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Novel PtCuO/CeO_2/α-Al_2O_3 sponge catalysts for the preferential oxidation of CO (PROX) prepared by means of supercritical fluid reactive deposition (SFRD)

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ABSTRACT

Ceramic sponges (α-alumina) supporting ceria wash-coats and PtCuO layers of varying compositions were tested in the preferential oxidation (PROX) of CO in the presence of excess hydrogen. Copper and platinum were loaded simultaneously on the ceria-coated sponge by means of supercritical fluid reactive deposition (SFRD) which includes adsorption and reduction of metal-organic complexes dissolved in supercritical CO_2. Products were characterized by means of SEM, STEM HAADF, EDX, H_2-TPR, CO-TPD, CO_2-TPD and N_2-adsorption. Catalysts prepared after the SFRD-method exhibit high selectivity. The CO oxidation activity roughly correlates with the copper content and is superior as compared to the activity of PROX-catalysts reported in the literature so far.

1. Introduction

CuO/CeO_2-catalysts have many fields of application such as the combustion of CO and methane [1], the water–gas shift reaction [2–4], the reduction of SO_2 by CO [5], reduction of NO_x [6] methanol synthesis [7], and the wet oxidation of phenol [8]. Most frequently they are being investigated as catalysts for the preferential oxidation of CO in the presence of hydrogen (PROX) [9] for application in the context of a fuel cell economy.

Fuel cells find increasing proliferation due to their high efficiency in small scale power generation. In those cases in which fuel cells act as an auxiliary power sources, overall efficiency might be further increased by not making use of a dedicated hydrogen fuel tank, but by utilizing the chemical fuel (i.e., methane, methanol, petrol, diesel, etc.) already at hand and converting it to hydrogen. In this scenario, a reforming of the fuel is followed by a water–gas shift stage to increase the H_2-content of the feed. Because the CO-concentration is required to be lower than 10 ppm [10], a further purification has to be carried out, since this concentration is below the thermodynamic equilibrium concentration that could be reached at water–gas shift temperatures. The most straightforward method to achieve this goal is the preferential oxidation of CO (PROX). The PROX process is a unit operation step during which CO is selectively oxidized to CO_2 while the simultaneous oxidation of H_2 is avoided.

It is agreed upon that the dispersion of copper on ceria is the key parameter to a high catalyst activity [11–13]. In the literature, a multitude of preparation routes for CuO/CeO_2-type catalysts has been reported to date. In this present study, we apply supercritical fluid reactive deposition (SFRD) as a novel method to produce highly dispersed copper (and platinum) particles on a ceria wash-coat. Previously, SFRD has been employed to prepare Pt/SnO_2 catalysts with a high dispersion of platinum [14]. The concept is also employed to create thin metal films for optical and microelectronic applications [15]. In which case, however, an excess of the complexes melting point is sought after in order to create a film rather than separate particles.

Our method comprises dissolution of suitable metal-organic complexes in supercritical CO_2, adsorption of the complexes on the catalyst support, and *in situ* reduction in the supercritical state with dissolved hydrogen. Upon pressure relief, CO_2 is vaporized and removed together with the organic ligands and residual hydrogen. Because disturbing effects of capillary pressure and gravitation are absent, SFRD is particularly useful to achieve even distributions of metallic nanoparticles on supports of complex geometry and/or with fine pores [14,16]. We have chosen ceramic sponges as catalyst carriers because they combine low pressure drop with good heat and mass transfer characteristics [17,18].

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2. Experimental

2.1. Catalyst preparation

The catalysts discussed here consisted of copper oxide with minor amounts of platinum deposited on ceria wash-coats. Cylindrical pieces of α-Al_2O_3 sponges with a pore density of 20 ppi provided by *Vesuvius* were used as catalyst supports. Fig. 1 shows exemplarily a blank support, a sponge with ceria wash-coat and a finished catalyst.

Wash-coating was performed with a nitrate-stabilized ceria sol with an oxide content of 20% m/m (*Nyacol*), followed by drying and calcination in air for 3 h at 400 °C. The supercritical fluid reactive deposition (SFRD) of copper and platinum was carried out in a horizontal tubular steel batch reactor equipped with a magnetic stirrer (Fig. 3). A wash-coated sponge was placed in the reactor together with the solid metal precursors copper-t-methyl-heptanedionate ($Cu(tmhd)_2$) and 2-Me–Pt(II)-cyclooctadien (2MePtCOD) (Fig. 2). After evacuation to 10 Pa, the reactor was pressurized with CO_2 to 5 MPa and heated to 80 °C. Thereafter, the pressure was slowly and isothermically raised to 15.5 MPa using a screw press (SP-1). At these conditions, CO_2 is in supercritical state, and the metal complexes are dissolved. After 20 h, the adsorption equilibrium between the supercritical solution and the ceria surface is established, and the stirrer is switched off. Subsequently, 1.12% (molar) of the CO_2 is isobarically exchanged with H_2 by pressing a defined amount of H_2 from the opposite direction into the reactor with a second screw press (SP-2) while simultaneously pulling fluid from the reactor with the first screw press (SP-1). Upon contact with the dissolved H_2, the organometallic complexes are reduced to the respective metals, and the organic ligands are dissolved in sc-CO_2. After 2 h of reduction at 80 °C, the vessel is depressurized and CO_2 together with organics are flushed out.

