Journal of Catalysis 286 (2012) 137–152

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Oxidative steam reforming of ethanol over Ir/CeO_2 catalysts: A structure sensitivity analysis

Weijie Cai [a], Fagen Wang [b], Cécile Daniel [a], Andre C. van Veen [a,c], Yves Schuurman [a], Claude Descorme [a], Hélène Provendier [a], Wenjie Shen [b,*], Claude Mirodatos [a,*]

[a] University of Lyon – Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON, UMR 5256, CNRS – Université Claude Bernard Lyon 1), 69626 Villeurbanne Cedex, France
[b] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[c] Ruhr University Bochum, Laboratory of Industrial Chemistry, 44780 Bochum, Germany

ARTICLE INFO

Article history:
Received 11 January 2011
Revised 16 October 2011
Accepted 22 October 2011
Available online 30 November 2011

Keywords:
Oxidative steam reforming
Ethanol
Iridium
Ceria
Hydrogen production
Structure sensitivity

ABSTRACT

A series of Ir/CeO_2 catalysts of different oxide and metallic phase dispersions was investigated by XRD, TPR, HRTEM, CO_2 TPD/calorimetry, *in situ* DRIFT spectroscopy, and oxygen isotopic exchange techniques in order to elucidate the specific influence of catalyst morphology and structure on the oxidative steam reforming (OSR) of ethanol. Structure/texture sensitivity is demonstrated on the basis of the OSR mechanism, which involves, in order: (i) ethanol adsorption on the ceria surface, (ii) partial oxidation to acetate and surface migration of the C2 intermediates along the ceria support toward the Ir particles, (iii) cracking and further oxidation into Ir carbonyls and ceria carbonates, and (iv) hydrogen and carbon monoxide desorption from the Ir particles. Structure sensitivity is established by considering two types of sites: the ceria surface sites, which are essentially pairs of oxygen vacancies and basic OH groups, as well as interfacial sites between Ir and ceria phases, involving pairs of Ir coordinately unsaturated sites (CUSs) and the aforementioned peripheral ceria sites. This structure sensitivity is revealed by TOF calculations based on these two types of sites, which correspond to the two main rate controlling steps of the ethanol OSR mechanism, namely steps (ii) and (iii). The materials considered display activity, selectivity, and resistance to aging (manifested by coke deposition and sintering) that are closely related to their initial structure and texture. Two domains in terms of iridium and ceria particle size are identified, leading either to stable and selective catalysts or to unstable and unselective catalysts. Such an original and quantified structure sensitivity analysis should prove useful for further process development.

1. Introduction

Hydrogen, a clean energy carrier, presents the potential to generate electricity in a highly efficient manner through the use of fuel cell technology. While the direct distribution and storage of hydrogen are the principal drawbacks to domestic or remote area uses, on-site generation from various H-containing feedstocks deserves to be investigated. Hydrogen production by oxidative steam reforming of bio-ethanol is therefore a valuable strategic target due to: (i) its ease of feedstock transport compared to conventional natural gas steam reforming, (ii) the renewable character of bio-ethanol compared to fossil fuels, and (iii) its increasing industrial production, which now makes it available for various domestic uses [1,2].

Metals such as Ni, Cu, Rh, and Pt [3,4] have been found to exhibit reasonable intrinsic activity for the oxidative steam reforming of ethanol. Furthermore, numerous oxides such as CeO_2, Al_2O_3, MgO, and ZrO_2 have been investigated as a support for the metal phase in order to ensure optimal metallic dispersion and stability but also to participate directly in the catalytic process [5–7]. It has frequently been shown that both the active metal and the support play a critical role in the activity and stability of the catalyst for hydrocarbon or oxygenate reforming [8,9]. In this respect, the excellent performance of CeO_2-supported catalysts, which present high catalytic activity and resistance against carbon deposition, has been tentatively related to the high oxygen storage capacity (OSC) of ceria [10,11] and to the strong interaction between ceria and the supported metal [12,13]. For example, Kugai et al. [14,15] found that Ni–Rh catalysts supported on high surface area CeO_2 nanocrystals showed better performance for the oxidative steam reforming of ethanol than did catalysts with a lower specific surface area. They stressed that significant differences in catalytic properties (such as metallic dispersion) and in performance (such as activity and selectivity) could be linked to the differences in CeO_2 supports. An explanation for these effects remains to be established; however, while the structural and textural

---

* Corresponding authors.
E-mail address: claude.mirodatos@ircelyon.univ-lyon1.fr (C. Mirodatos).

0021-9517/$ - see front matter © 2011 Published by Elsevier Inc.
doi:10.1016/j.jcat.2011.10.021

morphology of the catalyst (metallic dispersion and specific surface area of the ceria support) deserves more thorough investigation and control in view of industrial application.

Our group has previously described the outstanding performance of a well-dispersed Ir/CeO_2 catalyst for the oxidative steam reforming of ethanol [16,17]. Upon long-term testing, moderate ceria sintering was observed but had negligible impact on the iridium dispersion. Nevertheless, the full conversion of ethanol in the aforementioned experiments prevented the precise investigation of the potential effect of the specific surface area of the ceria support on catalyst performance and aging. We consequently performed an in-depth study of the combined effect of the ceria surface area and the iridium dispersion on the performance of the Ir/CeO_2 catalyst for the oxidative steam reforming of ethanol. For this purpose, catalysts with different ceria grain sizes but with the same Ir loading, including the catalyst already described in [16,17], were compared under identical reaction conditions. In order to further analyze the performance of the catalysts, their intrinsic properties were characterized using Temperature-Programmed Reduction (TPR), X-Ray Diffraction (XRD), oxygen storage capacity (OSC), oxygen isotopic exchange (SSITKA), *in situ* DRIFT spectroscopy, and High-Resolution Transmission Electron Microscopy (HRTEM) imaging, with an aim to establish possible structure–activity relationships.

