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CO_2 hydrogenation reaction over pristine Fe, Co, Ni, Cu and Al_2O_3 supported Ru: Comparison and determination of the activation energies

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Fe, Co, Ni and Cu are the main non-noble industrially significant catalysts in the CO_2 and CO gas phase hydrogenation reaction towards hydrocarbons and alcohols. These catalysts are typically supported on metal oxides such as SiO_2, TiO_2, Al_2O_3 and ZnO, in order to maximize the activity towards the desired reaction. The role of the supporting material is to stabilize the catalytic nanoparticles and to prevent sintering at the elevated reaction temperatures and pressures. The supporting phase can improve the reaction activity or even have a crucial role in the reaction, as is the case, e.g. for the Methanol synthesis over Cu based catalysts supported on ZnO. Studying the metals without a supporting oxide phase is of great importance for the fundamental understanding of the catalytic activity of the metal phase. Therefore, we investigated the pristine transition metals Fe, Co, Ni and Cu (diluted with silica glass beads to avoid sintering) towards their activity in the CO_2 hydrogenation reaction and determined the activation energy. An Al_2O_3 supported Ruthenium catalyst with 0.5 mass percent of Ru loading was taken as reference system. It was found that Co, Ni and Ru/Al_2O_3 are mostly active in the Sabatier reaction, while Fe is active in the reverse water gas shift reaction. Cu as pristine metal shows no catalytic activity. C2+ hydrocarbons were formed on Co in low concentrations. For the calculation of the activation energy, the kinetically determined temperature range of the reaction is identified with a high resolution in time by means of a quantitative gas analysis method with an online mass spectrometer. The observation activation energy of the CO_2 hydrogenation reaction was determined to be 50 kJ/mol over Fe, 77 kJ/mol over Co, 74 kJ/mol over Ni and 73 kJ/mol over the Ru/Al_2O_3 catalyst. This indicates similar reaction pathways over Co, Ni and Ru/Al_2O_3 and a different reaction mechanism on Fe.

1. Introduction

Energy storage is crucial for the development of an energy supply based on renewable energy. The energy supply from wind -and solar power plants is intermittent in time due the day/night cycles, weather conditions, and seasonality. Since the supply of electricity must correspond to the demand in the power grid at all times to keep the grid frequency stable, energy storage is required to buffer the fluctuations from the stochastically producing energy converters such as wind- and solar power plants. Batteries are favorable for efficient short term storage, but are too costly to provide long-term storage capacity [1]. Liquid synthetic fuels are a promising energy carrier for seasonal energy storage due to their high gravimetric -and volumetric energy density and stability in ambient conditions which is up to a hundred times larger than in batteries [2,3]. CO_2 extracted from air can be hydrogenated with hydrogen produced by electrolysis driven by renewable energy. The energy is then stored in the chemical bond of the hydrocarbons and is released upon combustion which is net CO_2 emission free. Today's technologies allow CO_2 hydrogenation via the reverse water gas shift reaction (RWGS) to CO, followed by the Fischer-Tropsch reaction (FTR) [4]. The FTR is an unselective reaction which leads to a wide hydrocarbon product distribution ranging from low molar weight gaseous hydrocarbons, alcohols and long chained waxes [5]. Therefore, energy intensive refining of the products is required to obtain a specific hydrocarbon fraction. The CO_2 hydrogenation via the Sabatier reaction is instead a selective reaction, with methane as the major product. Fe, Co, Ni, Cu, Ru and Rh

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are the most active elements known for the CO and CO_2 hydrogenation reaction and they are the key building blocks of the industrially significant catalysts [6,7]. In order to increase the surface area, the catalysts are typically nanosized particles supported on metal oxides such as Al_2O_3, SiO_2, TiO_2, ZnO and ZrO_2 to stabilize the active species, prevent sintering [8] and adapt the reaction selectivity [9]. In particular in the case of Cu, the support phase has a principal role in the CO_2 hydrogenation reaction mechanism [6,10]. The metal-support interactions and the influence on the reaction's activity and selectivity are not fully understood yet and a full understanding of these phenomena is crucial for the design of new, more selective catalysts. Therefore, it is of great interest to investigate the direct CO_2 hydrogenation over the unsupported pristine metal catalysts. This has been done on single crystal catalysts in Ultrahigh Vacuum (UHV) conditions [11,12] and by means of density functional theory calculations (DFT) [13–15] and micro kinetic reaction modeling [16,17]. The CO_2 hydrogenation reaction on Fe, Co, Ni and Cu catalyst on different supports – and also in their pristine form, was the object of numerous studies in the 1970s after the interest in synthetic fuels increased due to the oil crisis [18–20]. Nevertheless, a direct comparison of the pristine metal catalysts in similar reaction conditions with the determination of the activation energy has not been reported so far.

In this paper the activity of the pristine transition metals Fe, Co, Ni and Cu for the CO_2 hydrogenation reaction is investigated. The reaction was carried out in a micro reactor in quasi equilibrium conditions, meaning that the space velocity (around $1000\ h^{-1}$) and heating rate (1 K/min) were relatively low. For the product gas composition analysis, a quantitative gas analysis method by means of mass spectrometry (MS) has been developed, allowing the determination of the product gas stream composition, and therefore the calculation of the kinetic parameters, with a high resolution in time. The catalyst activity results are discussed in the frame of a thermodynamic reaction analysis.

