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Co–Cu–La catalysts for selective CO_2 hydrogenation to higher hydrocarbons

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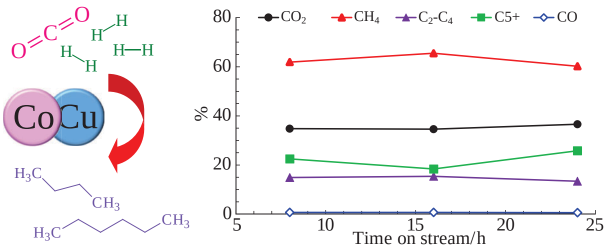
Copper and lanthanum promoted cobalt catalysts for CO_2 hydrogenation to higher hydrocarbons are described. The catalysts were prepared by the self-propagating high-temperature synthesis followed by alkaline leaching. They are active in CO_2 hydrogenation at 200 °C under 10 bar pressure ($CO_2 : H_2 = 1 : 3$) with selectivity to C_{2+} alkanes up to 39%; no alkenes and alcohols are formed under these experimental conditions.



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Growing utilization of carbonaceous fossil fuels such as coal, oil and natural gas caused unprecedentedly fast growth of carbon dioxide emission in the past and present centuries. The concentration of CO_2 in the atmosphere has risen from ~ 280 ppm before the industrial revolution to ~ 412 ppm in 2019, with predicted further increase.[1,2] Meanwhile, CO_2 is a known greenhouse gas that is believed to contribute in harmful global warming and upcoming climate change.[3] To overcome this unwanted trend of CO_2 accumulation in the atmosphere, carbon dioxide capture and storage[4] (CCS) and carbon dioxide capture and utilization[5] (CCU) concepts have been proposed. CCS implies using natural geological cavities, hence, it has significant drawbacks such as shortage of available reservoirs in many world regions and possible leakage. On the contrary, CCU in chemical syntheses not only decreases CO_2 concentration in air but contributes to the implementation of sustainable development principle inasmuch as CO_2 becomes a renewable feedstock.[6]

Catalytic hydrogenation of CO_2 to higher hydrocarbons has attracted a great attention as a promising route for the production of clean transportation fuels and chemicals.[1,2,7,8] The same metals that catalyze Fischer–Tropsch synthesis[9] (FTS) are active in CO_2 hydrogenation. However, their selectivity differs significantly. Supported Co, Ni and Ru produce mainly methane in CO_2 hydrogenation while target higher hydrocarbons yield is negligible.[10,11] Iron catalysts are more suitable because they are active in both FTS and reverse water–gas shift reaction (RWGS).[12] As is generally believed, CO_2 conversion into higher hydrocarbons proceeds in two steps.[13] In the first step, carbon monoxide is formed in RWGS. Second step is hydrocarbon chain growth reaction utilizing CO and H_2:

$$CO_2 + H_2 \longrightarrow CO + H_2O \qquad \Delta_1 H\,(500\ \text{K}) = 40\ \text{kJ mol}^{-1}, \qquad (1)$$

$$n\text{CO} + 2n\text{H}_2 \longrightarrow \text{–(CH}_2)_n\text{–} + n\text{H}_2\text{O} \quad \Delta_2 H\,(500\ \text{K}) = -165\ \text{kJ mol}^{-1}. \ (2)$$

Along with paraffins, olefins and alcohols are generally formed over iron catalysts. Although RWGS is thermodynamically unfavorable at typical FTS temperatures, the second step makes the whole process possible and highly exothermic.

