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Promoting effect of Fe in preferential oxidation of carbon monoxide reaction (PROX) on Au/CeO_2

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ABSTRACT

Ce–Fe mixed oxides were prepared by impregnation (IM) method and co-precipitation method (CP). Gold supported on Ce–Fe mixed oxides prepared by direct anionic exchange (DAE) was used as catalyst for preferential oxidation of carbon monoxide (PROX). The influence of the atomic ratio Ce/Fe and of the preparation method (CP or IM) was investigated. It was found that gold supported on modified ceria by iron displayed better catalytic performances. However, the selectivity of Au/CeFe-CP was lower than that of Au/CeO_2 catalyst, which could be ascribed to the formation of defects in CeFe support prone to accumulate carbonate species on the surface. The characterization by means of XRD, XPS, H_2-TPR and HRTEM indicated that the doping of iron in ceria prepared by CP promoted the formation of a Ce–Fe solid solution, decreased the particle size of ceria and enhanced the dispersion of gold. In the case of the IM catalysts, iron is segregated in the form of Fe_2O_3, which impedes the activity in PROX. The strong interaction between CeO_2 and Fe_2O_3 supports led to higher oxygen mobility and to the formation of Au^{3+}, which may also contribute to the higher catalytic activity of $Au/Ce_{85}Fe_{15}$.

1. Introduction

In the recent years, fuel cells and especially proton-exchange membrane fuel cells (PEMFC) have been the subject of intense studies as they are a very promising technology to utilize hydrogen as a substitute to carbon fossil energies. As it is known, the presence of trace amounts of carbon monoxide (<1%) in hydrogen could result in the poisoning of the electrodes [1]. The selective oxidation of carbon monoxide in the presence of high H_2 concentration, namely PROX reaction, is the best effective way to purify hydrogen [1,2]. The research on PROX reaction focuses on the catalysts containing precious metal (Pt, Au, Rh, Ru, Ir) [3–8], metal oxide (CuO, CoO_x, MnO_x) [9–12] or alloy catalysts [12,13]. Supported nanosized gold showed the best catalytic performance at low temperature in agreement with the operation conditions of fuel cells.

Ceria is one of the most interesting oxide supports for catalysis applications because of its ability of oxygen storage and transportation. Vacancy defects can be rapidly formed in ceria oxide with fluorite structure, which allows high oxygen storage capacity (OSC) [14]. In one of our previous studies, gold supported on ceria showed good oxygen selectivity to convert CO to CO_2 in PROX reaction [15]. However, the CO conversion at operation temperature of fuel cell should still be improved for a potential industrial application.

Ceria doped with lower valence ions, such as Fe^{3+}, has shown enhanced oxidation activity and catalytic properties through the formation of surface structural defects and a ceria-like solid solution [16–18]. But in certain cases, above a certain amount, iron is not incorporated in the ceria network but segregated and then plays the role of an electronic modifier [19] and allows a better dispersion of the added noble metal.

The aim of this work was therefore to investigate the influence of the preparation method of Ce–Fe mixed oxide with different Ce/Fe atomic ratio to serve as support for gold deposited by direct anionic exchange (DAE) in PROX reaction. Another objective was the evaluation of the level of modifications induced by the addition of the Fe^{3+} ion on the structure of CeO_2 network and to show how this modifier whether incorporated in a solid solution or segregated on the surface will affect the catalytic activity in PROX reaction.

2. Experimental

2.1. Catalyst preparation

2.1.1. Supports

Ceria support was prepared by precipitation reaction using NaOH as precipitate agent. A 1 M NaOH solution was slowly added

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to a 0.2 M $Ce(NO_3)_4, 6H_2O$ solution to adjust the pH value to 9 under vigorous stirring for 3 h at 70 °C. The precipitate was aged overnight, filtered and washed with distilled water to remove completely Na^+ ions. The solid was then dried at 110 °C for 12 h and calcined in air at 500 °C with a 2 °C min^{-1} ramp rate and the temperature was kept constant for 4 h. The Ce–Fe oxide supports were prepared by the co-precipitation method using $Fe(NO_3)_3, 9H_2O$ as a precursor. After the same calcination procedure, the obtained supports were abbreviated as Ce_x–Fe_y-CP (where x and y represent the atomic proportions of each element; the 4 following atomic Ce/Fe were prepared 95/15, 90/10, 85/15 and 80/20). To study the effect of the interaction between cerium oxide and iron oxide on supported gold catalyst, the cerium oxide was modified using $Fe(NO_3)_3, 9H_2O$ by wetness impregnation method. The support prepared by the same thermal treatment was abbreviated as Ce–Fe-IM. In this case samples with a Ce/Fe ratio of 90/10, 85/15 and 80/20 were prepared.

2.1.2. Gold impregnation

All the gold catalysts were prepared by impregnating the support with an aqueous solution of $HAuCl_4$ by direct anionic exchange (DAE) as described previously [20–22]. The chloroauric aqueous solution (10^{-4} M, pH = 3.2), was heated and stirred at 70 °C and the support (40–60 mesh) was then introduced to the gold solution. After an hour of support–liquid contact under agitation followed by addition of a 4 M ammonia solution, the suspension was filtered and washed with cold water several times to remove the Cl^- and NH_4^+ ions. The catalysts were dried in an oven at 100 °C for 12 h and then calcined at 300 °C for 4 h with a 2 °C min^{-1} ramp rate of temperature. The target loading was 2% of Au by weight.

