



## Research article

# Conversion of CO<sub>2</sub> into liquid hydrocarbons in the presence of a Co-containing catalyst based on the microporous metal-organic framework MIL-53(Al)

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## ABSTRACT

A novel 10%Co/MIL-53(Al) nanohybrid based on the microporous metal-organic framework MIL-53(Al) prepared by MW-assisted synthesis exhibits the properties of a bifunctional catalyst with activity in CO<sub>2</sub> hydrogenation to CO and consecutive synthesis of liquid hydrocarbons from carbon monoxide formed. The observed increase in the CO<sub>2</sub> conversion in comparison with the thermodynamically possible conversion is assumed to be due to the expected shift of the equilibrium toward the formation of CO as a result of its further rapid conversion to hydrocarbons by the Fischer-Tropsch reaction.

## 1. Introduction

An efficient approach to the problem of CO<sub>2</sub> utilization is the conversion of carbon dioxide to carbon monoxide [1]. This gas can be further converted into liquid hydrocarbons and valuable oxygenates by Fischer-Tropsch synthesis (FTS) and hydroformylation. FTS is considered as one of the most prospective and economical ways to clean fuel production, because this heterogeneous catalytic process can produce a variety of products such as paraffins, olefins, alcohols and aldehydes using synthesis gas (CO and H<sub>2</sub>) [2–5]. Ni and Ru-containing systems are the effective catalysts for the methanation reaction (4H<sub>2</sub> + CO<sub>2</sub> = CH<sub>4</sub> + 2H<sub>2</sub>O, ΔH<sub>298K</sub> = –252.9 kJ/mol) [6,7]. Bimetallic Ru-Ni nanoparticles (3–5 wt%) supported on zirconium oxide provide practically complete conversion of CO<sub>2</sub> with a selectivity to methane reaching ~100% (300–400 °C, 10 atm, space velocity ~36,000 h<sup>–1</sup>) [6].

The catalytic conversion of carbon dioxide to CO (CO<sub>2</sub> + H<sub>2</sub> = CO + H<sub>2</sub>O, ΔH<sub>298K</sub> = 41.2 kJ/mol) known as the reverse water-gas shift reaction (RWGSR) is more interesting due to the higher reactivity of carbon monoxide at moderate temperatures compared with methane. The catalysts of this process are, inter alia, copper-containing systems [8–10]. In the study of bimetallic Cu-Ni/Al<sub>2</sub>O<sub>3</sub> catalysts

in the CO<sub>2</sub> hydrogenation reaction, it was found that the presence of Cu promotes the formation of CO, while Ni accelerates the formation of methane [11]. However, the production of liquid hydrocarbons from CO<sub>2</sub> requires an additional step of conversion of CO produced at the first step by the consecutive Fischer-Tropsch reaction.

In connection with the problem of CO<sub>2</sub> utilization, once-through synthesis of hydrocarbons from CO<sub>2</sub> is most promising. In the early works, various mechanical mixtures of Fe-Zn-M oxide catalysts (where M = Zr, Al, Cr, Mn, and Ga) were studied for the production of heavier hydrocarbons from a mixture of H<sub>2</sub>/CO<sub>2</sub> = 3 at a high pressure with different zeolites, such as HY, HZSM-5 etc. [12]. The research methodology was the production of oxygenates on oxide catalysts with the simultaneous production of hydrocarbons (including liquid C<sub>5+</sub>) on the zeolite component of the composite catalysts. However, even at an elevated pressure (50 atm); the yield of liquid hydrocarbons did not exceed 2%.

In studying the gas-phase reaction of CO<sub>2</sub> hydrogenation on diverse cobalt-containing nanocatalysts (10–40% Co) supported on SiO<sub>2</sub>, as well as on catalysts modified with palladium, manganese, molybdenum with alkali metal additives, the formation of liquid hydrocarbons was observed at an atmospheric pressure. The maximum selectivity for C<sub>5+</sub> hydrocarbons on a complex three-component catalyst 20%Co-1%Na-

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1%Mo/SiO<sub>2</sub> was only 10.4%, and the liquid yield did not exceed 3.7% [13].