Co, Ni and Ru possess almost no intrinsic activity in RWGS. That is why methane is a principal product in CO_2 hydrogenation over these catalysts:

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad \Delta_3 H\,(500\ \text{K}) = -175\ \text{kJ mol}^{-1}. \qquad (3)$$

Most publications on CO_2 hydrogenation are devoted to iron catalysts with various structural (*e.g.* MgO and SiO_2) and chemical (Mn, La and alkali elements) promoters. Bimetallic Fe–Co and Fe–Cu catalysts have been also reported.[8,13] Copper is known to be good RWGS catalyst[14,15] while cobalt possesses high chain-growth activity in FTS.[12,16] Combining these two metals into a composition would give active and selective catalyst for CO_2 hydrogenation to higher hydrocarbons. Surprisingly, Co–Cu bimetallic catalysts for CO_2 hydrogenation stay almost unexplored. The only work describes Co–Cu/TiO_2 catalysts prepared by deposition–precipitation method.[17] In rather harsh reaction conditions (250 °C, 50 bar) C_{5+} selectivity was as low as 5%. Adding potassium to the catalyst formula increased the selectivity up to 23%, albeit at the expense of lower CO_2 conversion and considerable selectivity to CO.[17]

Lanthanum has been tested as promoting additive for cobalt catalyst by many research groups. Reportedly, doping with lanthanum enhances Co reducibility[18–21] and the selectivity to higher hydrocarbons[19–23] in CO hydrogenation.

We have previously proposed the new class of polymetallic catalysts which are the products of self-propagating high-temperature synthesis (SHS).[24] The method allows one to combine several metals, which could be active components and promoters for variety of catalytic reactions, in one material.[25] In particular, we have demonstrated high activity and selectivity to

Table 1 BET surface area of polymetallic catalysts.

Catalyst formula with wt% of metals on Al-free basis[a]	BET surface area/m^2 g^{-1}
65Co–30Fe–5La	6.1
85Co–10Cu–5La	12.5
65Co–30Cu–5La	12.7
45Co–50Cu–5La	10.0

[a] The catalysts always contain residual aluminum in an amount of about 10 wt%.

C_{5+} hydrocarbons of Co–La and Co–La–Zr catalysts in low-temperature FTS.[26]

With a view to elaborate a new active catalyst for CO_2 hydrogenation we prepared several Co–Cu–La intermetallides by SHS method.[24,25] For comparison, Co–Fe–La melt was prepared by the same procedure. The melts were crushed, sieved and treated with NaOH water solution to leach the alumina. Finally, the materials were washed with deionized water and stabilized by diluted H_2O_2. Their specific surface areas are shown in Table 1.

Microcrystal phases on the surface of the copper-containing catalysts were revealed by the X-ray diffraction analysis (XRD) and assigned using the JCPDS-ICDD database. All the catalysts contain reduced metals such as face centered cubic (fcc) Co, hexagonal close packed (hcp) Co and fcc Cu. Notably, hcp Co was found in 85Co–10Cu–5La while in the other two catalysts containing less cobalt only fcc Co was detected. Also, $Co_{13}La$ intermetallide (JCPDS-ICDD reference card 47-1528) was found in 45Co–50Cu–5La. Oxide phases were represented by CoO (75-0393), $Co_{2.73}Cu_{0.27}O_4$ mixed oxide (78-2173) and Cu_2O (05-0667). The last was found in the most copper rich 45Co–50Cu–5La. 65Co–30Cu–5La seemed to be ‘the most reduced’ sample. Indeed, the only oxide phase there was represented by weak diffuse CoO reflections (Figure 1).

In the reference sample (65Co–30Fe–5La) Co–Fe intermetallides as well as Co_3O_4 were revealed (see Online Supplementary Materials, Figure S1).

The samples after activation and catalytic testing for 24 h (*vide infra*) were also analyzed by XRD. Their diffractograms look much simpler and contain metal phases reflections only. Interestingly, $Co_{0.52}Cu_{0.48}$ intermetallide (50-1452) appeared in all the spent samples, thus indicating Co–Cu interaction in the course of high temperature reductive treatment (Figure 2).

