



Temperature-Scanning Method for the kinetic studies of CO oxidation over ceria–zirconia supported gold catalysts



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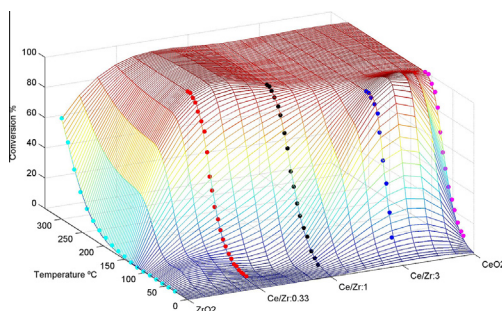
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HIGHLIGHTS

- Variation of Temperature Scanning Method let to optimize catalyst composition.
- Extended reaction surface plot identifies Au/Ce_{0.75}Zr_{0.25}O₂ catalyst as optimal one.
- For all catalysts activation energy and pre-exponential factors were determined.
- Support redox properties controlled the performance of the Au/Ce_{1-x}Zr_xO₂ catalysts.
- Fitted MvK model predicted superficial reaction and catalyst surface re-oxidation.

GRAPHICAL ABSTRACT

Predicted surface plot of conversion – temperature – catalyst composition (2 wt.% Au/Ce_{1-x}Zr_xO₂ washed with ammonia) as a tool for catalyst optimization (dots represent experimental data).



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ABSTRACT

The experimental data of CO oxidation over the series of 2 wt.% Au/Ce_{1-x}Zr_xO₂ ($x = 0, 0.25, 0.5, 0.75, 1$) catalyst were analyzed using a variation of the Temperature Scanning Method with the aim of catalyst's composition optimization. The catalysts were prepared by the Direct Anionic Exchange technique. The kinetic of CO oxidation was quantified by conversion–rate–temperature (X, r, T) triplets, calculated from raw data obtained using a plug flow reactor, working at oxygen stoichiometric, rich, and lean conditions. The data were fitted to the Mars-van Krevelen adsorption–reaction model (MvK). The results showed that the MvK model is able to predict the superficial reaction and the re-oxidation of the catalyst surface. Additionally, the data at oxygen lean conditions revealed the distinctive characteristic of Ce-containing catalysts, which act as oxygen buffer by releasing–uptaking oxygen. The obtained values of the fitted parameters allowed re-mapping raw data onto the conversion–temperature–catalyst composition surface plot and their application as a tool for the optimization of catalyst composition.

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1. Introduction

Catalytic oxidation of CO has received extensive attention due to its significance in practical applications, particularly in the context of breathing air purification in the closed spaces and reduction of cold start automotive exhaust emissions. This reaction, developed on platinum group based catalysts, has been studied and extensively reviewed [1] since the classic work of Langmuir [2]. Afterwards, several research groups have also demonstrated high efficiency of gold nanoparticles supported on partly reducible oxides in CO oxidation [3–7].

For this reaction, several kinetic rate models have been proposed in the open literature [1,8]. They are based on two widely accepted possible reaction mechanisms: Langmuir–Hinshelwood (LH) and Mars van Krevelen (MvK) [5]. The LH reaction model (i) includes the following set of steps: (i.1) competitive adsorption of CO and oxygen molecules from the gas phase on catalyst surface, (i.2) oxygen dissociation, (i.3) reaction between the adsorbed molecules/atoms, and finally (i.4) desorption of CO₂ to the gas phase. On the other hand, the MvK mechanism (ii) consists of: (ii.1) the metal/support oxidation in a separate and independent steps, (ii.2) adsorption of CO from the gas phase on the oxide, (ii.3) reaction between the adsorbed CO and catalyst surface oxygen, accompanied with the creation of oxygen vacancies, (ii.4) CO₂ desorption from the catalyst surface, and (ii.5) fast and irreversible refilling of the resulting oxygen vacancies by oxygen from the gas phase, in separate step (as in ii.1). As a consequence, LH and MvK models can be described by different kinetic rate expressions. One of the most important differences could be the fact that LH model presents a controversial tendency to predict low CO oxidation rates at high temperatures [8–12], as it could be seen for a set of experimental data obtained in this work (Appendix 1). Consequently, the reversibility of CO oxidation at these reaction conditions can be expected; statement that has not been confirmed experimentally using noble metal based catalysts. Moreover, the other authors [9] have already claimed that the permanence of oxygen radicals' on catalyst surface and their constant availability for the reaction are inconsistent with restrictions of LH model. Therefore, in this work, the MvK model was selected to fit the experimental data.

