15 and 0.25 mm, which is suitable for a fluidized bed reactor. The content of the acid function is 85 wt% for the bifunctional catalyst with γ -Al₂O₃ and 50 wt% for the bifunctional catalysts with zeolite.

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