Co nanoparticles exhibit a high activity and selectivity for linear hydrocarbons combined with a low activity in the WGS reaction [14,15]. The specific feature of Co-containing catalysts is that they require a H<sub>2</sub>:CO ratio close to the stoichiometric ratio, with the methane yield increasing sharply with increasing temperature. Also, because of the high hydrogenating activity of Co-containing catalysts, mainly alkanes are formed in the FTS process, but not oxygen-containing compounds [16].

Commonly used carriers for cobalt-containing catalysts are porous inorganic materials, such as SiO<sub>2</sub>, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> [15]. Among them, Al<sub>2</sub>O<sub>3</sub> has an excellent thermal stability, high mechanical strength, a large specific surface area and an appropriate pore size distribution [17]. However, strong interaction of the supported active phase with the carrier leads to the formation of cobalt-aluminate spinels that are not active in FTS. These drawbacks can be overcome by using carbon carriers characterized by chemical inertness and a high specific surface area for deposition of cobalt [18]. However, such catalytic systems are characterized by a rapid decrease in the activity due to the migration of cobalt particles to the external surface of the carbon support and agglomeration. Effective catalysts for the FT process are also cobalt-containing zeolites. Thus, cobalt-containing zeolites provide selective conversion into C<sub>4</sub>-C<sub>10</sub> hydrocarbons with the isoparaffin content up to 80% [19].

At present, considerable attention is paid to the study of a new class of hybrid materials - metal-organic frameworks (MOF) [20–23]. The inorganic-organic lattice structure of MOF is formed by cations or metal oxide clusters and organic linkers. A high degree of crystallinity, a large specific surface area, a controlled pore size and the possibility of varying the pore functionality over a wide range provide advantages to these matrices as carriers of heterogeneous catalysts in comparison with inorganic micro- and mesoporous carriers [24–27].

5–15% Co catalysts based on the metal-organic porous carrier MIL-53(Al) were studied in a FT reaction in an H<sub>2</sub>/CO mixture at 20 atm and a temperature of 240 °C [28]. It was found that the catalysts perform the FT reaction quite efficiently. The CO conversion was 47.1%, while the selectivity to liquid C<sub>5+</sub> hydrocarbons achieved 68.6%. However, as already mentioned, it is of great practical interest to obtain liquid hydrocarbons directly from CO<sub>2</sub> in mixtures with hydrogen.

The purpose of this study was to study the possibility of implementing the process of CO<sub>2</sub> hydrogenation combining simultaneously two stages - the formation of synthesis gas (a mixture of CO with hydrogen) and the subsequent conversion of CO formed at the first stage to liquid hydrocarbons by the Fischer-Tropsch reaction. A 10%Co/MIL-53(Al) sample was chosen as a catalyst, with Co nanoparticles being immobilized in a microporous matrix of the metal-organic framework MIL-53(Al) prepared under microwave-activated synthesis conditions and characterized by improved chemical and thermal stability [29,30].

Our work is thus focused on the preparation of the novel effective MOFs-based catalysts for carbon dioxide conversion into liquid hydrocarbons C<sub>5</sub>-C<sub>8</sub> via a two-step process including CO<sub>2</sub> hydrogenation followed by Fischer-Tropsch synthesis with carbon monoxide formed at the first step. The Al<sup>3+</sup>-derived microporous framework MIL-53(Al) (Al(OH)bdc, bdc = benzene-1,4-dicarboxylate) was selected as a host matrix for Co nanoparticles, because of its exceptional chemical and thermal stability. According to experimental results, novel Co/MIL-53(Al) nanohybrids display a behavior of bifunctional catalysts promoting both CO<sub>2</sub> hydrogenation into CO and FT synthesis.

The cobalt-containing catalysts were characterized by a combination of physico-chemical methods: PXRD, STEM, DRIFT spectroscopy, and volumetric N<sub>2</sub> adsorption.

