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Effect of Ba and K addition and controlled spatial deposition of Rh in Rh/Al$_2$O$_3$ catalysts for CO$_2$ hydrogenation

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ABSTRACT

The effect of Ba and K addition to Rh/Al$_2$O$_3$ catalysts for CO$_2$ hydrogenation was investigated. Catalysts with preferential deposition of 1 wt% of Rh either on the alumina support or the Ba or K component were prepared by the two nozzle flame spray pyrolysis method and characterized by nitrogen adsorption, CO chemisorption combined with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and scanning transmission electron microscopy. XRD and thermoanalysis combined with mass spectroscopy indicated that the Ba existed mainly as BaCO$_3$, while K was present in the form of KHCO$_3$ and KOH. DRIFTS combined with CO adsorption measurements revealed a strikingly different CO adsorption behavior of Ba- and K-containing catalysts.

The pure Rh/Al$_2$O$_3$ catalyst as well as the Ba-containing catalysts showed a high selectivity to CH$_4$ below 500 °C with a maximum yield at 400 °C. Above 400 °C, the reverse water gas shift reaction leading to CO and H$_2$O started to become dominant, in accordance with thermodynamics. In contrast, the K-containing catalysts produced no CH$_4$, all CO$_2$ was directly converted to CO in the entire temperature range (300–800 °C). Preferential deposition of the Rh on the additive components (Ba, K) or the alumina support had comparably little effect on the catalytic behavior. The CO$_2$ capturing additives, Ba and K, did not result in enhanced catalytic performance, probably due to the relatively high stability of the corresponding carbonates at the optimal reaction temperatures.

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1. Introduction

The steady increase of carbon dioxide emission caused by human activities contributes to harmful global warming and climate change [1]. Various strategies have been proposed to mitigate the carbon dioxide concentration in the atmosphere, such as separation [2], storage [3] and utilization in chemical synthesis [4,5]. A variety of chemical processes have the potential for CO$_2$ fixation, among them the exothermic methanation of CO$_2$ with sustainable H$_2$ [6], the so-called Sabatier reaction [7], is one of the most prominent:

$$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(g),$$
$$\Delta G_0 298K = -113 \, kJ \, mol^{-1} \qquad (1)$$
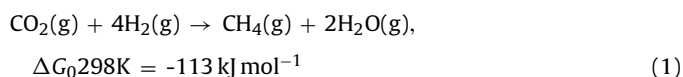
In the case of incomplete reduction, CO is formed by the endothermic reverse water gas shift (RWGS) reaction:

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g), \Delta G_0 298K = 29 \, kJ \, mol^{-1}.$$
$$\qquad (2)$$
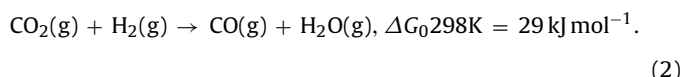
From a thermodynamic point of view, the synthesis of CH$_4$ is favored at normal conditions, but at elevated temperature (>500 °C) and pressure, the equilibrium shifts to CO production. Early on, the Sabatier reaction was recognized for its role in the synthesis of substitute natural gas (SNG) [8].

A variety of different metals catalyze CO$_2$ methanation, including supported Ni, Pd, Pt, Ru, Co and Rh. A comprehensive survey of suitable catalysts for CO$_2$ hydrogenation and the progresses made in the past years has been reported in a recent review [4]. In the present work we focused on Rh, which has been the subject of various previous investigations [9] and since Rh proved to have a comparatively good sulfur tolerance [10,11]. High sulfur tolerance is important when the H$_2$ feed contains sulfur compounds, as for instance in bio-fuels processing [12]. Depending on
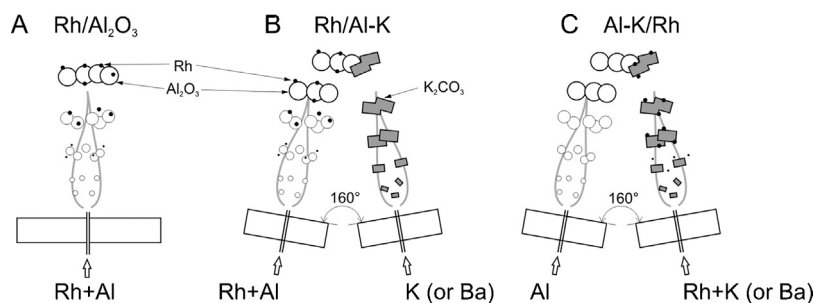
Fig. 1. Schematics of single nozzle FSP and two-nozzle FSP. With the latter, preferential deposition of noble metals is achieved.

the support material, the Rh particle size, and the experimental conditions (CO_2/H_2 ratio, temperature, pressure) different catalytic behavior is reported. Most frequently applied supports are: TiO_2 [9,13–15], Al_2O_3 [16,17], SiO_2 [18–21]. The activity of Rh on these supports at given conditions was reported to follow the order: $TiO_2 > Al_2O_3 > SiO_2$ [22]. To the best of our knowledge the effect of Ba- and K- additives has not been reported so far. Both additives are known to be prone to store CO_2 (e.g. as carbonates) and thereby are supposed to change the CO_2 adsorption on the catalyst surface which in turn might influence the catalytic performance.

