

# The water-gas-shift reaction over Ir/TiO<sub>2</sub> and Ir–Re/TiO<sub>2</sub> catalysts

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Received 8 December 2005; received in revised form 2 February 2006; accepted 7 February 2006  
Available online 20 March 2006

## Abstract

Water-gas-shift reactions over Ir/TiO<sub>2</sub> and Ir–Re/TiO<sub>2</sub> catalysts were studied, employing a closed gas circulation system. Addition of Re to Ir/TiO<sub>2</sub> catalysts clearly accelerated the WGS reaction, as is in the cases of our previous study over Pt/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> catalysts. The FT-IR analyses of the adsorbed species during the reaction exhibited the enhancement of the adsorbed CO peaks in the lower wavenumber region with the increase of Re content. These peaks are supposed to be the adsorbed CO neighboring to the adsorbed OH function, which was formed by the dissociation of water on the Re metal or ReO<sub>x</sub> species of Ir–Re/TiO<sub>2</sub> catalysts.

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*Keywords:* Ir/TiO<sub>2</sub> catalyst; Ir–Re/TiO<sub>2</sub> catalyst; Water-gas-shift reaction; FT-IR

## 1. Introduction

The technology to obtain pure hydrogen conveniently, which contains less concentration of CO with low cost, is one of the most important technologies in the coming hydrogen-energy society. The water-gas-shift reaction (WGS reaction) has been applied to decrease the concentration of CO and increase the hydrogen production for the most hydrogen processing units. More recently, with the development and beginning of commercialization of polymer electrode fuel-cells (PEM-FC), for both automotives and stationary (home) use [1,2], the interests in the WGS reactors and catalysts are growing, especially on the more efficient, the more compact, and the higher cost-performance reaction systems. For these purposes, advanced low-temperature shift (LTS) catalysts are needed to produce hydrogen containing less concentration of CO (less than 1 vol.% in the process gas) in higher space velocity (usually 5000–20,000 h<sup>-1</sup>). Such material will be introduced, in most fuel-processors used for PEM-FCs, to the further CO-removal reactors such as CO-preferential oxidation (PROX) reactor, where concentration of CO is suppressed below 10 vol.-ppm. For this purpose, conventional base-metal (Cu/Zn) LTS catalysts are no longer suitable due to their poor

activities per catalyst volume [3], and the lack of durability against higher temperature or air-exposure [4], all of which are the obstacles to reduce catalyst volume and to achieve easy-handling reaction systems.

As the alternative solution to base-metal catalysts, the precious metal (PM) WGS catalysts, especially supported Pt catalysts, are well known and many incentive studies are reported [5–12]. These catalysts, however, still have some problems; (i) insufficient activity in lower reaction temperature, compared with Cu/Zn catalysts; (ii) greater amounts of Pt are needed to load in order to obtain enough reaction rate; (iii) Pt metal is expensive owing to the limited resources, and is used by many other reactors including PEM electrode. So we focused on Ir metal for the design of the new WGS catalysts.

We have already reported that the addition of Re accelerates the WGS reaction over Pt/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> catalysts, and that the effect of Re addition was more remarkable in Pd/TiO<sub>2</sub> system than in Pt/TiO<sub>2</sub> [13]. There we concluded that the formation of Pt–Re and Pd–Re bimetallic clusters might be responsible for the initial acceleration of H<sub>2</sub> formation rate, which was found by the FT-IR analysis during the WGS reaction over these catalysts. FT-IR analysis also revealed that different types of CO adsorption occurred by addition of Re; these are assigned to linearly adsorbed CO next to dissociated OH function, and to bridge-type adsorbed CO peaks. These peaks are specific in Re-added reaction system under actual

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Table 1  
H<sub>2</sub> and CO chemisorption, Ir dispersion and Ir particle size determined by CO adsorbed volume over Ir/TiO<sub>2</sub> and Ir–Re/TiO<sub>2</sub> catalysts

Catalyst	H <sub>2</sub> total volume (mL/g)	CO total volume (mL/g)	Dispersion (%)	Ir particle size (nm)
Ir–Re (1:0)/TiO <sub>2</sub>	0.0763	0.892	77	1.4
Ir–Re (1:1)/TiO <sub>2</sub>	0.116	1.144	98	1.1
Ir–Re (1:3)/TiO <sub>2</sub>	0.188	1.874	161	0.7

reaction conditions where both CO and H<sub>2</sub>O exist. It is already known that WGS reaction over precious metal catalysts proceeds via the formation of the surface-formate anion, and the formation of formates is the rate-determining step of WGS reaction [13]. The role of Re is mainly the dissociation of H<sub>2</sub>O to form OH(a), which then reacts with CO to produce HCOO(a).

In the present study, we have investigated the mechanistic similarity and difference of WGS reaction over TiO<sub>2</sub>-supported Ir compared with Pt and Pd catalysts with and without Re addition, employing kinetic and infrared spectroscopic techniques, and we discuss the activity-determining factors and the role of added Re for these catalysts.

