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CuO/CeO$_2$ washcoated ceramic monoliths for CO-PROX reaction

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ABSTRACT

CuO/CeO$_2$ catalysts, with 7 and 9 wt.% copper loading was prepared by wet impregnation, and later was washcoated over cordierite monoliths in order to study their performance in CO-PROX reaction. The powder sample with low copper loading shows high concentration of easily reducible copper species. SEM images of the monoliths show an average thickness of 9 and 12 μm of the catalyst layer for 7% and 9% copper containing samples. EDX analyses suggested that copper has been deposited non-uniformly on the ceria surface. In the absence of CO$_2$ and H$_2$O, monolith washcoated with 7% Cu loaded catalyst shows better performance than its 9% counterpart in terms of activity and selectivity towards CO$_2$ in CO-PROX reaction. However, CO$_2$ substantially inhibits the activity and selectivity of both monoliths, in particular 7% Cu loaded catalyst. Also, H$_2$O inhibits the activity and selectivity of both monoliths, although in lower extent than that of CO$_2$.

1. Introduction

Selective oxidation of CO in H$_2$-rich streams (CO-PROX) is considered as the most efficient and straightforward method to obtain CO-free hydrogen (maximum CO content of 10 ppm in steady-state operation) to feed PEM fuel cells, especially for small scale mobile (such as vehicles) and portable auxiliary power units [1]. Traditionally, supported noble metals have been used for this purpose [2–4]. Gold-based catalysts, supported on reducible oxides, such as CeO$_2$ [5], or Fe$_2$O$_3$ [6] have been reported to be more active than Pt-based catalysts, but they show less resistance in the presence of H$_2$O and CO$_2$ in the feedstream [7]. Recently, base–metal oxide catalysts, especially CuO, have received attention because they exhibit high activity and selectivity towards CO oxidation [8]. In the recent years, CuO–CeO$_2$ catalysts have been proposed as candidates for the CO-PROX reaction [9–13]. These catalysts are more active and remarkably more selective than noble metal ones, and are also active at significantly lower temperatures than Pt-based catalysts [14]. The easy Ce^{+4}/Ce^{+3} redox cycle leads to outstanding oxygen storage capacity with reversible addition and removal of oxygen in the fluorite-type structure of the ceria [15]. A large number of investigations on CuO–CeO$_2$ catalysts preparation have been carried out in order to achieve catalyst with intimate CuO–ceria interface as strong metal–support interactions in the interface cause synergism which is responsible for their high activity towards oxidation reactions [10,16]. From the standpoint of process efficiency, it is desirable to select the CO-PROX catalyst and operating conditions that lead to selectivity close to unity as possible.

Ceramic monoliths with straight channels are considered to be suitable as supports for CO-PROX catalysts, since the geometric surface area of monoliths are much larger than that of the particulate catalysts [17]. On the other hand, the very high open frontal area of the monolithic support minimizes the gas pressure drop and also the low heat capacity provides a rapid response to changes in the operating conditions [18]. Monolithic catalysts have being extensively used for automobile exhaust gas purification [19]. To our knowledge only a few references have been found for CO-PROX application with copper–ceria washcoated monoliths [20]. Similar systems formed by three-dimensionally ordered CuO–CeO$_2$ or CuO–CeO$_2$ deposited on micro-channel reactor have been reported for CO-PROX [21,22].

The aim of this work is to study the performance of CuO/CeO$_2$ washcoated ceramic monoliths in CO-PROX reaction, for which we have prepared two different copper loaded CeO$_2$ as powder (close to optimum loading found in previous work [14]) to later be deposited onto ceramic monolith. Studies on the effect of the ratio O$_2$/CO as well as the influence of CO$_2$ and H$_2$O in the feedstream on the catalytic performance of the monoliths were studied.

