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Gold catalysts supported on CeO_2 and CeO_2–Al_2O_3 for NO_x reduction by CO

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Abstract

The reduction of NO_x by CO was studied over gold catalyst supported on ceria and ceria–alumina. The mixed supports with different CeO_2/Al_2O_3 ratios were prepared by co-precipitation. The catalysts were characterized by means of XRD, TPR, XPS and Raman spectroscopy. The addition of alumina led to a slight enlargement of the gold particles, while the ceria particle size was decreased. Deeper oxygen vacancies formation in the presence of alumina was detected by TPR, XPS and Raman spectroscopy, compared to the pure ceria support. The samples exhibited a high and stable activity and 100% selectivity towards N_2 was reached at 200 °C.

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Keywords: Gold; Ceria; Ceria–alumina; NO_x reduction by CO; XRD; TPR; XPS; Raman spectroscopy

1. Introduction

Catalysis is a key technology providing an effective solution of many environmental problems, and the most important one among them is the removal of NO_x. This is a major pollutant in the exhaust gases of various combustion processes. A widely applied method for NO_x removal is the catalytic reduction, using different reducing agents such as CO, hydrogen or hydrocarbons. In practice, there are two different sets of conditions for the catalytic reduction of exhaust gases produced, at the stoichiometric air-to-fuel ratio and under oxygen rich exhaust gases conditions. Diesel and lean-burn gasoline engines operate at high air-to-fuel ratios, as oxygen is fed in excess. Currently, the selective catalytic reduction is one possible solution of the NO_x problem; another one is the NO_x storage concept recently developed by Toyota [1]. The operating conditions of internal combustion engines, equipped with three-way catalysts (TWCs) are fixed around the stoichiometric air-to-fuel ratio, where the amount of supplied air is maintained on a level just sufficient for the complete combustion of the fuel. The supported noble metals—rhodium, platinum or palladium are currently used as the active components in the commercial TWCs. Oxides like ceria are used as supports, which enable widening of the operating air/fuel window, due to their high oxygen storage capacity (OSC). The efforts to optimize the performance of TWCs are mainly related to improvement of the OSC and catalytic stability under normal operating conditions. Recently, gold has also been reported as a catalyst for NO reduction with H_2, CO or hydrocarbons [2–5]. Gold is not able to match the high temperature performance of the platinum group metal (PGM) TWCs; however, a high activity during the catalytic operation at relatively low temperatures is characteristic of supported gold catalysts. To enhance the performance of the TWCs at low temperatures is still a challenging problem. It is needed in order to decrease the emissions immediately following the start-up of the vehicle's engine ("cold start" phase).

The present study is focused on the NO_x reduction by CO over gold catalysts supported on CeO_2 and CeO_2–Al_2O_3. The presence of alumina is aimed, on the one hand, to improve the gold and ceria dispersion and stability and, on the other hand, to study the effect of oxygen vacancies formation due to Al^{3+} ions on the catalytic activity. An interesting finding in the literature [6] is the doping of CeO_2 with metal (3+) oxides soluble in it, causing the creation of the so-called extrinsic oxygen vacancies in the mixed oxide support. The extrinsic oxygen vacancy

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formation caused by the presence of Al^{3+} in ceria structure has already been confirmed by some of us in the case of gold/ceria–alumina catalyst synthesized by a method different from that in the present study [7]. These vacancies are different from the intrinsic oxygen vacancies, formed by the reduction of Ce^{4+} to Ce^{3+} and removal of oxygen leading to an improvement of the oxygen transport characteristics. The prerequisite for the enhancement of the intrinsic oxygen vacancies is the presence of a noble metal, which promotes the redox behaviour of ceria. In the review by Trovarelli [6] it was shown that oxygen vacancies are associated with reduced ceria in the proximity of platinum metal particles. These have been supposed by many researchers as active sites for NO and CO conversion mainly due to their effective role in promoting NO dissociation. In the present study the gold-based catalysts were characterised by several techniques—XRD, Raman, XPS, TPR. The aim was to look for a relationship between the structural features and catalytic behaviour and especially to clarify the role of alumina for the catalytic activity and stability in NO_x reduction by CO.

