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CO oxidation on nanosized Au/Al_2O_3 by surface hydroxyl groups and in the absence of O_2, studied by inverse gas chromatography

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ABSTRACT

In catalysis by gold, the term "decomposition" is used in order to describe CO oxidation by surface hydroxyl groups in the absence of O_2, at which carbon dioxide is formed without the deposition of carbon. This process is not only important due to its contribution in the activity of CO oxidation but also because it can offer significant information concerning the mechanism of CO oxidation on gold catalysts. In the present work reversed-flow inverse gas chromatography (RF-IGC) is utilized in order to compare the kinetics of CO oxidation by surface hydroxyl groups, the adsorptive capacity and the nature of the active sites related to CO sorption over bare γ-Al_2O_3 and Au/γ-Al_2O_3 catalyst, in a wide temperature range (50–300 °C).

The rates related to CO surface binding exhibit exactly the same behavior, as the activity of CO oxidation by surface hydroxyl groups does over bare γ-alumina and Au/Al_2O_3 respectively, indicating that at higher temperatures a much stronger binding of CO molecules over γ-Al_2O_3 can occur. While, the strong bonding of CO over Au/Al_2O_3 catalyst, is attributed to CO on active sites of cationic Au^{x+} near the alumina support, in the case of bare γ-Al_2O_3 is related to CO insertion in surface Al-hydroxyls, which are inactive at lower temperatures.

Rise of temperature affects the topography in a different way resulting in homogeneity in the case of γ-Al_2O_3 and heterogeneity in that of Au/Al_2O_3. Gold phase enhances the sorption of bigger amounts of CO over Au/Al_2O_3 catalyst in comparison to bare γ-Al_2O_3 support, in agreement with the fact that CO is activated preferably at small particles of metallic Au. Although, a certain amount of CO is stored on the studied solids as inactive spectators of CO oxidation e.g. as carbonate like species during CO adsorption particularly over γ-Al_2O_3, Au containing catalyst exhibits higher adsorptive capacity towards CO. Slight decrease of the amount of surface CO with rising temperature is observed due to the enhancement of CO oxidation by surface hydroxyl groups over both bare alumina and Au/Al_2O_3.

CO oxidation by surface hydroxyl groups indicates a "periphery" mechanism in which CO molecule activated on metallic gold (Au^0...CO) is attacked by an hydroxyl group either on a support cation or on a peripheral Au^{III} ion, forming an intermediate carboxylate group attached to the latter.

1. Introduction

Catalytic technologies have played a key role in the economic development and growth. Due to the early inability to understand the performance of "poor" and "good" catalysts, nominally having the same bulk composition, it was very common to refer particularly to heterogeneous catalysis, as either an "art" or "magic". The rise of surface science in the early '70s led to the discovery, development and enhanced understanding of several catalyst systems. Many of the early surface science techniques, along with the newly developed techniques, continue to and will play a very important role in the future development of next generation catalysts and catalytic processes, for industrial use and environmental protection [1–4].

On the end of 2013, fifty years of research in catalysis and surface science were completed at the Leiden University. Wolfgang Sachtler first established the group of heterogeneous catalysis at the Leiden Institute of Chemistry and the flourish of surface science was largely influenced by Vladimir Ponec, Ben Nieuwenhuys, Aart Kleyn and Marc Koper. During the last five decades, SURFCAT groups at the Leiden University contributed significantly not only to exploring new materials and processes but also developing and optimizing surface science techniques [5–24]. Moreover, they have built a broad multinational network of collaborations with

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individual or groups of experimental and theoretical scientists, promoting heterogeneous catalysis and catalytic surface science. One of these collaborations was with the Laboratory of Physical Chemistry, at the University of Patras, in which framework well-studied silica supported Pt-Rh alloy catalysts prepared and characterized at Leiden [21,22], have been utilized in order to develop and evaluate novel inverse gas chromatographic methodologies.

Reversed-flow gas chromatography (RF-GC) is an inverse gas chromatographic (IGC) technique, in which the study is focused on the stationary phase and its interaction with injected solutes. Physicochemical measurements are based on the broadening and the shape distortion of the elution peaks, due to physicochemical processes taking place in a specific chromatographic column, called "*diffusion column*". Using suitable mathematical interpretation of the experimental chromatographic data, various physicochemical parameters pertaining to gas–gas and gas–liquid interactions were initially estimated, among of the others: gas diffusion coefficients in binary and ternary mixtures [25–27], mass transfer coefficients across the gas–liquid interphase [28–32] and Lennard–Jones parameters [33].

