



Effect of support of Co-Na-Mo catalysts on the direct conversion of CO₂ to hydrocarbons



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ABSTRACT

This study of the effect of support of Co-Na-Mo based catalysts on the direct hydrogenation of CO₂ into hydrocarbons (HC) provides guidelines for the design of catalysts for CO₂ conversion. We demonstrate that the surface area of the support and the metal-support interaction have a key role determining the cobalt crystallite size and consequently the activity of the system. Cobalt particles with sizes <2 nm supported on MgO present low reverse water gas shift conversion with negligible Fischer-Tropsch activity. Increasing the cobalt particle size to ~15 nm supported on SiO₂ and ZSM-5 supports not only substantially increases the CO₂ conversion but it also provides high HC selectivities. Further increase of the cobalt particle size to 25–30 nm has a detrimental effect on the global CO₂ conversion with HC:CO ratios below 1, however, lower methane selectivity and enhanced formation of unsaturated HC products are achieved. Additionally, the metal-support interaction potentially also has a strong effect on the growth chain probability of the formed hydrocarbons, increasing as the metal-support interaction increases. These evidences demonstrate that CO₂ conversion and hydrocarbon distribution can be tuned towards desired products by controlled catalyst design.

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1. Introduction

Hydrocarbons, currently derived from crude oil, represent a vital source of fuel as well as an important feedstock for many industrial chemical processes. Despite the dependency of our lifestyle on this energy source, governments around the world, driven by environmental and social pressures, have recently agreed upon a global agreement for the decrease of CO₂ emissions associated to hydrocarbons derived from fossil fuels. While in the long term, a substitution of fossil fuels by renewable ones is desirable, the transition period is expected to be facilitated by an alternative, environmentally friendly production route of hydrocarbons.

One possibility for the production of carbon-containing chemicals, which is gaining increasing attention, is the capture of CO₂ and its conversion into hydrocarbons [1]. Atmospheric CO₂ levels are rising rapidly, recently passing the symbolic 400 ppm

level and are set to continue to rise [2]. The increasing CO₂ concentration in the atmosphere is one of the largest contributing factors to global warming and as such, there is currently an increasing pressure on countries and industry to reduce CO₂ emissions. The possibility of considering CO₂ as a valuable chemical feedstock rather than a waste product is consequently becoming increasingly attractive as an exemplar of the circular economy.

A highly attractive route of CO₂ conversion is its two-step direct hydrogenation process consisting of the reduction of CO₂ to CO via the reverse water-gas shift (RWGS) reaction followed by the tandem conversion of the more reactive CO molecule into hydrocarbons through the Fischer-Tropsch (FT) process. The production of renewable hydrogen, as a way of storing excess renewable energy from solar and wind sources, is currently attracting significant attention with many extremely promising technologies currently being developed [1,3].

Focusing on the conversion of CO₂, one of the main challenges is associated with the development of catalysts not only with high activity but also with high selectivity to high value hydrocarbon products, specifically long chained hydrocarbons (C₅+) and short

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chain olefins (C₂–C₄) [1,4]. Additionally, having both steps of the process occur simultaneously over a single catalyst under the same reaction conditions can reduce the cost and complexity of a large scale implementation of such technology [5].

Most of the work to the date in this field has been focused on the use of conventional Fischer-Tropsch catalysts designed for CO-fed systems [6]. Iron-based systems have so far proved to be the most successful due to the RWGS activity of certain iron species which allows the formation of CO to be further converted into hydrocarbons [6]. On the other hand, cobalt-based catalysts are desirable for the production of heavier hydrocarbons in the industrial Fischer-Tropsch process due to their high activity, good selectivity and superior stability [7]. However, they normally present poor activity in the first CO₂ hydrogenation step [8]. Additionally, when CO₂ is added to a CO/H₂ stream, the hydrocarbon distribution is strongly affected with a shift in selectivity towards undesired products such as methane [5,9]. When the feed-gas is completely shifted to a CO₂/H₂ mixture, cobalt systems tend to act as methanation catalysts with almost exclusively (generally >90%) methane formed [5,10].

To improve the catalyst performance, small concentrations of dopants are often added to both iron and cobalt based catalysts [11]. Promoters typically utilised with cobalt Fischer-Tropsch catalysts such as platinum and palladium have little effect on the product distribution when CO₂ is utilised as the carbon source [12]. Recent work conducted within our group has shown that addition of molybdenum and sodium as promoters to cobalt enhances the selective production of C₂₊ hydrocarbons [13]. Most of the work in the area is focused on the use of Al₂O₃ supports, generally used in industrial Fischer Tropsch processes [14]. However, some studies have demonstrated that other inorganic oxide supports such as TiO₂ can outperform Al₂O₃ in the Fischer Tropsch process using CO/H₂ feeds [14,15]. This work presents for the first time a systematic study of the effect of the support on Co-Na-Mo catalysts for the direct conversion of CO₂ into hydrocarbons, revealing the importance of the support not only on the cobalt crystallite size but also the key effect of the metal-support interaction on the hydrocarbon distribution.

