



Synthesis of methanol using copper-*f* block element bimetallic oxides as catalysts and greenhouse gases (CO₂, CH₄) as feedstock



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ARTICLE INFO

Article history:

Received 22 April 2016

Revised 9 June 2016

Accepted 10 June 2016

Keywords:

Methanol

CO₂ and CH₄

Copper

f block elements

Intermetallic compounds

ABSTRACT

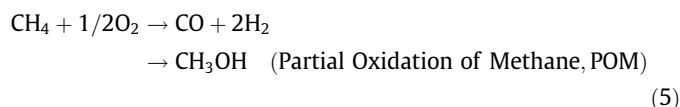
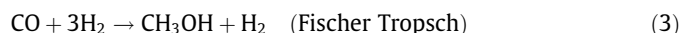
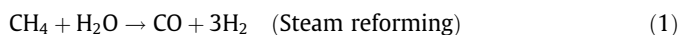
The study of methanol production using copper-*f* block element bimetallic oxides as catalysts was undertaken. Carbon dioxide and hydrogen were used as reagents, but the addition of methane to this mixture was also studied. Catalysts were obtained by two methods: (i) Controlled oxidation of binary copper-*f* block element intermetallic compounds (IC) to obtain IC bimetallic oxides and (ii) impregnation followed by controlled oxidation to obtain copper-*f* block element oxide catalysts supported on alumina. Both types of catalysts proved to be more active for the production of methanol than a commercial Cu based catalysts (Alfa Aesar, 45776-0500). The selectivity is also very high (>90%), but the incorporation of CH₄ to the feedstock has a negative effect on the catalyst behavior. The best result was that obtained with copper-cerium IC bimetallic oxide, its intrinsic activity ($\approx 900 \text{ mL}_{\text{CH}_3\text{OH}}/\text{m}^2_{\text{Cu}}\text{h}$) is 2–9 times higher in comparison with the numbers reported in the literature. To our knowledge, copper-*f* block element bimetallic oxides were never tested for the synthesis of methanol and the results herein reported are new and among the best reported until now.

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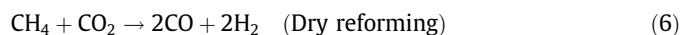
1. Introduction

The synthesis of methanol from CO₂ is particularly interesting, not only as a way to mitigate this greenhouse gas, but also due to the potential of CO₂ as an alternative and economical feedstock for the production of value-added chemicals [1–3]. Therefore, the activation of CO₂ and its hydrogenation to alcohols or other hydrocarbon compounds address simultaneously two internationally important issues: recycle of CO₂ and depletion of fossil fuels [4].

On the other hand, methane is an available and abundant feedstock, main component of natural gas that can be converted to syngas (hydrogen and carbon monoxide) and commercially used to produce methanol in two steps [5]: (i) Step 1, natural gas is converted into mixture of carbon monoxide, carbon dioxide and hydrogen (Eqs. (1) and (2)); and (ii) Step 2, synthesis gas is catalytically converted into methanol (Eqs. (3) and (4)). Conventional steam reforming is the simplest and commonly used route to synthesis gas production, but this process results in an excess of hydrogen. Methanol could be also produced through the partial oxidation of methane (Eq. (5)).



Alternatively, dry reforming of methane could be also a valuable option in the case of natural gas sources containing substantial amounts of CO₂ and any excess of hydrogen produced during conventional steam reforming could react with carbon dioxide or be added to the dry reforming to, ideally, produce more methanol (Eqs. (6) and (7)).



The potential use of methanol as fuel is also well known [6]. Many research groups are working on a single stage process for the manufacture of methanol. The partial oxidation route (Eq. (5)) offers a single step reaction and the advantage of directly converting methane to methanol [7,8,2]. Studies for a single step reaction via

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dry reforming are scarce and to our knowledge limited to the production of C2 hydrocarbons (ethylene, ethane) [9].

In the last decades, several reviews addressing the synthesis of methanol have been reported in the literature [10–14]. Liu et al. [10] reviewed the advances in catalysts for methanol synthesis via hydrogenation of CO and CO₂; Wang et al. [11] briefly discussed methanol production from CO₂; Waugh [12], Ganesh [13] and Vaidya et al. [14] present a comprehensive overview of important investigations on CO₂ conversion to methanol. Methanol is typically produced over copper based catalysts (Cu/ZnO/Al₂O₃) at high pressures (50–100 bar) and temperatures of a few hundred degrees C (200–300 °C). However, the preparation of catalytically active “copper catalyst” as well as the nature of their active site is, even today, not entirely understood [15]. Industrial Cu/ZnO-based catalysts are prepared by a co-precipitation method [16], which creates porous aggregates of Cu and ZnO nanoparticles (NPs), with size around 10 nm and large Cu surface area, up to ~40 m² g⁻¹ when enriched copper molar compositions (Cu:Zn ~ 70:30) are used [17]. Industrial catalysts contain low amounts of a refractory oxide as structural promoter [18], in most cases up to ~10% Al₂O₃ in their composition, and their activity depends both on the specific area and Cu accessibility. Activity, normally increases with both parameters [19,20]. Methanol synthesis over Cu appears to be also a structure-sensitive reaction [16,21,22]. Another important factor is the presence of ZnO, which is responsible for the increase in the activity of Cu-based methanol synthesis catalysts [23,16]. ZnO has the function of a physical spacer between Cu nanoparticles, which helps its dispersion during the catalyst preparation and favors the synthesis of Cu catalysts with high surface areas [17].

