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Short communication

Methanol synthesis over binary copper-ƒ block element intermetallic compounds

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A B S T R A C T

$LnCu_2$ (Ln = La, Ce, Gd, Tm) binary copper-ƒ block element intermetallic compounds were tested as catalysts for the production of methanol using greenhouse gases (CO_2 and CH_4) as feedstock. The best results were obtained with $PrCu_2$ and $LaCu_2$, which are more active for the production of methanol than a commercial Cu based catalyst (Alfa Aesar, 45776-0500) using $CO_2 + H_2$ (1:3) or $CH_4 + CO_2 + H_2$ (1:1:3) in the feed composition. The selectivity is also very high (>80%), but the incorporation of CH_4 to the feedstock has a negative effect on the catalyst's behavior. $LnCu_2$ also present a remarkable long term stability for at least 50 h on the gaseous stream. To our knowledge, the results herein described are among the best reported until now.

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1. Introduction

Among reactions that consumes CO_2, the dry reforming with CH_4 ($CO_2 + CH_4 \rightarrow 2CO + 2H_2$) offers a route for the conversion of large amounts of CO_2 and production of syngas [1,2]. This product can be subsequently used to yield other valuable products, namely: sulphur free diesel {$nCO + (2n + 1)H_2 \rightarrow CnH(2n + 2) + nH_2O$} and methanol {$CO + 2H_2 \rightarrow CH_3OH$}. The most active catalysts for the syngas production contain either Ni, Co or noble metals in its composition. A review of these catalysts was carried out elsewhere [2].

One of the main problems with the dry (CO_2) reforming of methane (DRM) is the risk of catalyst deactivation due to coke deposition. DRM is also a highly endothermic reaction ($\Delta H_{298K} = 247.3$ kJ/mol) and requires operating temperatures of 800–1000 °C to attain high equilibrium conversion of CH_4 and CO_2 to syngas. The addition of promoters to the catalysts is an effective way to improve performance and stability. The promotion effect of rare earths on Fischer-Tropsch catalysts, enhancing the dispersion of the catalysts active phase, which increases the amount of active sites on the catalyst, has been extensively described [3,4].

For what concerns the synthesis of methanol, the ICI process (1966) was the last major development: Cu-based catalysts were developed to replace the Zn catalysts used since 1923 (BASF process). Commercially, the production of methanol involves the steam reforming of CH_4 and

production of syngas over Ni catalysts at moderate pressures (40 bar) and high temperature (850 °C), followed by the reaction of the syngas over a second catalyst (mixture of $Cu/ZnO/Al_2O_3$), the ICI process, at elevated pressure (50–100 bar) and temperature (200–300 °C) [5]. Both reactions involve moderate or high pressure. As such, the development of catalysts which would be able to operate in more friendly conditions (less danger, but also less expensive conditions) and possessing the ability to produce methanol in only one step using CO_2 and CH_4 as raw materials is a major goal of considerable importance.

However, the preparation of active "copper catalyst" as well as the nature of the active sites on these high-performance catalysts is, even today, not completely understood [6]. Industrial Cu/ZnO-based catalysts are prepared by a co-precipitation method [7], which creates porous aggregates of Cu and ZnO nanoparticles (NPs, with size around 10 nm and large Cu surface area, up to ~40 $m^2\ g^{-1}$) when enriched copper molar compositions (Cu:Zn ~70:30) are used [8]. Furthermore, industrial catalysts contain low amounts of a refractory oxide as structural promoter [9], in most cases Al_2O_3 up to ~10% in their composition.