## 2. Experimental

### 2.1. Catalyst preparation

The carrier for the catalysts, MIL-53(Al), in the form of a nanopowder of the microporous metal-organic framework was prepared under conditions of microwave-activated synthesis [31]. AlCl<sub>3</sub> × 6H<sub>2</sub>O (1.21 g), 1,4-benzenedicarboxylic acid (0.42 g) and a mixed solvent of distilled water (3 mL) and DMF (5 mL) were charged into a glass ampoule with a diameter of 4 cm and a height of 30 cm. The reactor in a vertical position was placed in a hole in the chamber of a household microwave oven “Vigor” with a power of 200 W and the reaction mass was heated for 20–30 min (120–125 °C). The temperature of the process was monitored with a thermocouple placed in a glass pocket directly into the reaction mixture.

The 10%Co/MIL-53(Al) catalyst was prepared by impregnating the obtained support with a moisture capacity using an aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub> × 6H<sub>2</sub>O. After incipient-wetness impregnation, the sample was dried in air (90 °C, 3 h), and immediately before the reaction it was activated in a flow reactor in a stream of hydrogen (15 mL/min) at 450 °C for 2 h.

### 2.2. Physicochemical studies of the catalysts

N<sub>2</sub> adsorption data for the MIL-53(Al) material were obtained at –196 °C using an Autosorb-1 Quantachrome Instrument. Data analysis (BET) was carried out in the interval of relative pressures of 0.05–0.3, and according to Langmuir in the 0.07–0.2 interval, correspondingly. The experimental data were analyzed by a Quantachrome AS1Win Program.

Powder XRD patterns were measured in a reflection mode using a Panalytical EMPYREAN instrument with a linear X'celerator detector and non-monochromated Cu Kα radiation (λ = 1.5418 Å) in the 2θ range 7–40°.

Infrared diffuse-reflectance spectra were recorded at room temperature with a NICOLET “Protege” 460 Fourier-transform spectrometer equipped with a diffuse-reflectance unit [32,33] in the range of 6000–400 cm<sup>-1</sup> with a 4 cm<sup>-1</sup> increment. For a satisfactory signal-to-noise ratio, 500 spectra were collected. CaF<sub>2</sub> powder was used as a standard. Two samples of 10%Co/MIL-53(Al) catalysts were studied: after treatment in a stream of H<sub>2</sub> at 450 °C and after catalysis. Before adsorption of CO, the samples were evacuated under different conditions. The pre-reduced sample was subjected to alternating treatment in a vacuum and in H<sub>2</sub> (70 Torr, 440 °C, 2 h). The sample after catalysis was treated in a vacuum (440 °C, 2 h).

### 2.3. Method of catalytic measurements

Tests of the catalyst sample were carried out in a flow-through installation with a tubular metal reactor (D = 7 mm) with a fixed bed of a catalyst at a pressure of 1 and 30 atm in the regime of raising the temperature in the catalyst bed from 260 to 340 °C in 40 °C steps. A mixture of CO<sub>2</sub> and hydrogen with a molar ratio of H<sub>2</sub>/CO<sub>2</sub> = 2.7 was fed to the reactor at a space velocity of 800 h<sup>-1</sup> with a catalyst loading of 0.8 g (fraction 0.05–0.1 mm, volume of the catalyst bed 1 cm<sup>3</sup>). The reaction temperature was set by a Thermodat-17 controller coupled to a thermocouple located in the catalyst bed.

The gas at the outlet from the reactor was analyzed with a gas chromatograph, model “3700”, produced by the NPO “Granat” using two packed columns (2 m) with molecular sieves 5A (H<sub>2</sub>, CH<sub>4</sub> and CO) and HayeSep-Q (H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) using a catharometer detector, a heated loop of a constant volume was used as the sample inlet. The volumetric content of gases was determined from the ratio of the peak areas of the components in the chromatogram of the gas reaction mixture to the areas of individual gas peaks.

The hydrocarbon part of the reaction gas (C<sub>1+</sub>) including liquid

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