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Gold catalysts supported on ceria and ceria–alumina for water-gas shift reaction

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Abstract

Gold-supported catalysts on ceria and ceria–alumina with different ratios in the water-gas shift reaction were studied. It was shown that the addition of alumina leads to the deeper oxygen vacancies formation, detected by Raman and TPR measurements. It was established an increase of the ceria dispersion and as well as slightly increase of the gold particle size. In the presence of alumina after catalytic operation the dispersion of gold and ceria practically does not change. The lower WGS activity on gold/ceria–alumina can be explained on the basis of reduction–oxidation cycle of the reaction. It was established no efficiency re-oxidation of the catalyst surface at the temperatures of the reaction test by the water vapour and we consider this as a main reason of the lower catalytic activity.
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1. Introduction

The interest to the water-gas shift (WGS) reaction was grown significantly during the last years due to the pure hydrogen production in respect to fuel-cell power systems. A small amount of CO from the output of fuel reformers has to be converted, but the applied Pt catalysts are not resistant enough to the poisoning of CO. From other side, copper based catalysts traditionally used in the industry for low temperature WGS are not suitable for automobile application due to the contact with air and/or condensed moisture during start-up and start-down operation. Obviously, the new catalysts are needed being able to be avoided these problems and the gold catalysts could be applied successfully. The earlier works have shown that high activity in WGS was reached on Au/Fe_2O_3 and Au/TiO_2 [1–3]. Recently it was found that gold supported on ceria exhibited high and stable activity in low temperature WGSR [4,5]. The main results on WGS obtained in this laboratory have been summarized in [6]. Studying the mechanism of WGS by FTIR, it was found that the high activity of gold–ceria catalysts is due to the strong modification of ceria in the presence of gold. Small gold particles in a close contact with oxygen vacancies of ceria are the active sites of WGS reaction [7,8].

The present study continues the research works of this laboratory in LT WGS on gold-supported catalysts. The aim was to obtain catalysts with good performance by the formation of oxygen vacancies in ceria in the presence of alumina as well as to improve the stability both gold and ceria particles during catalytic operation. The mixed oxide supports were prepared by co-precipitation with two different ratios between ceria and alumina and the results were compared with gold supported on pure ceria.

2. Experimental

2.1. Catalysts preparation

The ceria and ceria–alumina supports were prepared by precipitation, respectively co-precipitation of the corresponding nitrates with a solution of K_2CO_3. The gold was deposited as $Au(OH)_3$ on the oxide supports, preliminary suspended in water, under full control of all parameters of preparation. After filtered and carefully washed, the precursors were dried and calcined at 400 °C for 2 h. The samples were denoted as: AuCe,

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AuCeAl10 (containing 10 wt.% Al_2O_3) and AuCeAl20 (containing 20 wt.% Al_2O_3). The amount of gold was 3 wt.%. Pure supports, denoted as Ce, CeAl10 and CeAl20 were also prepared and tested as references.

2.2. Catalysts characterization

The BET surface area of the samples was determined on a 'Flow Sorb II-2300' device.

The X-ray diffraction patterns were obtained on a DRON-3 automatic powder diffractometer, using Cu Kα_1 radiation. The crystal size of gold, ceria and alumina particles was calculated on the basis of the peak broadening using "Powder Cell" program. The program gives the possibility of approximation of XRD spectra based on the corresponding theoretical structures. The instrumental broadening was taken into consideration. XRD profiles were approximated by Lorenz functions.

The Raman spectra were recorded using a SPEX 1403 double spectrometer with a photomultiplier, working in the photon counting mode. The 488 nm line of an Ar^+ ion laser was used for excitation. The laser power on the samples was 60 mW. The samples were prevented from overheating during the measurements by increasing the size of the focused laser spot. The optimal conditions were chosen, checking the intensity, position and the width of the 464 cm^{-1} Raman line of CeO_2. The spectral slit width was 4 cm^{-1}.