2. Experimental

2.1. Catalyst preparation

Cylindrical shape ceramic honeycomb monolith (400 cpsi, Corning) was used as a support on which CuO/CeO$_2$ catalyst was washcoated. The catalyst was prepared as follows: during the

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first step, CuO/CeO_2 was prepared by incipient wetness impregnation from $Cu(NO_3)_2{\cdot}3H_2O$ precursor, over commercial high surface area CeO_2 (Rhodia, $S_{BET} = 164\,m^2/g$), with copper loadings of 7 and 9 wt.%. In order to adjust the powder size for washcoating, the as-prepared powder catalysts was suspended in distilled water (2 mL of water per gram of catalyst) and then wet milled for 3 h. Although lowering the pH achieves better suspension of particles in the slurry [23] in our case we did not add any acid in order to avoid copper leaching during milling [24]. Particle size distributions of agglomerates in the suspension were determined by laser particle size analysis carried out using Malvern Mastersizer X apparatus. For the washcoating, the slurry was prepared as a suspension of the catalyst in 60 mL of distilled water, and the pH was adjusted to 5 (by the addition of 1 M HNO_3). The actual amount of supported metal was determined by ICP-AES Horiba. Washcoating of CuO/CeO_2 catalyst was carried out by immersion of the cordierite monolith in the slurry for a period of 10 s; later, air was blown through the channels to remove the excess solution and dried at 393 K for 30 min. This procedure was repeated until the desired catalyst weight was achieved (to achieve the desired WSV during the lightoff experiments). Finally, the catalyst was calcined in air at 773 K for 5 h. The washcoat loadings on the monolith were calculated based on the following formulation:

$$W = \frac{m - m_0}{m_0} \times 100 \qquad (1)$$

where W is the washcoat loading, m is the weight of the monolith after each immersion and m_0 is the weight of blank cordierite before coating. The monoliths were denoted as 7CuCeM and 9CuCeM, the figure indicating the wt.% of copper in the powder catalysts; the powder catalysts have been denoted as 7CuCeP and 9CuCeP.

2.2. Catalyst characterization

Specific surface area and pore size distribution of the CuO/CeO_2 powder catalysts was determined by N_2 adsorption–desorption isotherms at 78 K (Micromeritics ASAP 2010). The crystalline structure of the catalysts was analyzed by XRD (Philips PW1710 diffractometer) with Cu Kα radiation in continuous scan mode. The particle size of ceria was calculated by X-ray broadening technique using Scherrer's equation ($d = K \cdot \lambda/\beta \cdot \cos\theta$) using the shape factor $K = 0.9$. The phase identification was carried out using reference files compiled by the International Centre for Diffraction Data (ICDD). The textural structure of the monoliths was analyzed using a scanning electron microscope (JEOL JSM-7000F) equipped with energy dispersive X-ray detector (EDX).

The redox properties of the catalysts were investigated by temperature-programmed reduction (TPR) using hydrogen. The sample was first oxidized by heating up from room temperature to 600 °C with a ramp of 10 °C/min with 60 mL/min flow of 5%O_2–He, later the sample was cooled down to −20 °C into He flow. The TPR experiments were carried out from −20 to 400 °C with a ramp of 20 °C/min with 60 mL/min flow of 5%H_2–Ar mixture. The TPR of the bulk CuO and support CeO_2 were carried out over calcined samples from 0 to 900 °C, at 20 °C/min. The water formed during reduction with H_2 was trapped using a cold trap and the hydrogen consumption was continuously monitored with a TCD. The catalyst ability to store and release oxygen (OSC, defined as the amount of CO_2 formed during a CO step pulse after oxidation in O_2) was conducted for the powder samples at a constant temperature of 120 °C, with the following procedure (repeated for 2 cycles, in order to check its reversibility): He → 5%O_2–He, 9 min → He, 6 min, 5%CO–He, 9 min → He, with a total flow of 100 mL/min in all steps. Mass spectrometer (MKS Cirrus 300) coupled to a NDIR selective detector for CO (Siemens Ultramat 23) was used for continuous monitoring of exhaust gases.

