

Role of Re in Pt–Re/TiO₂ catalyst for water gas shift reaction: A mechanistic and kinetic study

K.G. Azzam, I.V. Babich, K. Seshan*, L. Lefferts

*Catalytic Processes and Materials, Faculty of Science and Technology, IMPACT, University of Twente, P.O. Box 217,
7500AE Enschede, The Netherlands*

Received 19 September 2007; received in revised form 16 November 2007; accepted 20 November 2007
Available online 22 November 2007

Abstract

Transient kinetic studies and *in situ* FTIR spectroscopy were used to follow the reaction sequences that occur during water gas shift (WGS) reaction over Pt–Re/TiO₂ catalyst. Results pointed to contributions of an associative formate route with redox regeneration and two classical redox routes involving TiO₂ and ReO_x, respectively. Under WGS reaction condition rhenium is present at least partly as ReO_x providing an additional redox route for WGS reaction in which ReO_x is reduced by CO generating CO₂ and re-oxidized by H₂O forming H₂. The overall reaction rate, based on steady state kinetics, was given by $r_{\text{H}_2} = 0.075e^{31\text{kJ mol}^{-1}/RT} \times p_{\text{H}_2\text{O}} \times p_{\text{H}_2}^{-0.5}(1 - \beta)$, where β is the approach to equilibrium. Results obtained in the study indicated that the reaction between CO adsorbed on Pt and OH groups on titania is the rate-determining step.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Water gas shift (WGS); Platinum; Rhenium; Titania; Kinetics; Reaction mechanism; Reaction orders

1. Introduction

Recently, there is a growing interest in onboard H₂ production for automobiles-fuel cells. Water gas shift (WGS) reaction, $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$, $\Delta H = -41.1 \text{ kJ/mol}$, is the critical step in maximizing H₂ yield from syngas, produced by steam reforming or partial oxidation of hydrocarbons [1].

Current commercial WGS technology involves multiple stages/catalysts, i.e., (i) HTS (Fe₂O₃/Cr₂O₃) and (ii) LTS (Cu/ZnO/Al₂O₃). This is not suitable for mobile fuel cell applications because of its technical complexity, e.g., sensitivity to startup–shutdown cycles [1–4]. There is thus tremendous interest in the development of a single stage WGS conversion. Precious metals, such as Au [5,6], Pd [7,8] or Pt [4,9–12] on different oxide supports, e.g., CeO₂ [4,6,9,11,12], ZrO₂ [4,10], TiO₂ [4,8], Ce_xZr_{1-x}O₂ [4,13], Ti_xCe_{1-x}O₂ [4] have been explored and reported to be effective for WGS. It is commonly agreed [4,12–16] that these catalysts are bi-functional wherein noble metal sorbs/activates CO and the oxide supports activate H₂O. Based on DRIFT measurements

and SSITKA data, supporting evidence was obtained for the spillover mechanism of OH/H towards the noble metal and for the role of noble metal in chemisorption and activation of CO. We have shown earlier [4] that the oxide support strongly influences the catalyst performance in terms of activity and stability. For catalysts with the similar Pt loading/dispersion activity changes more than five times for different supports used. Among the catalysts tested in our study [4], Pt/TiO₂ showed the best intrinsic activity (TOF, s⁻¹), however, it deactivated with time on stream. Pt sintering was the cause of deactivation [4]. Deactivation could be overcome by adding Re to the catalyst [4]. The developed Pt–Re/TiO₂ catalyst showed excellent activity, selectivity to H₂ and stability for WGS [4].

WGS reaction is reported to occur mainly through two reaction routes, i.e., a redox [15,17,18] and an associative formate mechanism [16,19–22]. The redox mechanism involves successive reduction (by CO) and oxidation (by H₂O) of the support, while the associative mechanism involves reaction through an adsorbed surface intermediate (formate species). We have reported [23], based on transient kinetics and *in situ* FTIR studies, that WGS reaction mechanism is complex and depends strongly on the nature of the oxide supports and experimental conditions. An associative formate route with a redox regeneration of the oxide support was suggested as an

* Corresponding author. Fax: +31 53 489 4683.

E-mail address: k.seshan@utwente.nl (K. Seshan).

additional possibility. The difference between this and the conventional “associative formate route” is that the conversion of surface formate to H_2 and CO_2 occurs using oxygen from titania in the former while it is from water in the latter. In the case of Pt/TiO₂ (Fig. 1), we found that WGS reaction follows both (i) a redox and (ii) an associative formate with redox regeneration routes [23].

It is generally accepted that addition of Re to Pt/TiO₂ causes significant improvement in the catalytic activity [4,8,10,24,25]. However, there is still debate about the reason for the higher activity of Pt–Re/TiO₂ compared to Pt/TiO₂ despite the efforts by Iida and Igrashi [10,24] and Sato et al. [8,25]. The objective of this study is to establish the reaction sequences that occur in presence of Re and to understand the role of Re in Pt–Re/TiO₂ for WGS reaction.