The interaction of CO, O_2, CO_2 and light hydrocarbons with monometallic and/or bimetallic Pt-Rh alloy catalysts has been utilized in further developing novel IGC methodologies related to the gas–solid interphase. Surface studies related to the kinetics of the elementary sorption steps (adsorption, desorption, surface reaction), the thermodynamics and the nature of the catalyst active sites have been carried out, and the following physicochemical quantities have been determined: (i) conversions either under steady or non-steady state conditions [34,35]. (ii) Adsorption, k_1, desorption, k_{-1}, and surface reaction, k_2, rate constants and the respective activation energies [36–39]. (iii) Energy distribution functions revealing the topography of the various groups of active sites [40–42]. (iv) Local adsorption energies, ε, lateral molecular interactions energies, β, adsorption isotherms, $\theta(p, T, \varepsilon)$, surface concentrations, c_s^*, and adsorption energy distribution functions, $\varphi(\varepsilon; t)$ [41–44]. (v) Surface diffusion coefficients for physically adsorbed or chemisorbed species [45,46]. (vi) Adsorption entropies, Gibbs free energies, and enthalpies [47]. (vii) Investigation of the competition between mass transfer and kinetics on catalytic solids [48]. (viii) Standard free energy of adsorption, the total surface free energy $(\gamma_1^L \gamma_2^L)^{1/2}$ and their probability density functions [49]. The applications of RF-IGC methodologies for catalytic and surface studies and the main findings have been reviewed in detail [50–52]. During the last decade, our collaboration has been extended in studying the kinetics [53–55], as well as the topography and the nature of the active sites [56] of gold-based catalysts.

For several decades, gold was believed as inactive. Gold catalysis has derived benefits from the progress of nanoscience producing solid nanostructured surfaces showing unsuspected catalytic properties. In the last two decades, gold has attracted considerable attention as a catalytic material with surprising activity for oxidation reactions [56]. The selective oxidation of CO in the presence of H_2, also called as preferential CO oxidation (SCO or PROX) is a characteristic example of gold catalysis, especially in the form of Au nanoparticles on an oxidic support [58]. It is generally agreed that the exceptional catalytic activity of gold depends on the size of the gold particles, but the nature of support material, the preparation method, and/or the activation procedure have also all been suggested to play a key role [59]. Sites at the gold support interface have also been claimed to be responsible for the activity in CO oxidation [60]. Strain in the Au particles due to the mismatch of the lattices at the interface with the support and the effect of low-coordinated sites and roughness have also been suggested as important factors for high activity [61]. The availability of many low-coordinated gold atoms on the small particles is considered as very important factor for the catalytic activity of gold nanoparticles for the low temperature CO oxidation [62]. Effects related to the interaction with the support also contribute [62,63].

Although significant progress has been achieved in the area of gold catalytic activity, there are still unresolved issues concerning the nature, the structure of the active sites and the catalytic mechanism of CO oxidation. Some of the difficulty in this elucidation has been attributed to the extreme sensitivity of these catalysts to details in the preparation procedure and to the operating conditions. For example, there are several controversial suggestions for the oxidative state of Au species acting in CO oxidation: the partial nonmetallic character of Au [64], the existence of ionic (Au^{+x}) species [65], the action of metallic Au alone or in combination with oxidized Au [66] have been proposed for a good catalytic performance. Discrepancies between reported activities may also arise from the effect of water on CO oxidation, which activity on supported Au catalysts is enhanced by moisture [67]. The role of H_2O is related to a model of active site involving an ensemble of metallic Au atoms and Au^+ —OH^- [67–70]. It is generally accepted that the active site involves the perimeter of the Au particles or the Au-support interface [71–74] and the presence of Au cations [61,75], although their role in the reaction is not unequivocally accepted [74].

Conversion of CO to CO_2, in the absence of oxygen and without carbon deposition, has been observed on nanosized and highly dispersed Au particles on γ-Al_2O_3, ZrO_2 and α-Fe_2O_3 [53,76]. Both the mild character of gold as well as the inactivity of γ-Al_2O_3 support give more evidence to the role of surface hydroxyl groups and rule out CO dissociation. Although, this process is related to C—O bond scission, it is very important to discriminate from CO dissociation. Moreover the process takes place also on bare γ-Al_2O_3, ZrO_2 and α-Fe_2O_3, but key differences are attributable to the presence of Au nanoparticles. The peripheral mechanism of CO oxidation over gold also explains CO oxidation by surface hydroxyl groups.

The goal of the present work is focused on the study of CO oxidation by surface hydroxyl groups over the bare γ-alumina support and Au/Al_2O_3 catalyst. In this study RF-IGC is utilized in order to compare the kinetics of CO oxidation by surface hydroxyl groups, the adsorptive capacity and the nature of the active sites related to CO sorption over bare γ-Al_2O_3 and Au/γ-Al_2O_3 catalyst, in a wide temperature range (50–300 °C). We investigate the effect of the existence of gold phase on the kinetics of CO sorption and answer to the following questions: (1) What amount of CO is adsorbed on the surface? (2) CO molecules are bonded on Au or on the alumina support? (3) Which are the nature of the surface chemical bonds and the topography of the active sites?

2. Materials and methods

2.1. General

Conventional GC involves the flow of a gaseous mobile phase in a defined direction over a stationary phase or packing resulting in the selective retention of solute components. In RF-IGC the system is modified; and another column (diffusion column) is placed perpendicularly in the center of the conventional chromatographic column (sampling column). The carrier gas flows continuously through the sampling column, while it is stagnant into the diffusion column, at which open end the studied catalyst bed is placed, as shown in Fig. 1 of Ref. [42]. The displacement of the injected solute (e.g. CO) into the diffusion column depends on its interaction with the stationary phase (e.g. adsorption, desorption and surface bonding), as well as its diffusion into the stagnant carrier gas (mobile phase), while it is independent of the carrier gas flow-rate, making RF-IGC an ideal method for studying slow rate processes. Another feature

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