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Investigations on the properties of ceria–zirconia-supported Ni and Rh catalysts and their performance in acetic acid steam reforming

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ABSTRACT

The production of hydrogen via steam reforming of acetic acid was examined over Ni and Rh supported on a CeO_2–ZrO_2-mixed oxide. The catalysts were tested at 550–650–750 °C using steam/carbon = 3. Steam reforming, water gas shift, and decarboxylation are the main reactions taking place over the support alone. In parallel, dehydrogenation leads to the formation of carbon deposits on the surface of the mixed oxide. The addition of the metals enables the reforming reactions to proceed with high rates producing hydrogen yields close to thermodynamic equilibrium even at 650 °C. The oxygen exchange reactions are enhanced leading to much lower coke deposition. The nature of the metal affects not only the quantity but also the quality and the location of the carbon deposits, as evidenced from temperature-programing oxidation tests. The synergy of the support and metal is the key factor for the low coke deposition, which is even lower for the Rh catalyst.

1. Introduction

Hydrogen has great potential as an environmentally clean energy fuel. Since hydrogen does not exist on earth as a gas, it must be obtained from other compounds such as water, biomass, and natural gas. The two most common methods for producing hydrogen are steam reforming and electrolysis. Nowadays, a large amount of hydrogen that is commercially used for ammonia production and refining processes is produced from fossil fuels such as natural gas, naphtha, heavy oil, and coal via steam reforming and partial oxidation processes [1].

The depletion of currently used sources of hydrogen and the substantial amounts of CO_2 emitted to the atmosphere during the process steps associated with its production lead to apprehension. Biomass has been proposed as an alternative feedstock for hydrogen production not only because it is renewable but also because it is a CO_2 neutral energy source.

Hydrogen can be produced from biomass mainly via two thermochemical processes, gasification [2,3] and flash pyrolysis [4–6] followed by steam reforming of the pyrolysis oil. The pyrolysis oil, known as bio-oil, is a complex mixture of acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans, and multifunctional compounds [7]. Steam reforming can be used to convert the entire bio-oil or each of the oil fractions, the hydrophilic light fraction and the hydrophobic heavier fraction, to hydrogen-rich stream.

Thermodynamic calculations of steam and autothermal reforming of particular model compounds of bio-oil, acetic acid, ethylene glycol, and acetone showed that the oxygenates in the presence of steam are easily converted to hydrogen-rich mixtures achieving maximum hydrogen yield (80–90%) at 625 °C without any coke formation for operation under atmospheric pressure and steam/carbon > 1 [8,9].

Several studies have been reported for acetic acid steam reforming [10–20]. The influence of Ni and noble metals and the type of the support (Al_2O_3, La_2O_3/Al_2O_3, and MgO/Al_2O_3) on acetic acid steam reforming has been persistently studied. The main conclusions point to the crucial effect of the metal type and support on the hydrogen selectivity and yield and the high tendency of the thermally unstable oxygenates to decompose forming carbonaceous deposits which limit their large scale application especially in conventional fixed bed reactors [12].

Catalytic materials based on CeO_2–ZrO_2 have been demonstrated to be active in methane steam reforming with stable behavior, high methane conversions, and hydrogen yields approaching those of thermodynamic equilibrium. Above all, the ability of these catalytic materials to resist carbon deposition renders them attractive in reforming reactions. Partial oxidation, CO_2 reforming and steam reforming of methane using Ni and Pt over CeO_2–ZrO_2, CeO_2, and ZrO_2 have been widely examined in the literature

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[21–28]. In addition, the ceria–zirconia system has been investigated in phenol and ethanol reforming [29–36]. Despite the promising results of these materials concerning their high activity in combination with coke resistance in reforming reactions, their application in steam reforming of bio-oil and its components has received less attention [37,38].

Our recent publication [39], concerning acetic acid and acetone steam reforming over Ni and Rh supported on Ca–Al-mixed oxides, showed that hydrogen yield depends on the metal type and loading and the ratio of CaO to Al_2O_3. Both Ni- and Rh-containing catalysts were proved to be very effective in converting acetic acid and acetone to hydrogen with relatively low carbonaceous depositions.

The aim of the present work is to investigate acetic acid steam reforming over ceria–zirconia-mixed oxide-supported catalysts. The influence of active metal (Ni and Rh) on hydrogen yield, and the synergetic action of the support and metal on the nature and the quantity of carbon deposits are investigated using continuous flow experiments of acetic acid reforming and thermo-programing techniques.

2. Experimental

2.1. Catalyst preparation

The wet impregnation method was applied for the catalysts' preparation. Cerium-doped zirconium hydroxide provided by Mel Chemicals (XZO802) was calcined at 800 °C for 4 h. The calcined material with a composition $CeO_2/ZrO_2 = 15/85$(wt) was used as the support. $Ni(NO_3)_2{\cdot}6H_2O$ and $RhCl_3{\cdot}3H_2O$ were the precursors for the nickel (5 wt%) and rhodium (0.5 wt%) metals, respectively. The aqueous solution of the precursors was mixed with the support particles and stirred for 1 h at 70 °C. The solvent was removed via evaporation under mild vacuum conditions and the samples were dried afterward overnight at 120 °C. The catalytic materials were calcined in air flow at 400 °C for 2 h. Before the reforming experiments, the catalysts were reduced at 750 °C for 1 h in 25% H_2/He flow.