2. Experimental

2.1. Catalyst preparation

CeO_2 was prepared by precipitation, with diammonium cerium (IV) nitrate made to react with urea in aqueous solution, according to the procedure detailed in [17]. After filtration and thorough washing with water, the excess water was evaporated under vacuum, the precipitate was dried at 100 °C for 12 h, and finally calcined at 400, 550, 700, or 850 °C for 5 h in static air, yielding ceria samples with different specific surface areas (labeled as Ce400, Ce550, Ce700, and Ce850, respectively).

The series of Ir/CeO_2 catalysts loaded with 2 wt.% Ir was prepared by deposition–precipitation according to the procedure reported in [17]. The catalysts prepared were named Ir/Ce400, Ir/Ce550, Ir/Ce700, and Ir/Ce850. Their Ir content is reported in Table 1. Less than 0.03 wt.% sodium was detected by chemical analysis, which rules out any significant role of alkali for these catalysts.

2.2. Catalyst characterization

2.2.1. XRD

XRD patterns were recorded using a Rigaku D/MAX-RB diffractometer equipped with a Cu Kα radiation source operating at 40 kV and 100 mA. The mean crystallite sizes of ceria were calculated according to the Debye–Scherrer equation.

2.2.2. HRTEM

HRTEM images were obtained using a Philips Tecnai $G^2$20 microscope operating at 300 kV. The samples were prepared by ultrasonically suspending the sample in ethanol. A droplet of the suspension was deposited onto a thin carbon film supported on a standard copper grid and then dried in air.

2.2.3. BET

N_2 adsorption–desorption isotherms were recorded at −196 °C using a Nova 4200e instrument (Quantachrome). Prior to measurements, the sample was outgassed at 300 °C for 2 h under primary-pump vacuum. The specific surface area was calculated by multi-point BET analysis of the nitrogen adsorption isotherms.

2.2.4. H_2 chemisorption

The dispersion of the metallic phase obtained after reduction in hydrogen was calculated from H_2 chemisorption. Experiments were performed at low temperature to limit the "spillover" phenomenon [18,19] using a pulse chromatographic apparatus. After reduction under flowing hydrogen at 400 °C for 1 h, the sample was cooled to room temperature under flowing argon. The reactor was then placed in a dry ice–acetone mixture at −85 °C, and pulses of hydrogen were injected until saturation was indicated by constant peak area of the final pulses. This permitted the evaluation of total hydrogen uptake (H_{C1}). Subsequently, the catalyst was flushed for 10 min under argon to remove the physically adsorbed hydrogen molecules, and hydrogen was pulsed again until saturation (H_{C2}). The amount of chemisorbed hydrogen was calculated using $H_C = H_{C1} - H_{C2}$.

2.2.5. H_2-TPR

Hydrogen temperature-programmed reduction (H_2-TPR) was performed with a conventional setup equipped with a TCD detector. A 100 mg catalyst sample (40–60 mesh) was pretreated at 300 °C for 1 h under flowing He (40 mL/min). After cooling to room temperature, the sample was exposed to a flow of 5 vol.% H_2/He (40 mL/min), and the temperature was increased linearly at 10 °C/min.

2.2.6. OSC

The oxygen storage capacity (OSC) was measured in a microreactor coupled with a quadrupole mass spectrometer (Omnistar, Balzers). Before analysis, the sample (100 mg) was reduced with 5 vol.% H_2/Ar (50 mL/min) at 650 °C. The sample was purged for 15 min at 650 °C using flowing Ar. A stream of 5 vol.% O_2/Ar (50 mL/min) was then passed through the sample, and the oxygen consumption was quantitatively monitored with the mass spectrometer at $m/e = 32$.

2.2.7. Carbon deposition

The carbon deposition occurring during catalytic testing was investigated by temperature-programmed oxidation (TPO)

Table 1
Physicochemical properties and oxygen storage capacity of the fresh catalysts and in parenthesis, values measured after long-term aging treatments carried out at 650 °C for 60 h.

Catalyst	x_{Ir}[a] (wt.%)	D_{Ir} [b] (%)	S_{BET}[c] (m^2/g_{cat})	d_{CeO2} [d] (nm)	$S_{external}$[e] (m^2/g_{cat})
Ir/Ce400	1.92	67 (61)	153 (61)	6 (15)	140 (56)
Ir/Ce550	1.81	62 (46)	102 (43)	8 (19)	105 (44)
Ir/Ce700	1.87	59 (37)	45 (20)	15 (34)	56 (25)
Ir/Ce850	1.75	26 (23)	16 (12)	44 (60)	19 (14)

[a] Ir content from chemical analyses (no significant changes have been noted after long-run testing).

[b] Ir dispersion calculated from hydrogen chemisorption after reduction at 400 °C under flowing H_2 for the fresh samples and from HRTEM images for the used samples (see Fig. 14).

[c] BET surface area measured by N_2 adsorption before and after long-term runs.

[d] Ceria grain size, calculated from the XRD patterns (Debye–Scherrer equation).

[e] Ceria surface calculated from the ceria grain size using the formula $S_{external} = \frac{60{,}000}{\rho_{ceria}\ (g\ cm^3) \times d\ (Å)}$.