2. Experimental

2.1. Catalyst preparation

Titania (P25, Degussa) supported Pt and Re catalysts (0.5 wt% Pt/TiO₂, 0.5 wt% Re/TiO₂, 0.5 wt% Pt–0.5 wt% Re/TiO₂ and 0.3 wt% Pt–0.3 wt% Re/TiO₂) were prepared by wet impregnation, details of which are described elsewhere [4]. 5 wt% Pt/carbon (Activated Carbon, Norrit, ROX 0.8, 1100 m² g⁻¹) catalyst was prepared by wet impregnation of the carbon with aqueous solution of H₂PtCl₆ (Aldrich). The bimetallic (5 wt% of each) Pt–Re/C was prepared by sequential impregnation without intermediate drying or calcination. Carbon was first contacted with the required concentration of NH₄ReO₄ (Aldrich) in water for 1 h with continuous stirring. Solution of H₂PtCl₆ was then added and allowed to equilibrate for 1 h. Both catalysts (Pt/C and Pt–Re/C) were then dried at

75 °C for 2 h under vacuum in a rotary evaporator. Subsequently, the catalysts were reduced in H₂ at 300 °C (10% H₂/Ar, heating rate 10 °C min⁻¹) for 4 h. For all of the experiments described below, the gases (He, H₂, CO, and CO₂) used were of >99.9% purity.

2.2. Characterization

Surface areas were measured with N₂ physisorption using a Micromeritics ASAP 2400 device and applying the BET method. Pt loading was determined using a Philips PW 1480 X-ray fluorescence spectrometer.

FTIR spectra were recorded on self-supported catalyst pellets (about 10 mg of the catalyst) under flow conditions (5% CO/He, 10% H₂O/He and (5% CO + 10% H₂O)/He) at 300 °C using a Bruker Vector 22 with MCT detector. Pulse experiments were mimicked by fast switching between He and a mixture of He containing CO or H₂O. The catalyst pre-treatment was similar to catalytic test experiments. Spectra are presented in absorbance units. The empty IR cell was used as a background spectrum.

Pt dispersion was measured with CO chemisorption at room temperature using a Micromeritics Chemisorb 2750. The amount of sample used for each measurement was ~250 mg. Prior to measuring the CO uptake, the samples were reduced in pure H₂ (99.9%) from room temperature to 300 °C at a rate of 10 °C/min, flushed with He at 425 °C for 1 h and then cooled to room temperature (25 °C) in He. The CO uptake measurements were conducted at room temperature by injecting a series of pulses containing 1 mL of CO into a He stream flowing over the sample at a rate of 25 mL/min and measuring the amount of CO adsorbed per pulse. Our IR results on Pt–Re/TiO₂ showed, in agreement with finding of Peick et al. [26], that at room temperature, CO was only adsorbed on Pt.

2.3. Pulse experiments

Pulse transient experiments were performed at 300 °C at atmospheric pressure using a fixed-bed reactor, details of which are described elsewhere [4,22]. The catalyst (about 50 mg) was first reduced at 300 °C in 10 vol% H₂/He, 30 mL/min flow for 1 h. After this it was heated at 330 °C in He (30 mL/min) for 30 min. After cooling down to 300 °C the catalyst was contacted with fixed amounts of reactant gases using He as a carrier gas. Amount of CO in each pulse was 3.9 μmol. H₂O (1.0 μL) was injected manually directly into the reactor using a microsyringe. Pulses were repeated until the responses for reactants and products no longer changed. To determine the products formed, the outlet of the reactor was directly connected to a Porapak column (5 m, 100 °C) and a thermal conductivity detector (TCD). Downstream to the TCD detector, gases were analyzed by an online mass spectrometer (Balzers QMS 200 F). Quantitative determination of all gaseous products, except of H₂ and H₂O, was obtained from TCD data with accuracy not below ±0.1 μmoles g_{cat}⁻¹. H₂ was detected by MS; the data for H₂ are semiquantitative and comparison in H₂ formation between catalysts is not applicable.

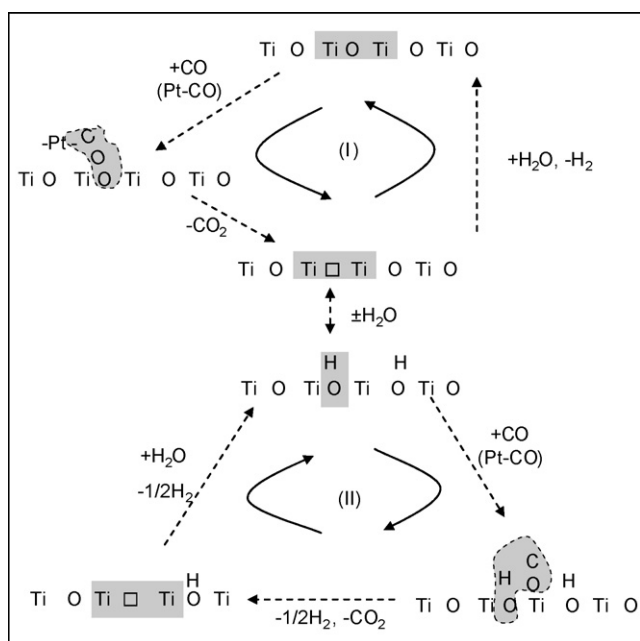


Fig. 1. WGS reaction pathways over Pt/TiO₂ catalyst as proposed in [22]: (I) redox cycle and (II) formate with redox regeneration.

Download English Version:

<https://daneshyari.com/en/article/48360>

Download Persian Version:

<https://daneshyari.com/article/48360>

[Daneshyari.com](https://daneshyari.com)