Available online at www.sciencedirect.com
ScienceDirect
Journal of Catalysis 243 (2006) 171–182
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

DRIFTS study of the water–gas shift reaction over Au/Fe_2O_3

B. Aeijelts Averink Silberova, G. Mul, M. Makkee *, J.A. Moulijn

DelftChemTech, Catalysis Engineering, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, NL 2628 BL Delft, The Netherlands

Received 28 February 2006; revised 30 June 2006; accepted 6 July 2006

Available online 28 August 2006

Abstract

The water–gas shift (WGS) reaction over Au/Fe_2O_3 was studied by *operando* diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) combined with mass spectrometry (MS). Au/Fe_2O_3 and Fe_2O_3 were exposed to high temperature (400 °C) in He, followed by CO, H_2, or H_2O treatment at 25 and/or 200 °C, respectively. The results showed that carbonate-like species and hydroxyl groups are present on the as-received sample, and not all of them are removed during high-temperature treatment at 400 °C. Although the dynamics of adsorbates on the catalyst surface have been observed at room temperature, at elevated temperature (200 °C)—that is, real operational steady-state conditions—the reduction–oxidation mechanism is the main pathway to the production of CO_2 and H_2. Formates have not been observed under these reaction conditions. At elevated temperature, the support Fe_2O_3, in the presence of Au particles is easily reduced and contributes the catalyst performance for the WGS reaction. The water introduced to Fe_2O_3 does not contribute to reoxidation to a large extent and, consequently, to high CO_2 production as observed over Au/Fe_2O_3. Furthermore, H_2 is evolved only in the presence of Au particles and when a certain degree of Fe oxide reduction is achieved.

© 2006 Elsevier Inc. All rights reserved.

Keywords: Water–gas shift reaction; Au; Mechanism; DRIFTS; TPR

1. Introduction

The pioneering work of Haruta et al. has initiated extensive research efforts on the application of nanosize gold in heterogeneous catalysis [1–5]. Haruta et al. have shown that gold on titania has extraordinary selectivity in epoxidation of propene, using a combination of hydrogen and oxygen as oxidant, as well as very high activity in low-temperature CO oxidation, which has been confirmed by others [3–10]. Various groups have analyzed the mechanism of Au-induced reactions [11–20], including the water–gas shift (WGS) reaction [20–39]. Various metal oxides have been reported to be active supports for Au particles in the latter reaction, including CeO_2 [20–29], TiO_2 [30–32], ZrO_2 [25,33], ZnO [25,33], Fe_2O_3 [25,28,31,33–37], Fe_2O_3-ZnO [25,33], Fe_2O_3-ZrO_2 [25,33], and zeolites [38], have all been discussed.

The reaction pathways of WGS reaction over gold-based catalysts have been addressed in some of these contributions [23,25,31,32,34]. Two reaction mechanisms generally can be considered for the WGS reaction: (i) the regenerative mechanism, which includes reduction of support sites by CO, yielding CO_2, followed by dissociation of H_2O to adsorbed O and H atoms (presumably on Au) and reoxidation of the reduced support sites with concomitant H_2 formation, and (ii) adsorptive mechanism comprising adsorption of CO and H_2O; formation of formate, carbonate, or bicarbonate intermediates (CO_yH_x); and finally decomposition of the intermediates to form CO_2 and H_2 [40]. The mechanisms are summarized as follows:

(i) regenerative

$H_2O(g) \rightarrow H_2O(s)$,

$H_2O(s) \rightarrow OH(s) + H(s)$,

$OH(s) \rightarrow O(s) + H(s)$,

$2H(s) \rightarrow H_2(g)$,

$CO(g) \rightarrow CO(s)$,

---

* Corresponding author.
E-mail addresses: b.aeijeltsaverink-silberova@tudelft.nl (B. Aeijelts Averink Silberova), g.mul@tudelft.nl (G. Mul), m.makkee@tudelft.nl (M. Makkee), j.a.moulijn@tudelft.nl (J.A. Moulijn).

0021-9517/$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2006.07.010

$$\mathrm{CO(s) + O(s) \rightarrow CO_2(s)},$$

$$\mathrm{CO_2(s) \rightarrow CO_2(g)},$$

(ii) adsorptive

$$\mathrm{H_2O(g) \rightarrow H_2O(s)},$$

$$\mathrm{CO(g) \rightarrow CO(s)},$$

$$\mathrm{H_2O(s) + CO(s) \rightarrow CO}_y\mathrm{H}_x,$$

$$\mathrm{CO}_y\mathrm{H}_x \rightarrow \mathrm{CO_2(s) + H_2(s)},$$

$$\mathrm{CO_2(s) \rightarrow CO_2(g)},$$

$$\mathrm{H_2(s) \rightarrow H_2(g)}.$$

Besides the adsorptive mechanism through (bi)carbonates, in cases of the WGS reaction over Au/CeO_2 catalysts, Tabakova et al. have proposed an adsorptive mechanism with the involvement of formate species [23]. Jacobs et al. confirmed that formate species can be formed on the surface of reduced CeO_2 during the WGS [27]. These studies on ceria-based catalysts found that in steady-state WGS conditions, the ceria surface is present in a reduced state, as evidenced by in situ measurements [23]. In contrast, Jacobs et al. have excluded a ceria redox mechanism based on the observation that adding H_2O has resulted only in the formation of bridging OH groups by reaction with ceria vacancies [25].