2. Experimental

The experiments were carried out in a stainless-steel plug flow reactor placed in a tubular furnace. Three thermocouples are placed in – or on the reactor in order to monitor the reaction temperature. The temperature measured in the reaction tube in close vicinity to the catalyst bed is used as reference temperature for the reaction. The gas flows were controlled via three mass flow controllers for CO_2, H_2 and He. The gas lines after the reactor to the analysis instruments were heated to 200 °C to avoid condensation of products and water.

The gas stream has been analyzed by means of a Mass Spectrometer (Pfeiffer OmniStar 320) with a Faraday and Secondary Electron Detector (MS-SEM) and a Gas Chromatograph (SRI 8610C) equipped with a Flame Ionization Detector (FID) and a Thermal Conductivity Detector (TCD).

For the gas analysis, a software application was developed within MATLAB R2016b for the GC and MS to quantify the partial pressures in the product gas stream as a function of the reaction temperature.

The metal powders of Fe, Co, Ni and Cu were obtained from Goodfellow (Table SI) and examined for their purity by means of X-ray photoelectron spectroscopy (XPS). No impurities were detected by means of XPS. The catalysts were reduced with Hydrogen at elevated temperatures prior to the experiment to obtain a purely metallic surface. The specific weight of the catalyst and the surface area of the catalysts used in this study were determined by means of SEM (to estimate the particle size) and liquid N_2 adsorption isotherms to determine the specific surface area.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2018.08.002.

2.1. Catalyst preparation and packing

In preliminary experiments, it was found that the metal powders can sinter during the reaction at elevated temperatures up to 650 °C. In particular, Co and Cu powders are prone to sinter. This caused clogging of the reactor, making the experiment not reproducible. Since it was the aim not to alter the reaction with a supporting phase, the catalyst powders were pressed to 8 mm pellets with a weight equivalent of four tons and then broken down to smaller grains with an approximate diameter of 1–1.5 mm. The grains were then mixed in an equal weight ratio with glass beads in the same size regime to prevent grain agglomeration. The glass beads are made of borosilicate glass and were purchased at Schäfer Glas. They have a diameter of 1 mm and were not affected by the reaction conditions. With this preparation method of the catalyst, no macroscopic sintering effects were observed after the experiments, thus enabling comparable reaction conditions among the four pristine metals.

2.2. Catalyst pretreatment with helium and hydrogen

To evaporate moisture from the catalyst and the tubing, the reactor and tubing were preheated with an applied He gas flow of 10 ml/min for a minimum time of 30 min. The reactor was preheated to 150 °C, the tubing to 200 °C. Subsequently, the catalysts were reduced with H_2 to obtain a metallic surface. This was done with a H_2 flow of 7.5 ml/min and 2.5 ml/min of He at a starting temperature of 150 °C. The temperature was then ramped up with 10 °C/min to a set point of 700 °C, while simultaneously measuring the gas composition with the MS. With this TPR, the temperature ranges at which the surface is reduced from oxides and carbides is determined via the formation of water (*m/z* 18 peak) and methane (*m/z* 16 peak). In case the surface reduction was not completed at the set point temperature after ramping up, the temperature was kept at the set point of 700 °C to further reduce the surface until the *m/z* 18 and *m/z* 16 peaks declined.

2.3. CO_2 hydrogenation experiment

After reducing the catalyst with H_2, the experimental gas flow was set with the gas stream going through the reactor bypass. The experimental gas flow was: CO_2 1.5 ml/min, H_2 6 ml/min and He 2.5 ml/min. Therefore, the total flow was 10 ml/min and the H_2:CO_2 ratio 4:1. The gas flow rate of 10 ml/min for the reaction gas stream was chosen as a tradeoff between quasi equilibrium conditions, MFC reliability (MFC models: Bronkhorst El Flow series. Flow range: 0.4–20 ml/min. Absolute measurement error in ml/min: 0.1% of maximum set point (20 ml/min) plus 0.5% of set point) and the time the gas product gas stream requires to reach the analysis systems (there is less than a minute of dead time between the reactor and the MS inlet at a flow of 10 ml/min). After the setpoint gas mixture was reached, the valve to the reactor was opened, the bypass closed, the temperature ramping set to 1 °C min and the measurement with MS and GC started. The maximum reactor oven temperature was set to 700 °C. The total time for the CO_2 hydrogenation experiment therefore takes 550 min since the ramping was started at 150 °C. The experiments were carried out in ambient pressure. The reactor is a plug flow reactor with a total length of 180 mm. The inner diameter of the reaction zone, which starts 75 mm after the inlet, is 7 mm in diameter ($d_{i,2}$). Before the reaction zone, the inner tube diameter is 4 mm ($d_{i,1}$). The catalyst is hold in place to the inlet site by a sintered steel filter with a pore size of approximatively 60 μm (Swagelok SS-2F-K4-60) and a diameter of 7 mm, which sits on a step of the inner tube at 75 mm from the inlet site. To load the catalyst, a small layer of glass wool is