## 2. Experimental

Spherically molded TiO<sub>2</sub> carrier (CS-300S-12, Sakai Chemicals) was used for all catalysts, and the precious metals were loaded by an incipient wetness method; the metal precursors were dissolved in pure water of the same volume as each carrier's water-pick-up volume, which was measured by preliminary water-soaking test. The content of Ir metal was fixed to 1 wt.%, and the contents of other precious metals as reference catalysts (Pt, Pd) were fixed to 2 wt.% for Pt–Re/TiO<sub>2</sub> and 1 wt.% for Pd–Re/TiO<sub>2</sub> catalyst; for each catalyst, various Re contents (from 1 to 10 wt.%) were tested. In the case of bimetallic catalysts such as Ir–Re/TiO<sub>2</sub>, Re was first loaded and then precious metals were loaded after drying under air atmosphere at 393 K for over 12 h. Used precursors for each metal are as follows: (NH<sub>4</sub>)ReO<sub>4</sub> (Kojima Chemicals) for Re, IrCl<sub>4</sub> (Kishida Chemicals) for Ir, H<sub>2</sub>PtCl<sub>6</sub> (Kojima Chemicals) for Pt, Pd(NO<sub>3</sub>)<sub>2</sub> (Mitsuwa Chemicals) for Pd. Metal-loaded catalysts were once calcined under air-flow at 723 K, then cooled and reduced in situ with H<sub>2</sub> at 573 K (LTR) or 723 K (HTR). The elemental analysis using ICP spectroscopy was carried out for all obtained catalysts to confirm the metal contents. The characterizations of catalysts were performed by XRD (Rigaku, RAD-γX), XPS (JEOL, JPS 9010MC), TEM (JEOL, JEM-2010) and CO-chemisorption methods (Beckman Coulter, Omnisorp 100CX).

A closed gas-circulation system was employed for the catalytic reaction. Catalyst activities were evaluated as initial H<sub>2</sub> formation rates in CO–H<sub>2</sub>O reaction (10 Torr each). Gas analysis was carried out with an on line TCD gas chromatograph (Shimadzu GC-17A) to obtain gas compositions for H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub>. On each circulating line, a catalyst disk (20 mm diameter) was installed, and adsorbed species were analyzed through the cell by IR spectroscopy (JASCO, FT/IR-610).

## 3. Results and discussion

### 3.1. Characterization of catalysts

Chemisorption analysis of H<sub>2</sub> and CO was carried out on 1 wt.% Ir/TiO<sub>2</sub> and Ir–Re (1:1 and 1:3)/TiO<sub>2</sub> catalysts after reduction by H<sub>2</sub> (LTR), followed by WGS reaction. Table 1 shows the adsorbed volume of H<sub>2</sub> and CO, and the Ir-dispersion and Ir-particle size calculated from the adsorbed volume of CO. Hydrogen atoms and CO were assumed to be adsorbed on the Ir surface atom in 1:1 ratio, and both species were adsorbed only on the surface of Ir even in the case of Ir–Re/TiO<sub>2</sub> catalyst. Correspondingly, the Ir-dispersion increased and the Ir-particle size was calculated to be smaller. We have already reported the quite opposite results in the cases of Pt–Re/TiO<sub>2</sub> and Pd–Re/TiO<sub>2</sub> catalysts, that is, the Re-addition to the Pt/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> catalyst caused the decrease of metal dispersion and the corresponding increase of metal particle size [13]. We attributed the phenomenon to the surface bimetallic cluster formation of the Pt or Pd metals with Re, which was confirmed by EDA analysis in TEM observation. As for the difference of the adsorbed H<sub>2</sub> volume from that of CO, which was commonly observed in the case of Ir–Re/TiO<sub>2</sub>, Pt–Re/TiO<sub>2</sub> and Pd–Re/TiO<sub>2</sub> catalysts, we consider the reason to be the strong electronic interactions between Ir and TiO<sub>2</sub> support, which weakened the metal–H(a) bonding more than the metal–CO(a) bonding.

Fig. 1 shows the XRD patterns and the assigned peaks of 1 wt.% Ir/TiO<sub>2</sub> and Ir–Re (1:1 and 1:3)/TiO<sub>2</sub> catalysts. Neither Ir nor Re peak was observed in all of these patterns, but only the peaks of TiO<sub>2</sub> lattice were observed. This result leads to the evidence of high dispersion of both Ir and Re metals, and enforces the results of chemisorption (vide supra). Fig. 2(a) and (b) are the TEM images of 1 wt.% Ir/TiO<sub>2</sub> and Ir–Re (1:1)/TiO<sub>2</sub> catalysts, respectively. In both pictures, small particles (less than 1 nm) were slightly confirmed other than the TiO<sub>2</sub> lattice; these were supposed to be highly dispersed Ir metals. Re was not observed, because Re are known to disperse finely after the calcination at high temperature (usually higher than 673 K) [14], which was a quite different result from our previous report about Pt–Re/TiO<sub>2</sub> and Pd–Re/TiO<sub>2</sub> catalysts [13]. In the present study, highly dispersed Re may play a role of anchor for Ir, which leads the high dispersion of Ir metal.

Fig. 3(a)–(c) shows the XPS results after reduction by H<sub>2</sub> at 573 K (LTR, upper), and followed by H<sub>2</sub>O introduced at 373 K (lower) on 1 wt.% Ir/TiO<sub>2</sub> and Ir–Re (1:1 and 1:3)/TiO<sub>2</sub> catalysts, respectively. All peaks were corrected as C 1s = 284.3 eV. In the three figures, the binding energy of Ir was 0.4–0.5 eV higher, which suggests that the Ir metal becomes slightly cationic compared with the ordinary zero-

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