It is also known that the role of CO is that of a reducing agent (formation of metallic Cu). Furthermore, it was also observed that the addition of CO₂ to the syngas gaseous feed increases methanol yield. CO₂ can be added up to 30% to the syngas mixture [24] and today much efforts address the conversion of pure CO₂ to methanol. However, as reported by Klier et al. [25] the production of methanol is promoted even with low concentrations of CO₂ in CO/H₂ gaseous feed, but high concentrations of CO₂ have an inhibited effect. Chinchin et al. [26] using isotope-labeled ¹⁴CO₂ confirmed that most of the methanol was produced from CO₂, whereas Sahibzada found that it is not the excess of CO₂ that is responsible for inhibition of methanol synthesis [27]. Instead it is the progressive and increased formation of water (Eq. (4)) that inhibits the formation of methanol at high concentrations of CO₂. Recently, the active sites for the activation of CO₂ and synthesis of methanol over Cu/ZnO/Al₂O₃ were identified [15]. They consist of Cu steps decorated with Zn atoms, where the synergism between copper and zinc oxide phases is responsible for a dramatic increase in the interaction with CO₂ (the interaction of Cu alone with CO₂ is very poor) that accelerates its transformation into methanol.

Efforts have been also made to modify and improve the industrial Cu/ZnO/Al₂O₃ catalyst. As an example, CuO/ZnO/Al₂O₃ catalyst activity can be improved by the addition of Pd and the effect was attributed to the existence of a hydrogen spill over mechanism [14,28]. Clearly, methanol synthesis via hydrogenation of CO₂ remains a top issue and more recently many efforts have been also put on the development of catalysts capable of operating at low temperature and near atmospheric pressure [29,30]. However, this approach is clearly not in the scope of this work.

It was also found that catalyst composition and catalyst preparation methods have huge influence on their catalytic behavior [31]. So many other catalysts were tested for the production of methanol [32–34]. Wang et al. [32] studied the behavior of CuO/CeO₂/ and CuO/YDC/ supported on alumina (YDC means yttria-doped ceria) and found that they are more active than the classical

CuO/ZnO catalyst, which was attributed to a synergistic effect between CuO and surface oxygen vacancies of CeO₂. Mao et al. [33] studied a series of Cu/ZrO₂ catalysts and found that the presence of La favors the production of methanol and that selectivity to methanol correlates with the distribution of basic sites on the catalysts surface. Sun et al. [34] studied the conversion of CO₂ to methanol over a series of La-M-Cu-Zn-O (M = Y, Ce, Mg, Zr) based perovskite-type catalysts and found that all catalysts are highly selective to methanol.

Therefore, the presence of *f* block elements on copper-based catalysts seems to improve the production of methanol. Actinides and lanthanides oxides were already studied with success in the partial oxidation of methane and other catalytic reactions evolving hydrocarbons [35–42] and the important role of *f* block element oxides as catalytic promoters and stabilizers is well established [43]. Therefore, actinides and lanthanides bimetallic oxides are promising candidates as catalysts for the conversion of methane and carbon dioxide into value-added chemicals, but their use for the production of methanol is, to our knowledge, scarce [32–34,41].

In our laboratories we have used binary intermetallic compounds of the type LnCu₂ (Ln = La, Ce, Pr, Nd) [44], LnNi (Ln = Pr, Gd, Lu) [45], ThCu₂ and AnNi₂ (An = Th, U) [46] as copper or nickel-lanthanide or actinide bimetallic oxide catalytic precursors (e.g., 3CuO·Ln₂CuO₄ or 2MO·AnO₂, M = Cu, Ni). The bimetallic nickel-*f* block element oxides were tested in the partial oxidation of methane (POM) [47,48] and both systems demonstrated to be very active and selective for the production of synthesis gas (CH₄ conversions ≈80% and selectivity to H₂ and CO ≈80% at 750 °C). More recently, the production of light hydrocarbons (ethane and ethylene) was successfully achieved using methane as feedstock and nitrous oxide as oxidizing agent over bimetallic copper or calcium or nickel actinide oxides (Th, U) [49,50] and potassium-lanthanide chloride molten salts (KCl–LnCl₃, Ln = La, Ce, Sm, Dy and Yb) [51]. In common, all these systems have the existence of a synergism between the transition metal (Ca, Cu, Ni) and the *f* block element, that influences their catalytic behavior.

Herein, we present the behavior of two types of copper based catalysts for the production of methanol using CO₂ and H₂ as main reagents. The addition effect of CH₄ to this mixture was also studied. The first type of catalysts was obtained by controlled oxidation of copper binary intermetallic compounds (CeCu₂ and ThCu₂) and the products are IC bimetallic oxides of the type 2CuO·MO₂ (M = Ce, Th), whereas the second type of catalysts was obtained by co-precipitation replacing ZnO in the industrial Cu/ZnO-based catalysts by an *f* block element oxide (2CuO·MO_x·Al₂O₃; M = Ce, Th). All products were characterized by powder X-ray (XRD), nitrogen absorption (specific surface area, BET), H₂ temperature-programmed reduction (H₂-TPR), CO₂ temperature programmed desorption (CO₂-TPD), N₂O reactive chemisorption and scanning electron microscopy (SEM), complemented with energy dispersive X-ray spectrometry (EDS).

2. Experimental

Intermetallic compounds (IC) containing Cu and *f* block elements (LnCu₂, Ln = La, Ce and ThCu₂) were prepared by direct melting of stoichiometric amounts of the elements (Goodfellow foil, Cu 99.99+%; La, Ce 99.9%; Th 99.5%) in a homemade arc furnace equipped with a water-cooled copper crucible under dynamic high vacuum (10⁻⁵ torr). The melting process was repeated at least three times in order to ensure a perfect homogeneity. The weight losses were less than 0.5 wt.%. No further thermal treatment was needed, e.g. annealing, since all compounds melt congruently. The 2–5 g ingots were kept under nitrogen inside a glove box (H₂O and O₂ contents < 5 ppm).

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