The catalytic materials are referred to as *z*Me/Ce–Zr (where *z* is the metal wt% and Me is Ni or Rh) for samples supported on CeO_2–ZrO_2.

2.2. Catalyst characterization

The surface area of the prepared materials was measured by N_2 adsorption at 77 K, using the multipoint BET analysis method with an Autosorb-1 Quantachrome flow apparatus. The samples were dehydrated in vacuum at 250 °C overnight, before surface area measurements. X-ray diffraction (XRD) patterns were obtained using a Siemens D500 diffractometer, with Cu Kα radiation.

NH_3 temperature-programed desorption (TPD-NH_3) was used to determine the acidic properties of the catalysts. The experiments were performed in a gas flow system using a U-tube reactor connected online with a quadrupole mass analyzer (Omnistar, Balzers). The catalysts (200 mg) were pretreated at 650 °C for 0.5 h and then cooled to 100 °C under He flow. The pretreated samples were saturated with 5% NH_3/He for 1 h at 100 °C, with subsequent flushing with He at 100 °C for 1 h to remove the physisorbed ammonia. TPD analysis was carried out from 100 to 700 °C at a heating rate of 10 °C/min. Quantitative analysis of the desorbed ammonia was based on (m/z) 15.

Temperature-programed reduction (TPR) experiments were performed in the same setup with the TPD NH_3 experiments. The catalyst sample (200 mg) was placed in a U-shaped quartz reactor and pretreated for 0.5 h at 650 °C in flowing 15% O_2/He followed by cooling at room temperature in He flow. The temperature was then raised from room temperature to 900 °C at a rate of 10 °C/min in a 5% H_2/He flow (30 cm^3/min).

The metal dispersion was measured with H_2 temperature-programed desorption (TPD-H_2). Using the same flow system as mentioned above the catalysts (300 mg) were treated at 600 °C for 1 h under 20% O_2/He flow, then cooled to 300 °C, and then reduced with 20% H_2/He for 1 h at the reduction temperature of the metal (470 °C for Ni and 300 °C for Rh). The reduced sample was heated to 500 °C in He flow to desorb any H_2 than might have been spilled over the support and then cooled down to room temperature. A flow of 5% H_2/He was applied for 30 min at room temperature followed by He flow for another 30 min. The TPD analysis was carried out from room temperature to 700 °C at a heating rate of 10 °C/min.

For the measurements of the oxygen storage capacity (OSC) of the Ce–Zr-mixed oxide catalysts the sample (50 mg) was first pretreated at 750 °C for 0.5 h under He flow. Injection of pulses of H_2 every 100sec, at 750 °C, was applied up to a maximum reduction of the sample (25 pulses). The OSC was also measured using pre-reduced samples at 750 °C for 1 h under H_2 flow to simulate the conditions as in catalytic-reforming experiments (Section 2.4). The amount of μmol of O_2/g of catalyst, calculated according to the H_2 consumption of the first pulse, is considered as the active oxygen of the catalyst and represents the OSC. The sum of the μmol O_2/g of catalyst of the first 10 pulses presented as OSCC characterizes the total amount of oxygen available in oxide [40].

The oxygen surface mobility was examined with the oxygen isotopic exchange experiments. The materials (300 mg) were first reduced at the specific reduction temperature of the metal (300 °C for Rh and 470 °C for Ni) to ensure that the support remains in oxidized form. Then, they were cooled under He flow to room temperature before the reaction. The isotopic exchange of oxygen (2% $^{18}O_2$/He) was temperature programed from 50 to 750 °C with a rate of 15 °C/min. The ratios m/z 32, 34, and 36 were monitored for the $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$, respectively.

The used catalysts were transferred to a CHN stoichiometric analyzer LECO 800, for the measurement of the solid carbon deposited on the catalyst. The oxidation temperature of the solid carbon was also measured in a thermogravimetric unit (STD2960 TA Instruments), by subjecting the catalyst in temperature-programed oxidation with a rate of 10 °C/min up to 1000 °C, under air flow. The morphology of the carbon deposits was examined by scanning electron microscopy (SEM) on a JEOL 6300 microscope.

2.3. Catalytic testing

The experiments were performed at atmospheric pressure in a laboratory unit equipped with a mass flow-controlled system for gases admission, a fixed bed quartz reactor, and an online gas chromatograph. An HPLC pump (Gilson 350) was used for the feeding of the liquid reactants (a mixture of acetic acid and water) to the reactor through a preheater. The fixed bed reactor was heated electrically by a tubular furnace, with three independently controlled temperature zones. The temperature in the middle of the catalytic bed was measured with a coaxial thermocouple. The hot gases exiting the reactor were cooled to condense the liquid products and the unconverted reactants. The gas phase products were analyzed with an online gas chromatograph (Varian 3700) equipped with TCD. To separate the gaseous products, two columns were used: Porapak Q for CO_2, C_2H_4, C_2H_6, and higher hydrocarbons and MS 5A for H_2, O_2, CO, and CH_4. The liquid products were analyzed offline in gas chromatograph (Varian 3300) equipped with FID using an HP-FFAP column.