2.2. Characterization of the catalysts

The specific surface area (S_{BET}), the specific pore volume (V_p) and the average pore diameter (d_p) were measured by N_2 absorption at −196 °C after degassing under vacuum at 300 °C for 3 h. The surface area was calculated by using the Brunauer–Emett–Teller (BET) method. The specific pore volume was calculated from the amount of vapor absorbed at a relative pressure (P/P_0). The actual gold loadings were determined by inductively coupled plasma emission spectroscopy (ICP-AES).

The analysis of the crystal phases was performed using powder X-ray diffraction. The XRD patterns were recorded on a DX-1000 diffractometer using Cu Kα radiation between 20° and 80°. The voltage and anode current were 40 kV and 25 mA, respectively, and the scan step was 0.06° S^{-1}.

Temperature programed reduction under hydrogen (H_2-TPR) was measured in a flow system using 5% H_2/N_2 with flow rate of 30 cm^3 min^{-1}. Approximately 50 mg of freshly calcined sample was used in each measurement. The temperature was raised from 100 °C to 800 °C at a rate of 10 °C min^{-1} using a programable temperature controller. The hydrogen uptake during the reduction was analyzed on-line by GC-2000 gas chromatograph with a thermal conductivity detector (TCD).

The X-ray photoelectron spectra (XPS) were recorded on a XSAM800 spectrometer with an Al Kα (1486.6 eV, 15 mA) X-ray source. Charging effects were corrected by adjusting the binding energy of C 1s peak from carbon contamination to 284.6 eV.

Transmission electron microscopy pictures (TEM) were obtained in Tecnai G^2F20 S-Twin instrument; the samples were prepared by dispersing the solid in ethanol. One drop of the solution was placed on a copper grid and dried for 1 h. The nanoparticle size distribution of gold was determined by counting approximately 200 particles from several TEM images obtained from different places on the grid. The formula to deduce the number average particle size was

$$\bar{d} = \frac{\sum_i n_i d_i}{\sum_i n_i}$$

Table 1
Element analysis of gold determined by ICP and textural properties determined by N_2 adsorption–desorption isotherms.

Sample	S_{BET} (m^2/g_{cat})	V_p (cm^3/g_{cat})	d_p (nm)	Au (%)
Au/CeO_2	90	0.1050	5.180	1.64
$Au/Ce_{85}Fe_{15}$-IM	77	0.1010	5.256	1.23
$Au/Ce_{95}Fe_5$-CP	93	0.1613	6.579	1.63
$Au/Ce_{90}Fe_{10}$-CP	103	0.1823	6.916	1.60
$Au/Ce_{85}Fe_{15}$-CP	120	0.1966	7.055	1.48
$Au/Ce_{80}Fe_{20}$-CP	113	0.2346	8.324	1.49

2.3. Measurement of catalytic performances

The catalytic activity tests were carried out in a quartz fixed-bed reactor at atmospheric pressure. The reaction mixture consisted of 1% CO, 2% O_2, and 48% H_2 with Ar as the balance gas. The weight of the catalyst was 100 mg and the total flow rate was 30 ml min^{-1} (GSHV = 6000 h^{-1}). The analysis of the effluent gas was performed by online gas chromatography. In some case, the durability and stability were measured using the same conditions but over a period of 48 h.

The conversion of CO to CO_2 is calculated from the following equation:

$$X_{CO}(\%) = \left(1 - \frac{[CO]\,out}{[CO]\,in}\right) \times 100$$

where CO_{in} and CO_{out} are the initial and outlet CO concentration, respectively. The selectivity of oxygen to oxidize CO is defined as follows:

$$S(\%) = \frac{0.5 \times ([CO]\ in - [CO]\ out)}{[O_2]\ in - [O_2]\ out} \times 100$$

For the most interesting samples, two complementary procedures, closer to real application conditions, were applied. The catalytic behavior of the best performing catalysts was tested in the presence of 10% CO_2 added to the original feed; in a second test, 10% H_2O was added through a saturator. In this case the H_2 concentration was adjusted to 35% instead of 48%. In both cases, the flow rate was increased to 100 ml $min.^{-1}$ (GHSV = 30,000 h^{-1}).

3. Results

3.1. Textural properties and bulk structure of the catalysts

The specific areas and porosities, as well as the gold contents of the obtained samples are given in Table 1. It is worth to note that the surface areas increase compared to Au/CeO_2 with an addition of iron prepared by co-precipitation, while the $Au/Ce_{85}Fe_{15}$-IM displays the lowest surface area (77 m^2/g). The actual gold loadings in each sample are c.a. 1.5% ± 0.15, except in $Au/Ce_{85}Fe_{15}$-IM. The gold content (1.6%) in Au/CeO_2 is slight lower than that of our previous work (1.9%) [15,22]. This could be associated with the different surface area or mesh of ceria support.

Fig. 1 shows the diffractograms of the catalysts. No diffraction peaks of gold are observed which indicates that the metal is highly dispersed on the support. Anyhow, to detect the characteristic Au (1 1 1) metallic gold peak it was necessary to deeply scan around $2\theta = 38°$ overnight with a scan step of 0.008° min^{-1} (see insert in Fig. 1a). In this case the ray of diffraction of Au (1 1 1) appears in a very moderate manner at $2\theta = 38.2$. The reflections observed