



Support effect on the catalytic performance of Au/Co₃O₄–CeO₂ catalysts for CO and CH₄ oxidation

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ABSTRACT

Gold-based catalysts supported on Co₃O₄, on CeO₂ and on mixed Co₃O₄–CeO₂ oxides were prepared by co-precipitation. They were tested in the catalytic oxidation of CO and CH₄, in separate tests, and their activities were compared with that of the bare oxides. Tests of CH₄ oxidation were performed in two consecutive runs in order to evaluate the catalysts stability. The effect of SO₂ in the reactant mixture was investigated. The fresh and spent catalysts were analysed by XRD, BET, TPR and XPS techniques. Among the fresh catalysts, Au supported on CeO₂ was the most active in CO oxidation whereas Au supported on Co₃O₄ was the most active for methane total oxidation. Synergy between the two oxides was not observed for gold on mixed Co₃O₄–CeO₂ system. However, in consecutive runs of methane oxidation and in the presence of SO₂, Au supported on mixed Co₃O₄–CeO₂ exhibited higher stability and superior SO₂ tolerance as compared to the single oxide catalysts.

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1. Introduction

Cold-start emissions are responsible for ~80% of the pollution emitted by gasoline vehicles, since conventional three way catalysts are not efficient at temperatures below 200 °C [1]. Carbon monoxide and unburned hydrocarbons are the main pollutants emitted during the cold-start operation. In order to comply with the new limits imposed by the legislation on pollution control, more efficient catalysts are needed. Recently, the catalytic combustion of alkanes, especially methane [2], has received particular attention due to the increasing use of lean burn natural gas vehicles (NGVs) [3]. Both classes of catalysts, metal oxides [4–6] and noble metals [7–9] are currently explored for this process. The noble metals, particularly Pd and Pt, are the preferred ones because of their high specific activity [10]. They are used in current commercial catalysts for cleaning exhausts from NGVs [11,12]. However, sulfur compounds, present as impurities or odorizer in the natural gas and/or in the lubricating oil cause serious deactivation of both Pt and Pd catalysts [2,7].

Gold has historically been considered an inert element. However, since the discovery of the high activity exhibited by supported gold particles of sizes 3–5 nm, in CO oxidation at low temperature, the interest in using gold as a catalyst component has

increased enormously [13]. Recently, gold in combination with platinum and palladium, was used as an automotive catalyst [14]. The application of supported gold catalysts for the total oxidation of hydrocarbons and carbon monoxide has been addressed in several papers [15–19]. In particular, Au/Co₃O₄ was recognized as one of the most active catalyst for methane oxidation, among a series of coprecipitated Au on several transition metal oxides [15]. Moreover, the structural promotion by CeO₂ of a Co₃O₄ catalyst was observed in methane total oxidation [20,21]. The positive effect was attributed to an improved thermal stability, and an increased dispersion of the active phase.

Aiming to explore the reciprocal effect of gold and mixed oxide system Co₃O₄–CeO₂, coprecipitated catalysts of gold on Co₃O₄, CeO₂ and mixed oxides were prepared, characterised by XRD, BET, TPR, XPS and tested in the CO and CH₄ oxidation. During the oxidation of CH₄, the effect of SO₂ in the reaction feed was evaluated.

2. Experimental

2.1. Catalyst preparation

The catalysts AuCo₃O₄, AuCeO₂ and AuCo₃O₄–CeO₂ (thereafter labelled as AuCoCe, with Co:Ce atomic ratio 1:1) were prepared by co-precipitation method, according to a published procedure [21]. An appropriate volume of H₂AuCl₄ water solution to yield a final 10 wt% Au loading and the calculated amounts of cobalt and

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cerium nitrates were mixed. Aqueous Na_2CO_3 0.25 M as precipitating agent was added drop-wise until a pH of 8.5 was attained. The resulting precipitate was aged at room temperature for 3 h, then filtered, washed several times with hot water and dried at 120 °C overnight. The obtained samples were calcined at 400 °C for 4 h and then at 600 °C for 1 h. For comparison, corresponding bare oxides Co_3O_4 , $\text{Co}_3\text{O}_4\text{-CeO}_2$ (indicated as CoCe) and CeO_2 were also prepared by co-precipitation method and were calcined at the same temperature as the gold catalysts.

2.2. Catalyst characterization

The X-ray diffraction analyses were carried out with a Philips vertical goniometer using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The spectra were collected with a step size of 0.05° and a counting time of 10 s per angular abscissa. The XRD profiles were reproduced using Rietveld refinement [22], in order to estimate the modification of the crystalline phases upon catalytic tests. The fit goodness was ascertained by low values (≤ 0.03) of R_p and R_{wp} [22]. The assignment of the various crystalline phases was based on the ICSD data base (Au, no. 58393; Co_3O_4 , no. 24210; CoO, no. 9865; CeO_2 , no. 28785) [23]. The fittings were performed by the GSAS package program and the particle sizes were determined, with an error of $\pm 2\%$, using the Scherrer equation on the basis of the calculated Lorentzian broadening [24,25].

The specific surface areas were determined by BET method [26] from nitrogen adsorption isotherms at -196°C using Sorptomatic 1900 (Carlo Erba) instrument.