Considering the WGS reaction over Au/Fe_2O_3 and Au/TiO_2, both the associated and regenerative mechanisms have been proposed to occur simultaneously [31,32,34,35]. The associative mechanism consisted of the dissociative adsorption of H_2O on small gold particles followed by spillover of activated hydroxyl groups onto adjacent sites of the ferric oxide [31,35]. This is followed by reaction of CO at the Au–support interface [34], eventually yielding CO_2 and H_2. Enhanced catalytic activity of Au/Fe_2O_3 compared with Fe_2O_3 was explained on the basis that Au/Fe_2O_3 contains more active OH groups [34]. In the event that the support is reduced by CO, H_2O molecules were reported to participate in the reoxidation Fe^{2+} to Fe^{3+} [34]. It should be noted that the IR spectra recorded by Boccuzzi et al. were obtained without measuring reaction products; that is, a direct connection between reaction products and the structure of the catalyst could not be made.

The present mechanistic study is focused on the WGS reaction over a reference Au/Fe_2O_3 catalyst of the World Gold Council (WGC) [3]. *Operando* diffuse-reflectance infrared Fourier transformation spectroscopy (DRIFTS) with mass spectrometry (MS) analysis of the gas composition has been applied to monitor the exposure of Au/Fe_2O_3 and Fe_2O_3 to CO, H_2O, and H_2 at 25 and/or 200 °C to correlate reaction products directly to compositional changes on the catalytic surface. The reducibility of the catalyst as measured by TPR is also discussed. The studies provide new insight into the initial morphological changes of the catalyst and reaction pathways at elevated temperature.

2. Experimental

2.1. Catalyst preparation and characterization

The applied Au/Fe_2O_3 reference catalyst was obtained from the WGC [3]. This catalyst was prepared by co-precipitation as described previously [47]. A final Au loading of 4.48% was determined by ICP analysis. Au particle sizes ranging from 3 to 5 nm [16,30] and a mean gold particle size of 2.8 nm [47] have been reported. The BET area of the calcined sample at 400 °C was 38.7 m^2/g [47].

Temperature-programmed reduction (TPR) of Au/Fe_2O_3 and Fe_2O_3 was performed with 7% H_2 in Ar and a total flow rate of 37 ml/min to further characterize the reducibility of the sample. The sample (100 mg) was diluted by SiC at a ratio of 1:1.5. A heating rate of 10 °C/min was chosen to reach 900 °C. The H_2 signal was recorded using TCD analysis.

2.2. DRIFT spectroscopy and mass spectrometry

DRIFTS studies were performed on a Thermo Nicolet Nexus IR with OMNIC software. The sample (~50 mg) was first treated in a flow of (~35 ml/min) He at 400 °C for 30 min (high-temperature treatment [HTT]) before each experiment. The heating rate during the treatment was 10 °C/min. After HTT, the sample was cooled under He to an operation temperature of either 25 or 200 °C. Unless stated otherwise, infrared (IR) spectra were recorded against a background of the sample at the reaction temperature under flowing He. IR spectra were recorded with co-addition 64 scans in single-beam spectra or absorbance spectra, by applying a resolution of 4 cm^{-1}. A Pfeiffer Vacuum ThermoStar mass spectrometer allowed direct identification of mass fragments of the reactants and products after interaction with the catalyst sample in the IR cell.

The catalyst (~50 mg) was further exposed to CO, H_2O, H_2, or a mixture of CO (CTS, 2.0) and H_2O in He. The total flow rate was 32.2 ml/min. The CO (20% CO in Ar) was diluted by He to obtain a content of 0.5%. When H_2O was added, the H_2O content was 2.70%, obtained by saturating He in distilled H_2O at 25 °C and mixing with the CO/Ar stream.

The mixing device connected to the IR cell was equipped with a four-way valve allowing switching between a bypass line for an inert gas and a main line for the reaction mixture. In some experiments, the sample was heated under He flow at the end of the experiment to evaluate the released adsorbed species.

3. Results

3.1. High-temperature treatment

The products that evolved and the compositional changes that occurred from HTT of the Au/Fe_2O_3 catalyst as-received are shown in Fig. 1A (MS analysis) and Fig. 1B (IR spectra). A large amount of H_2O was released during HTT. The highest rate of formation occurred around 100 °C, followed by a smaller maximum at 220–225 °C. Furthermore, a signal of mass

Download English Version:

https://daneshyari.com/en/article/63449

Download Persian Version:

https://daneshyari.com/article/63449

Daneshyari.com