2. Experimental

2.1. Catalyst preparation

Cobalt – sodium – molybdenum catalysts were prepared by wet impregnation using Co(NO₃)₂·6H₂O, NaOAc and (NH₄)₆Mo₇O₂₄·4H₂O as metal precursors. A variety of supports were used including SiO₂ (Davisil, 35–70 μm particle size, 500 Å pore diameter), CeO₂ (Aldrich, powder <5 μm), ZrO₂ (Aldrich, powder 5 μm), γ-Al₂O₃ (Fluka), TiO₂ (Aldrich, Anatase), ZSM-5 (NH₄⁺) (Alfa Aesar) and MgO (prepared by the calcination of Mg₅(OH)₂(CO₃)₄·xH₂O) (See Supplementary information). In a typical synthesis, the support was suspended in the minimum amount of methanol. 20 mL of methanol containing 20 wt.% of cobalt was added drop-wise under stirring. Following this step, 1 wt.% of sodium dissolved in methanol and (NH₄)₆Mo₇O₂₄·4H₂O dissolved in deionised water were added slowly into the solution. The resulting mixture was stirred for 10 min before being sonicated for 60 min. The solvent was removed under vacuum while being heated through the use of a rotary evaporator until a powder of constant mass was obtained. The obtained powder was then calcined in air for 16 h at 873 K.

2.2. Catalyst characterisation

Scanning electron microscopy characterisation was carried out on a JEOL 6480LV at 5–20 kV. Energy-dispersive X-ray spectroscopy

(EDS) was carried out *in situ* during SEM analysis. X-ray diffraction studies were conducted on a BRUKER D8-Advanced diffractometer. Cu Kα (λ = 1.5406 Å) radiation was used for all samples (step size 0.0164° and 0.6 s per step). N₂ adsorption was carried out at 77 K after degassing (at 120 °C for 12 h under high vacuum) using a Micromeritics ASAP 2020 gas sorption analyser. Surface area values were calculated using the Brunauer-Emmett-Teller (BET) theory. Temperature programme reduction (TPR) experiments were carried out using a Micromeritics Autochem II instrument equipped with a thermal conductivity detector (TCD). Samples were reduced using 30 mL min⁻¹ of 5% H₂/Ar from room temperature up to 1000 °C with a ramp rate of 10 K min⁻¹.

2.3. Catalyst testing

Catalysts were tested in a purpose built packed-bed reactor (See Supplementary information). Typically, 1.0 g of catalyst was diluted with silicon carbide (Sigma Aldrich, 200–400 μm particle size) and loaded into a stainless steel tube reactor (catalyst bed 150 mm length, 4.6 mm internal diameter). Prior to testing, the catalysts were reduced *in-situ* under a flow of pure hydrogen at 300 °C for 2 h. Carbon dioxide hydrogenation reactions were conducted at atmospheric pressure and 200 °C with a H₂:CO₂ ratio of 3:1 and a total flow of 8 sccm unless stated otherwise. Samples were taken from the exhaust gases of the reactor and analysed using an Agilent 7890A GC equipped with mass spectrometer as detector, this is further equipped with a TCD and FID detector. A 30 m HP-PLOT/Q column was utilised for product analysis. The GC-MS was calibrated using a BOC special gas mixture containing 1% v/v CH₄, C₂H₆, C₃H₆, C₃H₈, n-C₄H₁₀, CO, CO₂, in N₂. The mass balance was calculated based on the carbon content, being satisfied within ±5%. Product selectivity was calculated on the carbon basis defined as moles of carbon in product x/mol of CO₂ converted. Multiple repeats of the catalytic data reproduced well with values of conversion and selectivity being within ±5% of the values reported.

3. Results and discussion

3.1. Effect of support on CO₂ conversion and selectivity

In order to study the effect of the support of the activity of Co-Na-Mo-based catalysts on the direct conversion of CO₂ into hydrocarbons, a series of inorganic oxide supports were used namely SiO₂, CeO₂, TiO₂, Al₂O₃, MgO and ZrO₂ and ZSM-5(NH₄⁺). The catalysts were tested in a fixed bed reactor at atmospheric pressure at 200 °C using a H₂:CO₂ ratio of 3:1. Table 1 shows the conversion, selectivity and hydrocarbon distribution.

The Co-Na-Mo catalysts supported on SiO₂ and ZSM-5 showed the highest CO₂ conversion values, with similar CO and hydrocarbon selectivity. Catalysts supported on CeO₂, TiO₂, Al₂O₃ and ZrO₂ present a similar CO₂ conversion under the studied conditions (~15%), however, the hydrocarbon selectivity versus CO decreases in the order of ZrO₂ < Al₂O₃ < TiO₂ < CeO₂. Finally, the catalyst showing the lowest conversion utilises MgO as the support, with no hydrocarbons being formed, with the sole presence of CO in the outlet stream.

The difference in CO₂ conversion can be partially explained based on the difference of cobalt crystallite size. Fig. 1 shows the pXRD patterns of the different catalysts. In the Co-Na-Mo/SiO₂ catalysts, no diffraction peaks associated to the support are observed, confirming the amorphous nature of the silica. In contrast, diffraction peaks representative of CeO₂, TiO₂ anatase, γ-Al₂O₃, MgO, ZrO₂ and ZSM-5 are observed for the corresponding catalysts [16].

Additionally, the diffraction peaks at 2θ values of 19, 31, 37, 45 and 59°, corresponding to the crystalline Co₃O₄ phase [17] are

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