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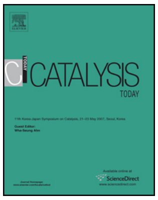

Methane dry reforming over ceria-zirconia supported Ni catalysts

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ABSTRACT

Nickel nanoparticles supported on $Ce_{1-x}Zr_xO_2$ mixed oxides prepared by different synthesis methods, as well as Ni-ZrO_2 and Ni-CeO_2, were evaluated for their catalytic performance in methane dry reforming (MDR). MDR is an interesting model reaction to evaluate the reactivity and surface chemistry of mixed oxides. Textural and structural properties were studied by N_2 adsorption and XRD. Mixed oxide preparation by co-precipitation resulted in catalysts with higher surface area than that of pure ZrO_2 or CeO_2. XRD analysis showed the formation of different $Ce_{1-x}Zr_xO_2$ solid solutions depending on using a surfactant or not. The catalyst prepared by surfactant assisted co-precipitation was not active for methane dry reforming most likely because of the encapsulation of Ni particles by ceria-zirconia particles, as revealed by TEM and H_2 chemisorption. The catalytic activity of the catalyst prepared by co-precipitation without surfactant was comparable to Ni-ZrO_2. Clearly, catalyst activity strongly depends on preparation and on the resulting phase composition rather than on nominal composition. Compared to Ni-ZrO_2 the ceria-zirconia supported Ni catalyst did not achieve higher activity or stability for methane dry reforming but, nevertheless, the formation of filamentous carbon was strongly reduced (100 times less carbonaceous species). Consequently, using ceria-zirconia as a support material decreases the risk of reactor tube blocking.

1. Introduction

Methane dry reforming (MDR) has attracted attention in recent years, not only because of synthesis gas production, but also due to environmental aspects. The MDR reaction (1.1) directly converts the greenhouse gases CH_4 and CO_2 to synthesis gas. Since a lower H_2:CO ratio is achieved by MDR than by methane steam reforming (MSR), synthesis gas produced by MDR is effective for olefins hydroformylation and carbonylation reactions. Additionally, MDR has great potential to be used for energy transformation and storage due to its reversibility via methanation [1].

$$CH_4 + CO_2 \rightleftarrows 2H_2 + 2CO \Delta H_r^0(25^\circ C) = +247\,kJmol^{-1} \tag{1.1}$$

However, other possible reactions such as reverse water-gas-shift RWGS (1.2), steam reforming of CH_4 (1.3), methane decomposition (1.4) and CO disproportionation (1.5) must be considered, resulting in H_2:CO ratios different from 1 and leading to carbon deposition on the catalyst.

$$H_2 + CO_2 \rightleftarrows H_2O + CO \qquad \Delta H_r^0(25^\circ C) = +41\,kJmol^{-1} \tag{1.2}$$

$$H_2O + CH_4 \rightleftarrows 3H_2 + CO \qquad \Delta H_r^0(25^\circ C) = +206\,kJmol^{-1} \tag{1.3}$$

$$CH_4 \rightleftarrows 2H_2 + C \qquad \Delta H_r^0(25^\circ C) = +75\,kJmol^{-1} \tag{1.4}$$

$$2CO \rightleftarrows C + CO_2 \qquad \Delta H_r^0(25^\circ C) = -171\,kJmol^{-1} \tag{1.5}$$

The effect of carbon deposition is a major problem and may lead to catalyst deactivation [2,3], by decoration (poisoning) of the active metallic sites and/or physical blockage of the tubes in fixed bed reformers [4]. Hence, intense research efforts have been focused on the development of catalysts that show high activity but are also resistant to carbon formation and sintering. Fischer and Tropsch showed already in 1928 that most group VIII metals display a significant activity for methane dry reforming [5]. Many years

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later various transition metals (Ni, Ru, Rh, Pd, Ir, and Pt) have been tested [6–10]. Even though Rh was the most stable and active of group VIII metals rather Pt catalysts have been developed as excellent methane dry reforming catalysts [11–15]. Besides the highly active noble metal catalysts, nickel based catalysts are the choice for industrial applications, due to better availability, lower cost and comparable activity [16]. Nevertheless, the active nickel particles tend to form coke, leading to catalyst deactivation [17].