The X-ray photoelectron spectroscopy analyses were performed with a VG Microtech ESCA 3000 Multilab, using the unmonochromatised $\text{Al K}\alpha$ source (1486.6 eV) run at 14 kV and 15 mA. For the individual peak energy regions, a pass energy of 20 eV was used. Samples were mounted with double-sided adhesive tape. Binding energies were referenced to the C 1s binding energy of adventitious carbon set at 285.1 eV. The software provided by VG was used for peak analyses and for the calculation of the atomic concentrations. The precision on the binding energy and on the atomic percentage values were respectively $\pm 0.15 \text{ eV}$ and $\pm 10\%$.

2.3. Catalytic activity

Catalytic tests were performed using a U-shaped quartz reactor with an inner diameter of 12 mm, electrically heated in a furnace. The catalyst powder (sieved fraction between 180 and 250 μm) was diluted 1:2 with inert SiC in order to avoid thermal gradients and it was placed on a porous quartz disk. The reaction temperature was measured by a K-type thermocouple in contact with the catalytic bed 12 mm long. Prior to the catalytic testing, the samples were treated “in situ” under flowing O_2 (5 vol.% in He, 50 ml/min) at 350 °C for 1/2 h and in He during cooling to room temperature. The standard reagent gas mixture consisting of 1 vol.%CO + 1 vol.% O_2 in He or 0.3 vol.% CH_4 + 2.4 vol.% O_2 in He was led over the catalyst (50 mg) at a flow rate of 50 ml/min (STP), equivalent to a weight hourly space velocity (WHSV) of 60,000 $\text{ml g}^{-1} \text{ h}^{-1}$. In order to assess the stability of the catalysts, two reaction runs were recorded consecutively, the first one from r.t. up to 600 °C, the second one up to 800 °C, keeping the catalyst under the reaction mixture during the cooling. The performance of the catalysts in both reactions is given in terms of the temperature corresponding to 50% conversion. For general comparison purpose pseudo-first order reaction rates were also calculated using differential reactor equation.

The inlet and outlet gas compositions were analyzed by on line mass quadrupole (ThermostarTM, Balzers), in order to follow the

evolution of all the species, CH_4 , CO, CO_2 , H_2 , H_2O and O_2 . Moreover, the concentration of CO and CO_2 was checked by an IR analyser (ABB Uras 14), calibrated in the range of 0–3000 ppm for CO and 0–10,000 ppm for CO_2 . The reaction products of methane oxidation were CO_2 and H_2O . No CO was detected in the overall range of temperature. Carbon balance was close to $\pm 5\%$ in all the catalytic tests. Experiments of methane oxidation in presence of SO_2 were performed by co-feeding 10 vol ppm of SO_2 .

3. Results and discussion

3.1. Catalytic activity

In Fig. 1 the CO conversion as a function of the temperature is displayed for Au supported catalysts and for the supports. In Table 1 the temperatures in correspondence of 50% CO conversion (T_{50}) and the specific reaction rates calculated at low conversion (at 70 °C) over Au supported catalysts and the corresponding bare oxides are listed. It is worth noticing that the supports containing cobalt are able to convert CO at temperature below 200 °C, differently from pure CeO_2 which starts to be active at higher temperature. Upon addition of gold the activity improves noticeably especially for the ceria supported catalyst. Among the catalysts, AuCeO₂ is the most active, followed by AuCoCe, and then by AuCo₃O₄. However, as expected, the activity of the co-precipitated gold ceria catalyst is lower with respect to the activity of a similar catalyst prepared by deposition-precipitation [27].

Light-off curves of methane oxidation in two consecutive runs are shown in Fig. 2. In Table 2 the temperatures of 50% methane conversion obtained with the gold catalysts and with the bare supports in different runs, together with the specific reaction rate calculated at low conversion (at 300 °C) for the 1st run, are listed. As for the CO oxidation, the presence of gold enhances the activity of the corresponding oxides. It is worth noting that, differently from the CO case, the activity of the Au catalysts changes as $\text{AuCo}_3\text{O}_4 > \text{AuCoCe} > \text{AuCeO}_2$, with the same trend as the activity of the corresponding oxides, suggesting a strong support effect. In the second run performed consecutively, a clear deactivation is observed, the extent of which strongly depends on the support. AuCo₃O₄ shows the most pronounced deactivation, with a T_{50} increase of 80 °C. Moreover, in accord with results from a study on similar oxides, a rapid deactivation due to the thermal decomposition of Co_3O_4 to the less active CoO occurs at $T > 700^\circ\text{C}$ [21]. AuCoCe deactivates less in the second run with a T_{50} increase of

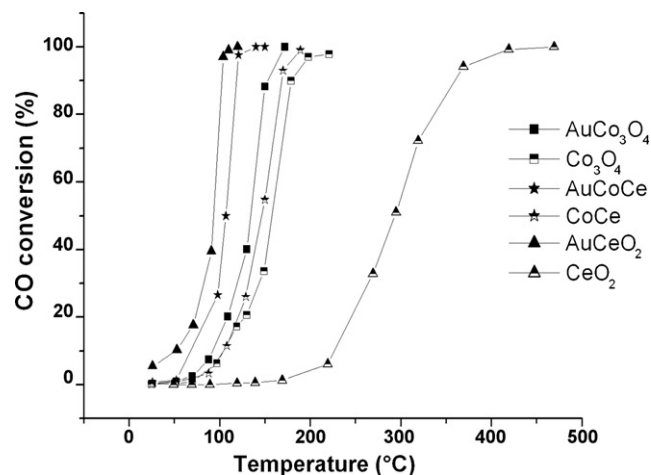


Fig. 1. CO conversion (%) as a function of the temperature for gold catalysts and the corresponding oxides.

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