

# Steam reforming of bio-ethanol for the production of hydrogen over ceria-supported Co, Ir and Ni catalysts

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## Abstract

Ceria-supported Co, Ir and Ni catalysts were investigated for steam reforming of ethanol in the temperature range of 300–700 °C with respect to the nature of the active metals and the catalytic stability. At low temperatures, ethanol dehydrogenation to acetaldehyde and ethanol decomposition to methane and carbon monoxide were the primary reactions, depending on the active metals. At higher temperatures where all the ethanol and the intermediate compounds, like acetaldehyde and acetone, were completely converted into hydrogen, carbon oxides and methane, steam reforming of methane and reverse water gas shift were the major reactions, which determined the outlet gas composition. More importantly, long-term stability test revealed that the Ir/CeO<sub>2</sub> catalyst showed rather stable catalytic performance for 300 h time-on-stream without any deactivation. The improvement was attributed to the effective prevention of the sintering of the highly dispersed Ir particles through the strong interaction between Ir and CeO<sub>2</sub> and to the significant resistance to coke deposition of ceria based on its higher oxygen storage-release capacity.

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## 1. Introduction

Bio-ethanol produced by fermentation of starch and sugar or lower-cost crop wastes is very attractive for hydrogen production due to its relatively high hydrogen content and renewable origination. The use of bio-ethanol for the production of hydrogen also provides significant environmental benefits, since the produced CO<sub>2</sub> is consumed for biomass growth and thus offering a carbon dioxide neutral energy supply. Bio-ethanol is practically produced by fermentation of biomass, and the aqueous mixture is then distilled to the level of 45–55 vol.% ethanol solution. Occasionally, this concentration of ethanol equals to a molar ratio of water/ethanol = 3:1, which is the stoichiometric proportion of ethanol steam reforming (C<sub>2</sub>H<sub>5</sub>OH +

3H<sub>2</sub>O → 2CO<sub>2</sub> + 6H<sub>2</sub>). However, there are also other undesirable side reactions that may greatly affect the selective production of hydrogen as well as the catalytic stability [1–3]. The production of hydrogen from ethanol steam reforming is critically dependent on the choice of both the active metal and the support.

Supported Ni catalysts [3,4] showed relatively good activity, but accompanied by the rapid deactivation due to the severe coke deposition and the higher methane formation. Co catalysts [1,5,6] exhibited good performance in hydrogen production from ethanol steam reforming, however, the significant deactivation through sintering and surface cobalt oxidation limited the practical application. Among the noble metals, Rh was found to be the most active and selective system [1,7–9]. But sufficiently large amount of Rh and excess of water were often employed to prevent the coke formation at high operation temperatures (700–900 °C). Obviously, the catalytic stability associated with the resistance to coke deposition still is the main

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challenge of the catalyst for ethanol steam reforming. By considering that fact that  $\text{CeO}_2$  often exhibits strong resistance to coke deposition based on its oxygen storage-release capacity [8,10], here we investigated the catalytic performance of ceria-supported Co, Ni and Ir catalysts for hydrogen production from ethanol steam reforming with stoichiometric feed composition, that is, 52 vol.% aqueous ethanol solution with a water/ethanol molar ratio of 3.0. The Ir/ $\text{CeO}_2$  catalyst showed rather stable catalytic performance for 300 h time-on-stream without any deactivation.

## 2. Experimental

### 2.1. Catalyst preparation

The M/ $\text{CeO}_2$  (M = 2%Ir, 15%Co and 15%Ni in weight) catalysts were prepared by deposition–precipitation method using a commercially available cerium dioxide with a BET surface of  $96 \text{ m}^2/\text{g}$ . The  $\text{CeO}_2$  support was first suspended into the aqueous solutions containing certain amounts of metal precursors ( $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ , respectively) and heated to  $75^\circ\text{C}$  under stirring.  $0.25 \text{ M Na}_2\text{CO}_3$  aqueous solutions were then gradually added until the pH value of the mixture reached 9.0 and further aged for 1 h. After filtration and washing with hot water, the obtained solids were dried at  $100^\circ\text{C}$  overnight and finally calcined at  $400^\circ\text{C}$  for 5 h in air.

### 2.2. Catalyst characterization

Power X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX-RB diffractor with  $\text{Cu K}\alpha$  radiation operated at 40 kV and 100 mA.

HRTEM images were taken on Philips Tecnai G<sup>2</sup>20 operated at 200 kV. Specimens were prepared by ultrasonically suspending the sample in ethanol. A drop of the suspension was then applied onto clean holey copper grids and dried in air.