For the purpose of comparison, a set of catalysts was prepared via impregnation. In this case, instead of the SFRD treatment, ceria-coated sponges were dipped for 5 min into a 0.7 M $Cu(NO_3)_2$ solution.

The weight gain after SFRD treatment and also after impregnation with $Cu(NO_3)_2$ was in the range of 5–9 mg, relating to about 0.3% of the final weight. Finally, the samples were calcined in air at 450 °C for 3 h.

2.2. Catalytic performance tests

PROX experiments were carried out in an isothermal tubular plug-flow reactor made of glass. A detailed description of the reactor can be found elsewhere [17]. A flowchart of the test rig is given in Fig. 4. The temperature was measured by two radially mounted thermocouples up- and down-flow to the catalyst bed. The reactor could be bypassed to measure inlet concentrations. Concentrations of CO and CO_2 were determined on-line using an *ABB Uras14* analyzer; O_2 was measured with an *ABB Magnos26* analyzer. Volumetric flow rates were varied between 20 l_{NTP}/h and 48 l_{NTP}/h. The corresponding weight-hourly space velocities (WHSV), defined according to Eq. (1), were ranging between 0.19 $h^{-1}$and 2.1 h^{-1}.

$$\mathrm{WHSV} = \frac{\dot{m}_{CO}}{m_{active}} \ (h^{-1}) \tag{1}$$

The active mass m_{active} of the catalyst is defined as the sum of the masses of CeO_2, Pt and CuO. It is determined by subtracting the weight of the blank α-Al_2O_3 sponge from the weight of the finished sample after calcination. The feed gas was composed of 0.5% CO, 0.5% O_2, 41% H_2, and nitrogen as the rest. The reactor temperature was varied between 90 °C and 150 °C. The conversion of CO was calculated as follows:

$$X_{CO} = \frac{C_{CO,in} - C_{CO,out}}{C_{CO,in}} \tag{2}$$

The selectivity to CO_2 was related to the oxygen consumption according to Eq. (3).

$$S_{CO_2,O_2} = \frac{C_{CO,in} - C_{CO,out}}{2(C_{O_2,in} - C_{O_2,out})} \tag{3}$$

External mass transfer limitation was ruled out by employing a correlation previously devised for ceramic sponges [17]. Temperature rise on the catalytic layer has been ruled out according to the Mears heat criterion in conjunction with a heat transfer correlation on ceramic sponges presented by Dietrich et al. [19]. Internal mass transfer limitations have been ruled out by the Weisz–Prater criterion. The rate coefficient k_m is related to the active mass and serves as an activity parameter. Assuming first-order kinetics in CO according to $r_m = k_m \cdot C_{CO}$, the coefficient k_m can be calculated from the CO-conversion according to

$$k_m\ (T) = \frac{-\ln(1 - X_{CO}(T))}{\tau_{mod}} \tag{4}$$

with τ_{mod} being defined as

$$\tau_{mod} = \frac{\dot{V}_0}{m_{active}} \tag{5}$$

2.3. Characterization

The contents of Cu, Pt, and Ce were determined by means of ICP-OES (*Varian Vista Pro CCD – Simultaneous* ICP-OES). SEM images were taken on a *LEO 1530 Gemini* microscope. BET surface areas and pore sizes of the catalyst samples were determined by means of nitrogen adsorption on a *Micromeritics ASAP2010*.

STEM HAADF images and according EDX data were obtained at a *FEI Titan 80–300 Cubed*. The sample was prepared for focused ion beam (FIB) milling at a combined SEM/FIB system (*ZEISS EsB 1540 Crossbeam*) by cutting a 5 × 10 μm cross-sectional slice from the surface layer of sample XII and consequently thinning it to about 50 nm in a Ga-ion beam.

Temperature-programmed reduction (TPR) and desorption (TPD) experiments were carried out on a *Micromeritics 2910* apparatus equipped with a thermal conductivity detector. An on-line quadrupole mass spectrometer (*Pfeiffer Vakuum QMG422*) served as an additional detector. TPR measurements were carried out at 10 °C/min in a flow rate of 25 ml_{NTP}/min of 5% H_2 in Ar after preheating in a flow of He for 1 h at 400 °C. TPD experiments were performed after preheating the sample at 450 °C in He and subsequent saturation of the sample surface with either CO_2 or CO at 30 °C. Desorption was achieved by heating in a flow of He at a rate of 2.5 °C/min with a holding step at 200 °C.

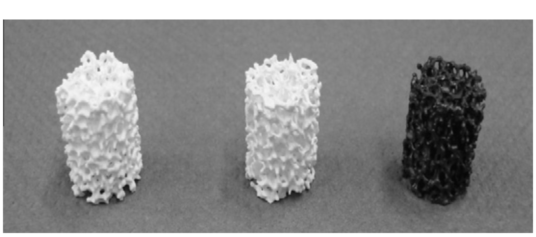

Fig. 1. Catalyst in its three stages of preparation (from left to right): blank α-Al_2O_3 sponge; yellowish after coating with CeO_2, matte black after SFRD treatment and subsequent calcination (deposition of CuO and Pt).