The TPR measurements were carried out by means of an apparatus described elsewhere [9]. A cooling trap (−40 °C) for removing water formed during reduction was mounted in the gas line prior to the thermal conductivity detector. A hydrogen–argon mixture (10% H_2), dried over a molecular sieve 5A (−40 °C), was used to reduce the samples at a flow rate of 24 ml min^{-1}. The temperature was linearly raised at a rate of 15 °C min^{-1}. The sample mass used was 0.05 g. It was selected by the criterion proposed by Monti and Baiker [10]. In addition TPR experiments after re-oxidation were performed. The re-oxidation with purified air was carried out at two different temperatures. In the first case of high temperature (HT) re-oxidation the H_2–Ar flow was switched over to air at the temperature just after the end of the corresponding TPR peak of the fresh sample. The sample was kept in air at this temperature for 15 min and the TPR spectra were recorded after cooling down to room temperature (RT) in purified argon. In the second case after the end of the TPR peak the sample was cooled in purified argon to RT and re-oxidized in air for 15 min, then the TPR pattern was registered (RT re-oxidation).

2.3. Catalytic activity measurements

The catalytic activity of the samples towards the WGS reaction, expressed as the degree of CO conversion, was evaluated over a wide temperature range (140–350 °C). The activity was measured in a flow reactor at atmospheric pressure. A gas mixture of initial composition 4.494 vol.% CO in argon was used. The samples are tested in WGS after pretreatment under different conditions—as prepared and after reduction at 100 °C for 1 h in a hydrogen–argon mixture (1% H_2), space velocity of the gas 2000 h^{-1}. The catalytic activity and stability of the catalysts in a long period of operation (40 h) was studied. It was applied different treatments (re-activations)—after maximum water vapour partial pressure (50 kPa) and after re-oxidation was carried out at 200 °C for 1 h in air, space velocity of the air 2000 h^{-1}.

The WGS activity was carried out under the following experimental conditions: catalyst bed volume 0.5 cm^3 (0.63–0.80 mm sieve fraction), space velocity of the dry gas 4000 h^{-1}, partial pressure of water vapour −31.1 kPa. The CO content at the reactor outlet was determined on an "Uras 3G" (Hartmann&Braun AG) gas analyzer.

3. Results

In Table 1 are presented the chemical composition and BET surface area of the studied catalysts. The deposition of gold causes an increase in the surface area of the catalysts.

3.1. Catalytic activity, pretreatment and re-activation

The WGS catalytic activity data, expressed as degree of CO conversion are presented in Figs. 1–3. The catalysts are tested as prepared (Fig. 1(1)–(3)) and after pretreatment in H_2/Ar mixture (1% H_2) at 100 °C ((1′)–(3′)). In the same figure are

Table 1
Chemical composition and BET surface

Catalyst	Chemical composition (wt.%)			S_{BET} (m^2 g^{-1})
	Au	CeO_2	Al_2O_3	
AuCe	3.0	97.0	–	108
AuCeAl10	2.8	87.5	9.7	103
AuCeAl20	2.9	77.7	19.4	140
Ce	–	100	–	84
CeAl10	–	90	10	83
CeAl20	–	80	20	83

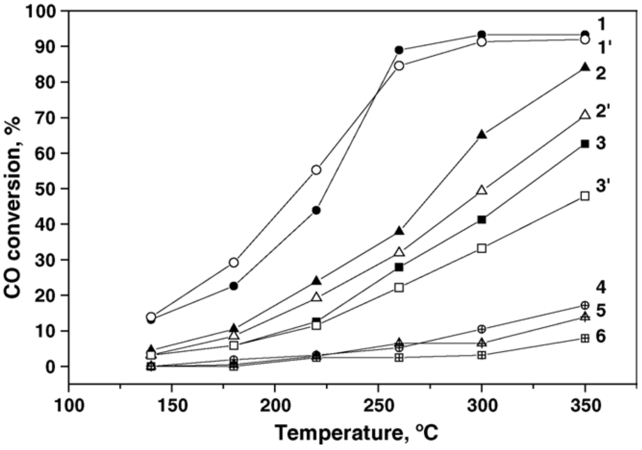

Fig. 1. Catalytic activity of initial supports and gold-supported catalysts as prepared (1–3) and after reduction (1′–3′): (1, 1′) AuCe; (2, 2′) AuCeAl10; (3, 3′) AuCeAl20; (4) Ce; (5) CeAl10; (6) CeAl20.

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