2. Experimental

2.1. Sample preparation

A series of three catalysts was studied: gold supported on ceria (AuCe); Au supported on ceria–alumina mixed support containing 10 wt.% alumina in ceria (AuCeAl10) and 20 wt.% alumina in ceria (AuCeAl20). The ceria–alumina mixed oxide supports were prepared by co-precipitation of the corresponding nitrates at a desired ratio with a solution of K_2CO_3. The gold was then loaded by deposition–precipitation under full control of the synthesis parameters (pH, temperature, stirring speed, etc.). After filtering and carefully washing, the samples were dried and calcined in air at 400 °C for 2 h. The amount of gold was determined by gravimetric analysis. The initial salts used $HAuCl_4 \cdot 3H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and K_2CO_3 were of analytical grade purity.

2.2. Sample characterization

The BET surface area of the samples was determined on a Micromeritics ‘Flow Sorb II-2300’ device with 30% N_2, 70% He mixture at atmospheric pressure and N_2 boiling temperature.

The X-ray diffraction patterns were obtained on a DRON-3 automatic powder diffractometer, using Cu $K\alpha_1$ 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 fitting the experimental XRD spectra, based on the corresponding theoretical structures. The instrumental broadening effect was taken into consideration. The XRD profiles were approximated by Lorentz 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 X-ray photoelectron spectroscopy analyses were performed with a VG Microtech ESCA 3000 Multilab, equipped with a dual Mg/Al anode. The spectra were excited by a non-monochromatized Mg Kα source (1254.4 eV) operated at 14 kV and 15 mA. The analyzer operated in the constant analyzer energy (CAE) mode. Pass energy of 20 eV was used across the hemispheres for the individual peak energy regions. The survey spectra were measured at 50 eV pass energy. The samples, analyzed as prepared, were pelletized and then attached on a double-sided adhesive tape. The pressure in the analysis chamber was in the range of 10^{-8} Torr during the data collection process. The binding energies of the support electrons were referenced with respect to the energy of the C 1s peak at 285.1 eV arising from adventitious carbon. The peaks were fitted by a non-linear least square fitting program using a properly weighed sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley and Sherwood [8,9]. The binding energy values are given with a precision of ± 0.15 eV. The surface atomic concentration was evaluated based on peak areas using appropriate sensitivity factors set in the VG software.

The TPR measurements were carried out by means of an apparatus described elsewhere [10]. A cooling trap (−40 °C) for removing the 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° min^{-1}. The sample mass charged was 0.05 g. It was selected based on the criterion proposed by Monti and Baiker [11]. The hydrogen consumption during the reduction processes was calculated using a previous calibration of the thermo-conductivity detector.

2.3. Catalytic activity measurements

The catalytic activity in NO_x reduction by CO was tested using a quartz glass U-shaped reactor, equipped with a temperature programmed controller. All the reactants and products were monitored by IR and UV analysers. The MS analysis of the reaction products was also performed using on-line Pffeffer quadrupole mass spectrometer and Balzers Quadstar software. The steady-state tests were made upon increasing the reaction temperature, waiting at each temperature for a constant conversion value. The catalysts were tested in a wide temperature interval charging 0.05 g of the sample at a flow rate of 50 ml min^{-1} corresponding to WHSV of 60,000 ml g^{-1} h.

The catalytic behaviour of AuCe, AuCeAl10 and AuCeAl20 samples pretreated using 5% H_2 in helium for 30 min at 120 °C was compared. Two series of experiments were performed using 3000 or 2000 ppm H_2 feed concentration in addition to the NO–CO reactant gas (3000 ppm of each component).

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