2.3. Catalytic studies

Catalytic tests over the CuO/CeO_2 monoliths were carried out in a down-flow plug flow reactor at atmospheric pressure (Microactivity-Reference, PID Eng&Tech). The prepared monoliths were cylindrical with dimensions of 2.1 cm in height and 0.9 cm in diameter, containing 21 channels (the channel in the centre was used to insert the thermocouple), other geometric characteristics of the monoliths are as follows: open frontal area fraction = 0.86, geometric surface area per volume unit = $2500\,m^2/m^3$, hydraulic diameter = 1.36 mm. The light-off curves were obtained for CO-PROX from 50 °C to 200 °C with a temperature ramp of 3 °C/min. A total flow rate of 200 mL/min at 1 atm (GHSV = $9000\,h^{-1}$, WSV = $0.43\,NL\,min^{-1}\,g^{-1}$) was fed to the reactor with the following composition (in vol%): CO(1%), O_2(0.5–1%), H_2(60%), He (to balance), for conditions without CO_2 and H_2O. When a more realistic reformate gas composition was simulated, 15% CO_2 and 15% H_2O were fed to the above mixture, initially either CO_2 or H_2O was used and later both together. The effect of oxygen-excess parameter ($\lambda = 2 \cdot P_{O_2}/P_{CO}$) on the catalyst performance was also studied for λ = 1, 1.5 and 2, in the absence of CO_2 and H_2O. The feed and exhaust gases were continuously analyzed by MS (MKS Cirrus 300) coupled to a NDIR selective detector for CO (Siemens Ultramat 23).

The CO and O_2 conversions (Eqs. (2) and (3)) and selectivity towards CO_2 (Eq. (4)) were calculated by their usual definitions, from the molar flow of CO and O_2 in the inlet and outlet of reactor:

$$X_{CO}(\%) = 100 \cdot \frac{[F_{CO,in} - F_{CO,out}]}{F_{CO,in}} \qquad (2)$$

$$X_{O_2}(\%) = 100 \cdot \frac{[F_{O_2,in} - F_{O_2,out}]}{F_{O_2,in}} \qquad (3)$$

In the case of no parasite reactions such as WGS or methanation, selectivity towards CO_2 can be calculated as the ratio of the oxygen reacting to CO and the total oxygen consumption.

$$S_{CO_2}(\%) = \frac{100}{2} \cdot \frac{\left[F_{CO,in} - F_{CO,out}\right]}{\left[F_{O_2,in} - F_{O_2,out}\right]} \qquad (4)$$

Taking into account the definition of oxygen-excess parameter (λ), the latter equation can be written as follows, which has been employed for selectivity calculations:

$$S_{CO_2}(\%) = 100 \cdot \frac{X_{CO}}{X_{O_2}} \cdot \frac{1}{\lambda} \qquad (5)$$

In the studied temperature range, neither WGS nor methanation reactions occurred, thus, the above equations were used.

The comparison of the activity of the samples has been done in terms of T_{50} (temperature required for 50% of CO conversion), T_{100} (lower temperature required for 100% of CO conversion) and T^* (highest temperature at which complete CO conversion is achieved). Note that the difference $T^* - T_{100}$ corresponds to the temperature window where 100% conversion is achieved, as reported in some works [21,25]. On the other hand, the comparison of catalysts selectivity towards CO_2 has been done with the aid of $S_{T_{1000}}$ (selectivity at the temperature T_{100}) and S_{T^*} (selectivity at the temperature T^*, i.e. the selectivity at the end of the 100% conversion temperature window).

3. Results and discussion

3.1. Powder catalyst textural and morphological characterization

The main textural and morphological properties of the catalysts (in powder) are shown in Table 1. The BET specific surface area of the catalysts decrease with respect to the pure support ($164\,m^2/g$)