A similar strategy, using a CO_2 capturing support, has recently been applied successfully by Park at et al. [23] to enhance the performance of metal catalysts for methanation. They investigated the effect of Mg as a CO_2 capturing agent on $Pd–Mg/SiO_2$ catalysts and concluded that the Mg fixed the CO_2 leading to higher CH_4 selectivity.

Here we investigated the effect of the addition of CO_2 capturing components (Ba or K) to Rh/Al_2O_3 catalysts for CO_2 hydrogenation. Furthermore the role of the location of Rh (different interfaces) either on support or on the CO_2 capturing component on catalytic performance was explored.

2. Experimental

2.1. Catalyst preparation

All catalysts were prepared by a two-nozzle flame spray pyrolysis (FSP) [24]. Fig. 1 shows its working principle schematically. The Rh could be selectively deposited on the support γ-Al_2O_3 (Fig. 1B) or the CO_2 capturing K- or Ba-containing components (Fig. 1C). The angle between both nozzles was chosen to be 160° [25]. Each nozzle used a premixed pilot CH_4/O_2 flame at a vol. ratio of 1/2 to ignite and sustain the spray [26].

The Al-precursor solution consisted of aluminum-tri-*sec*-butoxide (Fluka, 95%) dissolved in a 2:1 vol. ratio of diethylene glycol monobutyl ether (Fluka, 98%) and acetic anhydride (Riedel-de Haën, 99%). The aluminum concentration was kept constant at 0.5 mol/L. The Ba-precursor solution consisted of barium 2-ethylhexanoate (Aldrich, 98%) dissolved in 1:1 vol. ratio of toluene (Riedel-de Haën, 99%) and 2-ethylhexanoic acid (Riedel-de Haën, 95%) for a Ba concentration of 0.06 mol/L. For the K-precursor, potassium-acetate (Alfa Aesar, 99%) was dissolved in a 1:1 vol. ratio of toluene (Riedel-de Haën, 99%) and 2-ethylhexanoic acid (Riedel-de Haën, 95%) with a K concentration of 0.22 mol/L. Appropriate amounts of Rh-2,4 pentanedionate (Alfa Aesar, 99.99%) were added to either the Al-solutions or the Ba- or K-solutions. The Al-precursor solution was sprayed at 5 ml/min and the Ba or K ones at 3 ml/min. All precursor solutions were dispersed with 5 L/min O_2 (Pangas, 99,95%). The Al, Ba, K, and Rh- concentrations and spray rates were chosen to result in a nominal $Rh/M/Al_2O_3$ (with M = K or Ba or nothing) weight ratio of 1/20/100. In the present notation, the noble metal is written next to the material with which

it was co-produced and where preferential Rh deposition occurs [27]. For example, Rh/Al–Ba represents Rh deposited on the alumina support, whereas in Al–Ba/Rh the noble metal is deposited on the Ba-containing component.

2.2. Catalyst characterization

Nitrogen adsorption–desorption isotherms were measured at 77 K (Micromeritics Tristar instrument) and the BET method was used to determine the specific surface area (SSA) by a 5-point nitrogen adsorption isotherm. The estimated accuracy is ±3%. X-ray diffraction (XRD) patterns were recorded with a Bruker D8 Advance instrument (40 kV, 40 mA, λ = 0.154 nm). Crystallite sizes and mass fractions were calculated using the fundamental parameter approach and the Rietveld method with the TOPAS 3 software at ±10% accuracy [27].

For scanning transmission electron microscopy (STEM), the catalyst material was dispersed in ethanol and deposited onto a perforated carbon foil supported on a copper grid (Okenshoji Co. Ltd.). The STEM images were obtained with a high-angle annular dark-field (HAADF) detector attached to a Hitachi HD2700, aberration-corrected dedicated STEM (cold FEG, operated at 200 kV), showing the metal particles with bright contrast (Z contrast).
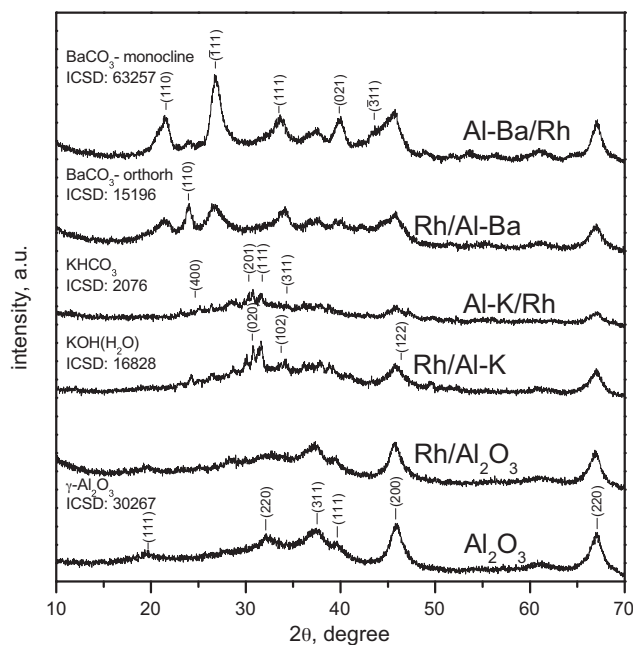

Fig. 2. Powder XRD analysis of as-prepared catalysts. The support material Al_2O_3 is present in all samples. The Ba-containing samples show additionally $BaCO_3$ while K-containing samples show $KHCO_3$ and $KOH(H_2O)$ reflections.