Research for alternative catalysts operating at lower pressures and temperatures has mainly been focused in the preparation of other Cu-based catalysts. An important impact on its performance comes from the use of copper catalysts with high specific surface areas and highly accessible Cu [10]. Indeed, it was observed that the catalyst's activity for samples having a similar preparation increase linearly with the catalysts surface area, Cu content and accessibility. So, the active phase is believed to be linked to metallic Cu [11]. Another important factor is the presence of ZnO, which is responsible for the increase of the intrinsic

activity of Cu-based methanol synthesis catalysts [7,12]. 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 [8]. On the other hand, the existence of a synergism between copper and zinc oxide phases is also responsible for increases in the interaction with CO_2 (the interaction of Cu alone with CO_2 is very poor) that accelerates its transformation into methanol [6]. In this context, actinides and lanthanides oxide based catalysts have been used as catalytic promoters and stabilizers for the partial oxidation of methane and other catalytic reactions evolving hydrocarbons [13–18] and their contribution is also associated to synergetic interactions with the catalysts main active phases [19]. However, their use as catalysts for the production of methanol is, to our knowledge, scarce [17].

The synthesis of methanol using binary copper–*f* block element intermetallic compounds as catalysts was evaluated in the past by several authors using CO and H_2 as reagents [17,20,21]. These studies shown that copper intermetallic compounds are active for the synthesis of methanol, but it was also reported that: i) the addition of CO_2 decreases the catalyst activity and selectivity to methanol; ii) catalysts decompose during reaction, leading to the formation of *f* block element oxides and metallic copper to which their catalytic behavior was ascribed. The activation of Cu-lanthanide catalysts has been described in detail by Owen et al. [22] and, in particular, the activation of copper-thorium samples leads to catalysts containing copper interspersed on ThO_2 that are 6–7 times more active for the production of methanol than the traditional $Cu/ZnO/Al_2O_3$ ICI catalyst at 280 °C and 60 atm pressure. The values reported for copper-thorium catalysts are among the best reported so far. Moreover, under typical synthesis conditions, copper–*f* block element catalysts are not only more selective than conventional catalysts, but they also produce less water and lower concentrations of higher alcohols as by-products. So, the catalytic behavior of copper–*f* block elements alloys and intermetallic compounds is inspiring but remains largely unexplored, with most of the work being done in the 80s and 90s of last century.

In our group, studies of the synthesis of binary intermetallic compounds with *f* block elements have been carried out aiming applications in different areas such as catalysis and the understanding of the lanthanide or actinide effect on the catalytic activity. In particular, binary copper or nickel–rare earth (La, Ce, Pr, Nd, Gd, Dy and Yb) intermetallic compounds and the corresponding bimetallic oxides proved to be active as heterogeneous catalysts for the activation of methane and production of syngas or C_2 hydrocarbons (ethylene and ethane) [14,15,18,23]. Their behavior is competitive either in terms of activity or selectivity when compared with commercial noble metal catalysts (Rh, Pt). Such catalysts were also successfully employed on the hydrogenation of propionitrile to the primary amine (so far nitrile hydrogenation over Cu catalysts yields exclusively secondary amines) in the gas phase using copper based catalyst ($LnCu_2$ and bimetallic oxides ($3CuO·Ln_2CuO_4$, Ln = La, Ce, Pr and Nd)) [14,24]. All these systems have in common the existence of a synergism between an alkaline earth metal or a transition metal (Ca, Cu, Ni) and the *f* block element, that influence their catalytic behavior. Herein, we present the behavior of binary copper-*f* block element intermetallic compounds ($LnCu_2$, Ln = La, Ce, Gd, Tm) as catalysts for the production of methanol using different feed compositions with CO_2, CH_4 or H_2. For comparison purposes, the behavior of a Cu commercial catalyst was also tested under the same conditions.

2. Experimental

Intermetallic compounds (IC) containing Cu and *f* block elements ($LnCu_2$, Ln = La, Ce, Gd, Tm) were prepared by the direct melting of stoichiometric amounts of the elements (Goodfelow, foil, Cu 99.97 + %; La, Gd, Tm 99%, Ce 99.9%) 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 homogeneity. The weight losses were <0.5 wt%. No further thermal treatment was needed, e.g. annealing, since all compounds melt congruently. After melting, the 2–5 g ingots were kept under nitrogen inside of a glove box (H_2O and O_2 contents < 5 ppm).

