Available online at www.sciencedirect.com

ScienceDirect

Journal of Catalysis 254 (2008) 238–243

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

On the usefulness of carbon isotopic exchange for the operando analysis of metal–carbonyl bands by IR over ceria-containing catalysts

H. Daly [a], J. Ni [a], D. Thompsett [b], F.C. Meunier [a,c,*]

[a] CenTACat, School of Chemistry and Chemical Engineering, Queen's University, Belfast, BT9 5AG, UK
[b] Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading, RG4 9NH, UK
[c] Laboratoire Catalyse et Spectrochimie, CNRS, University of Caen, ENSICAEN, 6 Boulevard du Marechal Juin, 14050 Caen Cedex, France

Received 12 October 2007; revised 19 December 2007; accepted 25 December 2007

Abstract

Operando diffuse reflectance FTIR spectroscopy (DRIFTS) combined with isotopic exchange techniques were used to investigate the bands located in the carbonyl-stretching region observed over a Au/$CeZrO_4$ catalyst under water–gas shift (WGS) conditions. The use of ^{12}CO and ^{13}CO in the feed was essential to distinguish between Au-carbonyl bands and an electronic transition band associated with Ce^{III} centers and to allow correct deconvolution of the carbonyl signal. The very active WGS catalyst used here as an example displays three main types of carbonyl species under reaction conditions, tentatively assigned to CO adsorbed on positively charged, neutral, and negatively charged Au entities. The DRIFTS data collected in the present work characterize the catalyst under reaction conditions and thus circumvent the difficulties associated with possible catalyst modifications during and after use. The possible presence of the electronic absorption (the maximum of which is at ca. 2120–2140 cm^{-1}) due to the presence of Ce^{III} centers always should be considered when analyzing metal–carbonyl IR bands. It also is crucial to realize that this band also may form in situ by reduction of the Ce^{IV} while under reaction conditions or when the sample is titrated with CO.

Keywords: FTIR; DRIFTS; In situ; Operando; Isotope; Exchange; SSITKA; Carbonyl; Ceria; Metal; Gold

---

1. Introduction

Catalysts based on ceria-supported metals (e.g., Cu, Pt, Au) display high activity for various reactions involving carbon monoxide, such as CO oxidation [1–4], the preferential oxidation of CO in the presence of hydrogen (PROX) [5–8], and the water–gas shift (WGS) reaction [9–17]. The adsorption of CO over the metal to form a metal carbonyl species is usually taken to be the first reaction step. Therefore, understanding the features of the metal–CO bond is valuable. This can be achieved by, for instance, analyzing the intensity and wavenumber of the carbonyl bands that are observable by IR spectroscopy. Such data may help in determining the nature (neutral or electronically charged) of the metal particles, the dispersion of the metallic phase, the type of bonding (e.g., on-top, bridged carbonyl), and the presence of lateral interactions between adsorbates.

Gold supported on ceria-containing supports has received particular attention in recent years in view of the high activity at low temperatures for the above-mentioned reactions that some appropriately prepared formulations can exhibit [18,19]. There has been much debate as to the nature of the active gold species, with the activity being related to various factors, including the size and shape of the metal particles, the nature of the support, and its electronic interaction with the metallic phase and the metal oxidation state [20,21]. Work by Boccuzzi et al. [22–27] and Hadjiivanov et al. [28–32] have provided some valuable insight into the state of Au particles by analyzing IR carbonyl bands.

Much of the previous work on the characterization of Au and Ce-based catalysts through metal carbonyl bands was not carried out under reaction conditions (operando), but rather was done using in situ methods, such as measures under dynamic vacuum after exposure to gas-phase CO or under varying pressures of pure CO. Operando techniques are invaluable for providing information on a working catalyst, because the structure

---

[*] Corresponding author. Fax: +33 (0) 231452822.
E-mail address: frederic.meunier@ensicaen.fr (F.C. Meunier).

0021-9517/$ – see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2007.12.013

of the Au particles and the oxidation state of the metal (and also that of the cerium atoms of the support) can evolve under reaction conditions. As an example, operando EXAFS and XANES of the Au/CeZrO$_4$ catalyst that we investigated in the present work revealed that the sample contained oxidized gold at room temperature in air, whereas only metallic gold could be observed at 100 °C under a WGS feed [33]. Similar results on Au and ceria-based catalysts were reported by Hanson et al. [34].

The extent of the catalyst modification under reaction conditions is not easily predictable and also will depend on the interaction between Au and the support. It has been shown that gold can significantly reduce the reduction temperature of ceria by several hundreds of degrees and that ceria surface reduction can be seen at temperatures as low as 100 °C [18,23]. The reducing nature of CO-containing atmospheres such as WGS feeds usually will lead to the formation of reduced species of cerium, at least on the catalyst surface [18,35–37]. This even occur even in the presence of $CO + O_2$ feeds with a large excess of O_2, because at low temperatures, the oxidation state of the surface under steady-state reaction conditions will be dictated primarily by the kinetics of the sample reduction by CO versus that of oxidation by O_2, rather than by the thermodynamics of the overall system.