Scanning electron microscopy demonstrated rather whimsical texture containing plates, granules, hexagonal prisms, rectangular bars and hollow columns. Cobalt, copper and lanthanum were detected on the surface by electron probe analyzer (see Online Supplementary Materials, Figures S2–S4, Table S1).

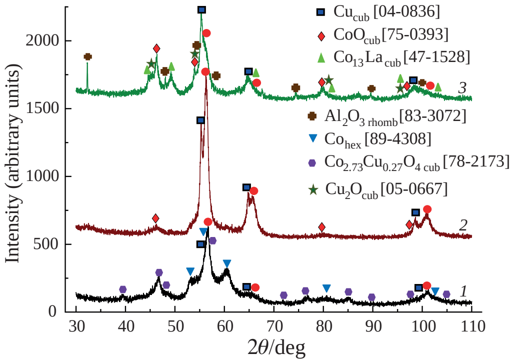

Figure 1 X-ray diffraction patterns of freshly prepared (*1*) 85Co–10Cu–5La, (*2*) 65Co–30Cu–5La and (*3*) 45Co–50Cu–5La. JCPDS-ICDD database reference card numbers are given in brackets.

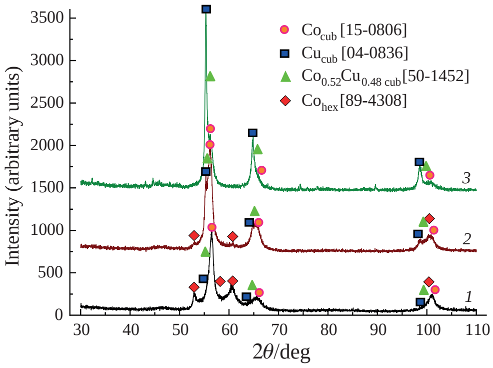

Figure 2 X-ray diffraction patterns of spent (*1*) 85Co–10Cu–5La, (*2*) 65Co–30Cu–5La and (*3*) 45Co–50Cu–5La. JCPDS-ICDD database reference card numbers are given in brackets.

The reducibility of the catalysts was studied by temperature-programmed reduction (TPR). The curves recorded after drying in He flow at 300 °C showed a distinct peak at 245–250 °C that was accompanied by wide shoulder at higher temperatures. Notably, TPR profiles of 85Co–10Cu–5La and 65Co–30Cu–5La look similar while 45Co–50Cu–5La is characterized by sharper peak and weak shoulder (Figure S5). We attribute the peak to the reduction of copper oxides.[17,27,28] Bulk CuO is reduced reportedly at 280 °C[27] or 300 °C[28] and bulk Co_2O is reduced at 300 °C.[27] Much lower temperature of the reduction in our case may be referred to higher reducibility of small oxide particles.[27,29] High-temperature shoulder represents cobalt oxides reduction.[30] Relatively low H_2 consumption at the temperatures above 250 °C for the sample 45Co–50Cu–5La corresponds to the lowest percentage of cobalt in this catalyst.

To examine the catalyst in CO_2 hydrogenation, 1 g of 100–300 μm fraction was placed in the isothermal zone of stainless steel tubular reactor between two quartz sand layers. Catalyst was activated in H_2 flow at 400 °C for 4 h. Then the feed gas (22% CO_2, 70% H_2, 8% Ar as an internal standard) was passed through the reactor under pressure of 10 bar at a flow rate of 2 nl h^{-1}. Reaction temperature was kept constant at 200 ± 1 °C. Tail gas was analyzed *via* online gas chromatograph to determine CO_2 conversion and products selectivity.