Hydrogen temperature programmed reduction (TPR) measurement was performed with a conventional setup equipped with TCD detector. At each measurement, 50 mg (40–60 mesh) samples were heated to  $500^\circ\text{C}$  under  $\text{N}_2$  flow (40 ml/min) and kept at this temperature for 1 h to remove the adsorbed carbonates and hydrates. After cooling down to room temperature and introducing the reduction agent of 20 vol.%  $\text{H}_2/\text{N}_2$  (40 ml/min), the temperature was then programmed to rise at  $10^\circ\text{C}/\text{min}$ .

### 2.3. Catalytic measurement

Steam reforming of ethanol was conducted in a continuous flow fixed-bed quartz micro-reactor under atmospheric pressure within the temperature range of  $300\text{--}700^\circ\text{C}$ . Three hundred milligram of catalyst (grain size of 40–60 mesh) were loaded and sandwiched by two quartz wool

layers. Prior to reaction, the catalyst was reduced with 5 vol.%  $\text{H}_2/\text{He}$  (30 ml/min) at  $400^\circ\text{C}$  for 3 h. Ethanol (52 vol.%) aqueous solution with a molar ratio of  $\text{H}_2\text{O}/\text{EtOH} = 3:1$  was fed by a micro-pump and vaporized at  $200^\circ\text{C}$ . The gas hourly space velocity (GHSV) was  $6000 \text{ ml g}^{-1} \text{ h}^{-1}$ . The effluent was analyzed on-line by gas chromatography.  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  were separated by a packed column (Hayesap D) and detected by a TCD using helium as carrier gas, and hydrocarbons and oxygenates were separated with a capillary column (INNOWAX) and analyzed with an FID. The concentrations of the outlet products were calculated by excluding water, that is, dry-based gas composition.

## 3. Results and discussion

### 3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of the M/ $\text{CeO}_2$  catalysts. The distinct fluorite oxide diffraction of  $\text{CeO}_2$  was observed in all the samples, and the Co/ $\text{CeO}_2$  and Ni/ $\text{CeO}_2$  catalysts exhibited diffraction patterns of  $\text{Co}_3\text{O}_4$  and  $\text{NiO}$ , respectively. While, the absence of diffraction from iridium oxide in the Ir/ $\text{CeO}_2$  catalyst may suggest that the Ir particles are too small (probably less than 5 nm) to be detected and highly dispersed over ceria. Fig. 2 shows the HRTEM images of the M/ $\text{CeO}_2$  catalysts. Clearly, the spherical metal particles were well dispersed over ceria. The Ir particle size was estimated to be ca. 5 nm in the Ir/ $\text{CeO}_2$  catalyst, and the particle sizes of the active metals in the Co/ $\text{CeO}_2$  and Ni/ $\text{CeO}_2$  catalysts were about 10–30 nm.

Fig. 3 illustrates the  $\text{H}_2$ -TPR profiles of the M/ $\text{CeO}_2$  catalysts. The Ir/ $\text{CeO}_2$  catalyst exhibited two overlapped hydrogen consumption peaks appearing at  $65^\circ\text{C}$  and  $120^\circ\text{C}$ . These hydrogen consumptions could be assigned to the combined reduction of the  $\text{IrO}_2$  species and the partial surface reduction of ceria, since the measured value of hydrogen consumption was higher than the amount

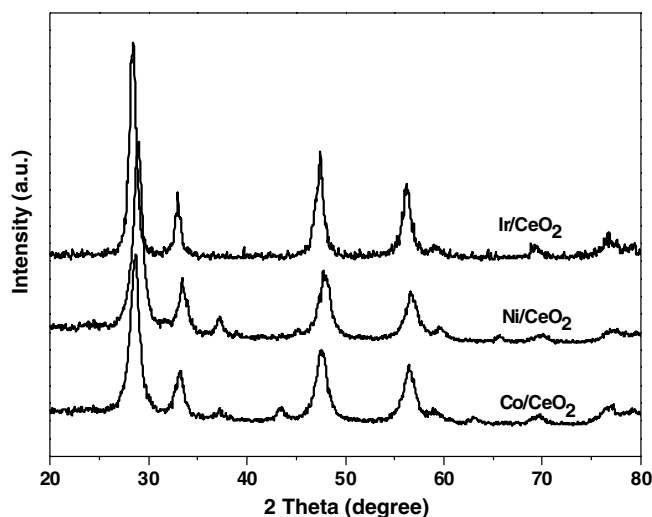


Fig. 1. XRD patterns of the M/ $\text{CeO}_2$  catalysts.

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