The reduction of Ce^{IV} to Ce^{III} leads to additional difficulties in the interpretation of metal carbonyl bands. Reduced ceria exhibits an absorption band in the infrared region at approximately 2120 cm^{-1} due to a normally forbidden electronic transition ($^2F_{5/2}$ to $^2F_{7/2}$) [38–42]. Binet et al. observed this band after H_2 or $^{12}CO/^{13}CO$ reduction of ceria. The band wavenumber did not shift regardless of whether treatment was carried out with ^{12}CO or ^{13}CO, demonstrating that the band is not due to any carbonyl species. Depending on the baseline correction method used, the position of the maximum of this band can (apparently) shift within the 2140–2120 cm^{-1} wavenumber range [42]. The presence of this electronic absorption band located in the same region as that associated with typical carbonyl-stretching modes may lead to misinterpretation of data even at very low temperatures, because metals such as Au lower the reduction temperature at the surface of ceria.

An example of the difficulty created by this electronic transition was recently provided by Behm et al. [43], who acknowledged the difficulty in interpreting the IR signal in the 2200–2000 cm^{-1} region (see their Fig. 5b). A possible explanation for this proposed by Behm et al. assigns most of the signal in this region to the electronic transition of reduced ceria. We favor this interpretation over a second possibility proposed by Behm et al. that this band is due to carbonyl species adsorbed on Au(0). The latter interpretation led to the unrealistic conclusion that "the constant CO(ads) intensity is most simply explained by a compensation of two counteracting effects, deactivation (intensity decrease) and formation of Au(0) nanoparticles (intensity increase)," [43] when trying to explain the fact that no signal change occurred while the surface state of gold was dramatically modified. The difficulty of rationalizing the IR signal in this region clearly supports the need for the work described in this report.

The combination of IR spectroscopy and steady-state isotopic transient kinetic analysis (SSITKA [44]) provides a powerful method for investigating the reactivity of surface species under reaction conditions [45–48]. Using SSITKA-DRIFTS-MS methods, we were able to prove that the IR-observable surface formates are not important factors in the WGS reaction mechanism for various catalysts: Au/CeZrO$_4$ [49], Pt/ZrO$_2$ [50], Au/Ce(La)O$_2$ [42], and Pt/CeO$_2$ [49,51]. Our findings underscore an additional advantage of using such a technique: the ability to monitor the structure of the metal carbonyl band under reaction conditions and ascertain deconvolution of the signal by comparing the data obtained under ^{12}C- and ^{13}C-containing feeds. The discrimination between the signal of metal carbonyl species and that of the reduced ceria electronic transition is made obvious, allowing straightforward spectrum corrections. The WGS data used in the present work were collected by operando DRIFTS over a Au/CeZrO$_4$ catalyst, which is among the most active low-temperature WGS catalyst based on noble metals reported so far [19,33,52].

2. Experimental

The experimental setup consisted of a high-temperature diffuse reflectance IR cell (from Spectra-Tech) fitted with ZnSe windows. The DRIFTS cell was located in a Bruker Equinox 55 spectrometer, operating at a resolution of 4 cm^{-1}. The reactor crucible was modified to ensure plug-flow conditions throughout the catalyst bed. The interface between the ceramic reactor and the metallic base plate was sealed with PTFE tape to prevent any sample bypass. The original porous bed for supporting the sample was replaced by an inert metallic mesh. The WGS reaction rates measured with this cell were equal to those measured in a conventional tubular plug-flow reactor [42].

The catalyst used was a 2 wt% Au/CeZrO$_4$, the details of which have been reported previously [33]. The catalyst sample of 60 ± 3 mg was placed in the crucible. The purity of all gases used (i.e., H_2, CO, Ar; all supplied by BOC) was >99.95%. The ^{13}CO (supplied by Cambridge Isotope Laboratories Inc.) was 99% pure. The DRIFTS cell was connected to the feed gas cylinders through low-volume stainless-steel lines. The gas flows were controlled by Aera mass flow controllers, which were calibrated regularly. A 4-way valve was used to allow rapid switching between two reaction feeds when appropriate. High-purity water was introduced using a single saturator that delivered a constant, accurate flow of water. Water delivery was completely unaffected by the valve switching (as determined by MS or GC analyses [51]).

A reference DRIFTS single scan was recorded over a mirror at room temperature and used as background; 28 and 128 scans were co-added for the sample and background spectra, respectively. Unless stated otherwise, the catalyst was brought up to reaction temperature under Ar, after which water was added to the Ar stream. The reaction mixture was subsequently introduced at a total flow rate of 100 mL min^{-1}. The reaction flow was down through the reactor bed; therefore, the upper layer of the catalyst (the layer mainly probed by the DRIFTS technique) was the front of the bed. Steady-state conditions in terms of the