Nickel-based catalysts have been proven to be sensitive to doping and structure modification by other metals, such as Cu, which affects the structure and morphology of the produced carbon [18]. We have studied CH_4 reforming activities and selectivity on Ni and CuNi-based catalyst systems by combining in situ spectroscopic techniques such as near atmospheric pressure X-ray photoelectron spectroscopy (NAP-XPS), Fourier transform infrared spectroscopy (FTIR) and X-ray absorption spectroscopy (XAS) [19–21]. The formation of CuNi alloy nanoparticles enhanced the stability against carbon deposition, but the CuNi alloy showed limited stability (i.e. Ni segregation) under reaction conditions [20,21]. For in situ studies on other bimetallics (PdZn, Pd-Ga, Pd(Pt)-Cu) we refer to [22–26]. Boron promotion of Ni-based catalysts was also reported to inhibit the formation of bulk carbide and weaken the on-surface carbon binding energies [27].

Clearly, in addition to the metallic component of the catalyst, the support material also plays an important role in the catalytic activity and stability towards carbon deposition. Indeed, nickel has been supported on various supports such as MgO [3,16,28–30], Al_2O_3 [3,30–34], SiO_2 [3,16,35], TiO_2 [3,16], La_2O_3 [31,32], CeO_2 [30,32,36], ZrO_2 [32,33,37,38] and $Ce_{1-x}Zr_xO_2$ [39–49]. $Ce_{1-x}Zr_xO_2$ solid solution is considered as a promising support [39–46] for Ni-based MDR catalysts. Mixing ZrO_2 and CeO_2 has been found to improve the thermal stability, catalytic activity and oxygen storage capacity. The latter refers to the ability to deliver oxygen from the lattice to the gas phase or to solid (adsorbed) carbon [39,46,50]. Several methods have been used to prepare $Ce_{1-x}Zr_xO_2$ solid solutions for catalytic applications. These include the high-temperature milling of a mixture of the oxides [51], co-precipitation [39–41,44,50,52–56], surfactant-assisted co-precipitation [42,43,45,57,58], thermal hydrolysis [59–61], sol-gel [46,62,63] and pseudo-sol-gel techniques [47,48]. Among these methods, the surfactant-assisted co-precipitation route has attracted considerable interest because of its effective soft-templating, reproducibility and simplicity [58]. However, detailed correlations of MDR catalytic activity with the oxides microstructures (e.g. determined by Raman spectroscopy or powder XRD via the Rietvield analysis) are still lacking. In order to understand the beneficial effect of the $Ce_{1-x}Zr_xO_2$ support is of great importance to establish relationships between the surface structural and physico-chemical properties with the catalytic activity.

Recent studies by Makri et al. [64] provided very important insights into the carbon formation pathways and carbon reactivity over 5 wt% $Ni/Ce_{0.8}Zr_{0.2}O_{2-\delta}$ and 5 wt% $Ni/Ce_{0.5}Zr_{0.5}O_{2-\delta}$ MDR catalysts. Using temperature-programmed methods and transient isotopic experiments it was demonstrated that the reaction temperature and support chemical composition had a strong effect of on the relative contribution of the CH_4 or the CO_2 activation routes towards carbon formation, as well as on the reactivity of the various carbons towards H_2 and O_2.