Specific surface areas (BET method; single point relative pressure P/P_0 = 0.3 using a mixture of 30% nitrogen in helium (flow 20 mL/min) were obtained on a Micromeritics ChemSorb 2720 instrument equipped with a high temperature module option (APX). Prior to measurements, all samples were degassed at 250 °C for 2 h under N_2. H_2-chemisorptions, including quantification, were also recorded on this instrument under a 10%H_2/argon mixture (flow 20 mL/min). H_2 chemisorption was estimated from the chemisorption of H_2 at −80 °C and was calculated from a two-step analysis consisting of (i) H_2 absorption at −80 °C and (ii) H_2 desorption, increase of temperature until room temperature (20 °C). Quantitative H_2-uptakes were evaluated by integration of the experimental profiles, basing on previous calibration measurements with CuO powder (Aldrich, 99.99995% purity). Before analysis, all intermetallic samples were cleaned with a pure He stream (50 mL/min) at 150 °C, 2 h. In the case of the commercial Cu based catalysts for methanol synthesis (Alfa Aesar, 45776-0500) its copper oxide phase was selectively reduced to Cu under a 10%H_2/argon mixture (0–500 °C, at 10 °C/min, flow 20 mL/min) before the H_2 chemisorption studies. The empty reactor (a glass lined U-tube) was found not to give any desorption of H_2 within the limits of detection. Cu metal surface areas, crystallite sizes and Cu dispersion were calculated from the volume of H_2 chemisorbed using the simplified equations described elsewhere [25, 26]. We have use also 0.0711 nm^2 and 8.92 g cm^{-3} as the average surface area per atom and density of Cu, respectively [27]. XRD patterns were obtained in reflection geometry with a PANalitycal X'Pert Pro diffractometer using Cu, kα monochromatic radiation (λ = 1.5406 Å). The operational settings for all scans were: voltage = 40 kV; current = 35·mA; 2θ scan range 19–80° using a step size of 0.03° at a scan speed of 0.003°/s. For identification purposes, the relative intensities (I/I_0) and the *d*-spacing (Å) were compared with standard JCPDS powder diffraction files [28]. Rietveld refinements were performed by fitting the peaks in the XRD patterns using Powdercell 2.3 software and used to determine the $LnCu_2$ binary intermetallic compound's crystallite size and strain.

Catalytic tests were carried out in a U-shaped stainless steel reactor (316S), plug flow type reactor (350 mm length, 12 mm external diameter, 8 mm internal diameter), with a fixed bed (Pyrex wool) and an inside volume of 17.5 cm^3. Catalysts grain size distribution was controlled using a 200 Mesh sieve (0.074 mm), m = 30–90 mg, catalytic bed height ≤ 1 mm. Mass flow controllers (Bronkhorst, EL-flow series) were used to control CH_4 (Air Liquide, purity 99.9995%), CO_2 (Air Liquide, purity 99.9995%), H_2 (Air Liquide, purity 99.9995%) flows and He (Air Liquide, purity 99.9995%) flows, whereas the reactor outlet pressure was controlled using a Bronkhorst EL-press series digital electronic pressure controller. Unless otherwise stated, gaseous mixtures of CO_2/H_2 (1:3 mol/mol) or $CO_2/H_2/CH_4$ (1:3:1 mol/mol/mol) were tested with an adequate Gas Hourly Space Velocity (GHSV, mL of CO_2 per g of catalyst per h) of 5000–40,000 mL CO_2/g_{Cat}·h (typically 40,000). Other reaction standard conditions include 50 bars for the pressure and 250 °C for the reaction temperature. The reactor outlet gas composition was online analyzed by gas chromatography using two Agilent systems: first, 7820 A GC equipped with a flame ionizing detector (FID) and a HP-PLOT-U capillary column (L = 30 m, 1/8 in., ID = 0.32 mm) for the detection of methanol and other condensable products and, second, 4890D GC equipped with a thermal conductivity detector (TCD) and a Restek ShinCarbon ST column (L = 2.0 m, 1/8 in., ID = 1 mm, 100/200 mesh) for the detection of all gaseous reagents and products. Each system uses a 6-port gas sampling valve with a 0.250 μL loop. Additionally, before TCD analysis the outlet gas was cooled in an ice-water trap in order to avoid column contamination, namely by water. Unless stated