All the catalysts exhibited comparable activity in CO_2 hydrogenation though their selectivity was essentially different (Figure 3). Methane prevailed in product gas for 65Co–30Fe–5La catalyst while selectivity to C_{2+} and CO did not exceed 2.5 and 1.5%, respectively. On the contrary, copper-containing samples produced significant amounts of higher hydrocarbons. Noteworthy, selectivity to CO was less than 1% for all these catalysts. Obviously, almost all CO formed in WGSR was immediately

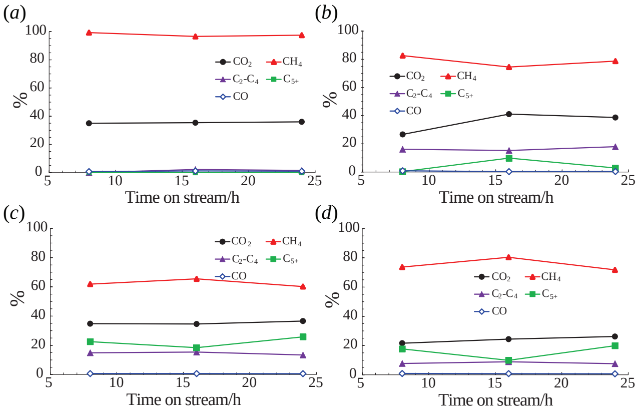

Figure 3 CO_2 conversion and product selectivity with time on stream for (*a*) 65Co–30Fe–5La, (*b*) 85Co–10Cu–5La, (*c*) 65Co–30Cu–5La and (*d*) 45Co–50Cu–5La. P = 10 bar, T = 200 °C, gas flow rate 2 nl h^{-1} g^{-1}, $H_2 : CO_2 : Ar = 22 : 70 : 8$.

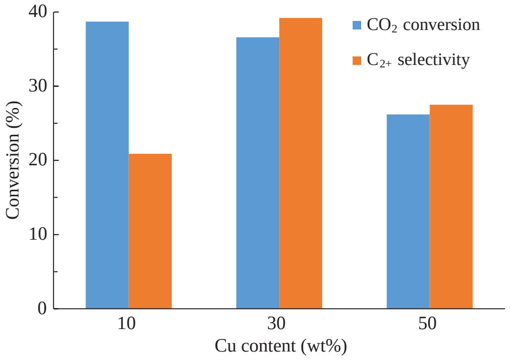

Figure 4 Effect of Cu amount in Co–Cu–La on CO_2 conversion and C_{2+} selectivity after 24 h on stream.

hydrogenated over cobalt. Another notable feature is that the synthesized hydrocarbons were completely paraffinic. No alkenes were detected by GC analyses both in gas and liquid fractions and only traces of methanol were found in product water.

Cobalt possesses strong hydrogenation activity, that is why alkanes commonly prevail in the products of FTS over cobalt catalysts.[4,12] Nevertheless, alkenes are usually detected in light FTS fractions. The absence of alkenes in the products formed over Co–Cu–La catalysts is remarkable.

It is safe to conclude that the replacement of Fe by Cu significantly affects product distribution. The reason is evidently the higher Cu activity in RWGS which serves here as a source of CO for FTS over Co catalyst. The strict optimum Co : Cu : La ratio has to be found for elaborating the most effective catalyst. Our preliminary results demonstrate gradual decrease of activity with increasing Cu amount in the catalysts whereas chain growth reaction proceeds faster at intermediate Cu content (Figure 4).

The long-term stability of catalysts is important for their industrial implementation. We performed extended catalytic testing of the best sample, 65Co–30Cu–5La. The CO_2 conversion decreased slowly during 100 h on stream. However, selectivity to target higher hydrocarbons remained stable (see Online Supplementary Materials, Figure S6).

In conclusion, we have demonstrated that Co–Cu–La catalysts prepared by self-propagating high-temperature synthesis are effective for CO_2 hydrogenation to higher hydrocarbons at relatively mild reaction conditions. While Cu serves as active RWGS catalyst, Co converts almost all CO formed *via* chain growth reaction. Synthesized hydrocarbons are completely paraffinic, contrary to that produced by conventional FTS. Among catalyst tested, the composition 65Co–30Cu–5La exhibited the highest C_{2+} selectivity of 39%.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.01.017.

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