In this contribution we have revisited the mixed oxide support and have compared the catalytic activity, stability and coke formation tendency of Ni based catalysts supported on $Ce_{0.6}Zr_{0.4}O_2$ (prepared by co-precipitation and surfactant assisted co-precipitation) with those supported by the individual supports ZrO_2 and CeO_2. MDR is an interesting model reaction to compare the reactivity and surface chemistry of different mixed oxides. The main aim of this work was to understand some of the influencing factors by correlating structure (governed mainly by the synthesis procedure) with catalytic performance. $Ce_{0.6}Zr_{0.4}O_2$ was chosen since Kumar et al. [42] reported Ni-$Ce_{0.6}Zr_{0.4}O_2$ to be the most effective methane dry reforming catalyst, as its activity was stable for up to 100 h at 650 and 700 °C. We have tested these catalysts during MDR at 600 °C for up to 24 h and characterized them carefully before and after exposure to the reaction mixture. The mixed oxide catalysts prepared by different co-precipitation methods showed very different catalytic behaviour. Even though the catalytic activity of the active ceria-zirconia supported Ni catalyst was not higher than that of Ni-ZrO_2, the $Ce_{0.6}Zr_{0.4}O_2$ support still strongly decreased deposition of carbonaceous species.

2. Experimental

2.1. Sample preparation

Ni-ZrO_2, Ni-CeO_2 and two types of Ni-$Ce_{0.6}Zr_{0.4}O_2$ catalysts were prepared by different methods. ZrO_2 was prepared from $Zr(OH)_4$ (MEL Chemicals, XZO 880/01) by heating from room temperature (RT) to 650 °C at a ramp of 2 °C/min and kept at 650 °C for 2 h. Commercial CeO_2 (Schuchardt, CE026) was calcined at 650 °C at a ramp of 2 °C/min and kept at 650 °C for 2 h. Two further binary ceria-zirconia materials were prepared by a co-precipitation (cp) method, both $Ce_{0.6}Zr_{0.4}O_2$ were composed of 60 mol% CeO_2 and 40 mol% ZrO_2. For preparation of the first oxide support (labelled as $Ce_{1-x}Zr_xO_2$_cp) stoichiometric quantities of zirconyl nitrate hexahydrate ($ZrO(NO_3)_2{\cdot}6H_2O$, Fluka) and cerium(III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, Aldrich) were dissolved in distilled water. The resulting solution was transferred to a round bottom flask and stirred for 1 h at 80 °C. Then, an aqueous solution of 20% w/w KOH was added drop-wise at 80 °C with constant stirring until a pH of 10.5 was reached. After digesting the precipitate at 80 °C for 72 h, it was filtrated and washed several times with distilled water to remove any potassium impurity. Then, it was air-dried for 72 h followed by drying at 120 °C for 6 h. Finally, the oxide was heated at a ramp of 2 °C/min and kept at 650 °C for 2 h. The second mixed oxide, labelled as $Ce_{1-x}Zr_xO_2$_ctab, was prepared by surfactant-assisted co-precipitation with cetyltrimethylammonium bromide (CTAB, Roth). The synthesis route was adapted from Sunkonket et al. [45] with a molar ratio c(CTAB)/c(Ce + Zr) = 1 and dropwise addition of aqueous ammonia for precipitation.

A nominal 5% w/w Ni was loaded over all supports by wet impregnation, using nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, Merck) aqueous solution. After drying overnight at 100 °C the catalysts were calcined at 450 °C for 2 h.

2.2. Catalyst characterization

2.2.1. X-ray diffraction measurements

Powder XRD patterns were recorded on a XPERT-PRO diffractometer with Cu Kα radiation operating at 40 kV and 40 mA with a 2θ scanning from 5 to 90° and a step size of 0.02°. The crystallite size t was estimated from X-ray line broadening using the Scherrer's formula [65] $t = 0.9{\cdot}\lambda/(B \cdot \cos(\theta))$, where λ is the X-ray wavelength (Cu Kα radiation: 0.154 nm) and B the full-width half-maximum of the Bragg diffraction angle θ.

2.2.2. Surface area analysis

The Brunauer-Emmet-Teller (BET) specific surface areas for all catalysts were obtained by N_2 physisorption acquired at liquid N_2 temperature using a Micromeritics ASAP 2020 apparatus. Prior to analysis, all powders were outgassed at 300 °C and <13 μbar for 1 h prior to acquisition of the adsorption isotherm. The average pore size and average pore volume were analysed by the BJH method