Many researchers have tried to perform temperature-programmed runs and to “deduce the kinetics” observing the light-off point during the temperature ramping program. Thus, Wojciechowski and Rice [9] developed the Temperature Scanning Method (TSM), at which experiments consist of operating the reactor over a period of time, varying the temperature in a programmed way. During each run, the temperature and conversion data are registered at the outlet of the reactor. Subsequently, the reaction rate can be calculated basing on the obtained raw data by splining the discrete conversion (X) – residence time (τ) data (at a constant temperature) and evaluating the $dX/d\tau$ to yield the rates, r , at these conditions (τ , X , T) [9]. Next, the (X , r , T) triplets can be used for rate law parameters fitting. Consequently, surface plots, usually, tridimensional correlation between residence time, temperature and conversion can be obtained. Finally, the catalyst performance can be predicted.

Thus, the goal of this work was to develop a numerical technique to analyze the reaction kinetics of CO oxidation using a variation of the TSM (including the catalyst composition as a variable for optimization). In fact, we show how to win more insight into the chemical reaction kinetics by extending the original methodology of Wojciechowski and Rice [8,9]. As far as we know, no similar analysis has been reported in the open literature. Thus, the kinetic of CO oxidation was quantified by conversion–rate–temperature (X , r , T) triplets obtained for a series of 2 wt.%

Au/Ce_{1-x}Zr_xO₂ ($x = 0, 0.25, 0.5, 0.75, 1$) catalysts and their corresponding supports. Finally, the obtained kinetic results were discussed based on morphological, structural and redox (using CO-TPR) properties of the studied catalysts.

2. Experimental

2.1. Catalyst synthesis

A series of Ce_{1-x}Zr_xO₂ ($x = 0.25, 0.5, 0.75$) solid solutions, characterized with different Ce/Zr molar ratio (Ce/Zr = 3, 1, 0.33, respectively), CeO₂ and ZrO₂, used as support for Au, were prepared by the sol-gel like method, based on a thermal decomposition of mixed propionates [13]. The starting materials, zirconium (IV) acetylacetonate [Zr(CH₃COCH₂COCH₃)₄, Avocado, purity 99.9%] and/or cerium (III) acetylacetonate hydrate [Ce(CH₃COCH₂COCH₃)₃·H₂O, Sigma–Aldrich, purity 99.9%] were dissolved in boiling propionic acid in concentration of 0.12 M. Next, boiling solutions were mixed and the solvent was evaporated until a resin was obtained. All samples were calcined in air at 550 °C for four hours. Hydrogen tetrachloroaurate (III) trihydrate [HAuCl₄·3H₂O, Sigma–Aldrich, purity 99.9%] was used as a gold precursor. The supported Au catalysts were prepared by the Direct Anionic Exchange (DAE) method of gold species with hydroxyl groups of the support [14,15]. The optimization of catalyst's synthesis conditions was in details presented previously [16]. In order to remove the residual chlorine from the catalysts, responsible for Au agglomeration during thermal treatment, an ammonia washing procedure prior to the drying process was applied, as described previously [10,11].

2.2. Catalyst characterization

Nitrogen adsorption/desorption isotherms at –196 °C were measured using Sorptomatic 1900 apparatus (Carlo-Erba). Prior to the measurement, all samples were degassed for 4 h at 250 °C. The specific surface area, S_{BET} , was calculated using BET equation [10,11].

Atomic Absorption Spectroscopy (AAS) analyses were performed with a Solaar M6 Unicam spectrophotometer in order to estimate the amount of Au deposited on supports, as described previously [11].

High Resolution Transmission Electron Microscopy (HRTEM) measurements were carried out using high resolution microscope EM-002B (TOPCON), at an acceleration voltage 200 kV, equipped with energy dispersive spectrometer (EDS). To determine an average Au particle size and to define their distribution more accurate, at least 500 particles of each catalyst were chosen for analysis. Moreover, many different HRTEM images of each catalyst sample have been analyzed, in details described previously [11].

Temperature Programmed Reduction (TPR–CO) experiments were carried out by PEAK-4 apparatus [17], using CO as reducing agent. The apparatus was equipped with an infrared gas analyser (Fuji Electric Systems Co., type: ZRJ-4) to follow CO₂ formation. TPR–CO experiments were performed using a CO/He (5 vol.% CO, 95 vol.% He) gas mixture, with a flow rate of 40 cm³ min⁻¹, in the temperature range of 25–850 °C, with a ramp rate of 15 °C min⁻¹. Powdered samples of 100 mg were exposed to dry Ar at 250 °C for 1 h before the reduction.

2.3. Reactor set-up

CO oxidation reaction was carried out at atmospheric pressure in a quartz flow microreactor containing 100 mg of sample in a

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