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Short Communication

Power-law type rate expression for WGS reaction over Au–Re/CeO_2 catalyst under realistic fuel processor conditions

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ABSTRACT

The kinetic behavior of 1Au–0.5Re/CeO_2 catalyst was investigated at 280–325 °C as a function of temperature and partial pressures of reactants and products of the forward WGS reaction under realistic feed conditions. Parameters estimated by non-linear regression analysis were found to predict the overall CO conversion rate within a 10% error margin.

1. Introduction

Fuel cells (FC) are electrochemical devices that use H_2 or H_2-rich fuels together with O_2 to produce electricity. Since a well-established hydrogen infrastructure is not present, present efforts are focusing on extracting H_2 from fossil fuels (reforming) at the point of use by employing serial chemical reactions in a fuel processor (FP). Polymer electrolyte membrane FCs (PEMFC) are seen as the most promising FC type for small power generators [1]; however, poisoning its anode catalyst by trace amounts of CO constitutes a main barrier to commercialization of this type of FC since reforming reactions produce considerable amounts of CO. Water–gas shift (WGS) reaction, $CO + H_2O = H_2 + CO_2$, is an equilibrium-controlled and mildly exothermic reaction and has a primary goal of maximizing H_2 while minimizing CO. This reaction is a well-established technology at industrial scale which typically combine a high-temperature shift (HTS) stage (300–400 °C) and a low-temperature shift (LTS) stage (200–260 °C) to take advantage of the fast reaction kinetics at higher temperatures and the shift of the equilibrium to lower CO concentration at lower temperatures. On the other hand; design and development of efficient WGS catalysts for FP-PEMFC applications, which require *non-pyrophoric* catalysts being robust under transient operations, is still a challenge.

Precious metal-based WGS catalysts have been seen as leading candidate WGS catalysts in FC applications and have been extensively studied [2–4]. Pt was found to be very active in several studies when compared to other precious metals such as Rh, Ru, Pd, Ir and Au [4,5]. The promotion effect of Re addition to Pt catalyst was also pointed out by several other studies [6,7] possibly due to a synergistic effect between Pt and Re. Another widely studied precious metal-based system for WGS reaction is Au supported on reducible oxides. In 1997, the activity of Au/TiO_2 was found to be far better than that of commercial LTS catalyst [8]. In 2001, the activity of Au/CeO_2 prepared by different methods was published [9]. In 2005, Sakurai et al. [10] compared the activity of Au/CeO_2 catalysts with Pt/TiO_2, and found that Au/CeO_2 catalyst was able to convert CO up to equilibrium limits without methane formation. Recently; Çağlayan has developed, characterized and studied Au–Re catalysts supported over CeO_2. Performance tests clearly showed that Re addition affected the WGS activity of Au/CeO_2 catalysts strongly such that CO conversion levels were close to equilibrium levels for ideal feed conditions. The results indicated that novel Au–Re/CeO_2 catalysts were highly active especially at high H_2O/CO ratios resulting from the presence of catalytically active and steam tolerant sites formed on the bimetallic catalysts for both ideal [11] and real feed conditions [12]. Under real feed conditions, additional H_2 production beside CO conversion was obtained for 1Au–0.5Re/CeO_2 catalyst with high H_2O/CO ratios in the feed.

Kinetic expressions are essential in reactor design. A number of WGS kinetic studies are present in the literature over different catalysts. A recent review published by Smith et al. [13] summarizes various kinetic expressions available in the open literature. Basically the kinetic expressions can be classified as the microkinetic approach and the empirical method. The microkinetic method provides accurate pathway and prediction of the reaction, but is computationally intensive. Alternatively, the empirical models are based on the experimental results and are typically expressed in power-law type rate expressions and provide an easy and computationally lighter way to

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predict the rate of reaction [14]. Most of the design works are known to use the empirical models [13]. The power-law type expression for WGS reaction is generally of the form:

$$-r_{CO} = \left[k_0 \exp\left(\frac{-E_A}{RT}\right)\right] P_{CO}^{a} P_{H_2O}^{b} P_{CO_2}^{c} P_{H_2}^{d} (1-\beta) \quad (1)$$

where, r_{CO} = reaction rate (mol gcat^{-1} s^{-1}); a, b, c, d = reaction order of CO, H_2O, CO_2, H_2 respectively; k_0 = pre-exponential factor; E_A = activation energy (kJ mol^{-1}); R = universal gas constant (kJ mol^{-1} K^{-1}); T = reaction temperature (K). β is defined as

$$\beta = \frac{1}{K_{eq}} \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}. \quad (2)$$

In FPs, the gas stream leaving the reforming reactor typically contains up to 8% CO on a dry basis; hence, a two-stage WGS converter with HTS and LTS sections may be needed to reduce the CO content first to 3–4% and then to 0.5–1%, respectively [15]. This situation inevitably increases the volume requirement of the FP as the WGS reactor volume constitutes for about 50% of the total volume [16]. Previously studied Pt–Ni catalyst system was able to produce hydrogen with 100% conversion level of propane in oxidative steam reforming (OSR) reaction at 400 °C, a lower temperature than typical reforming reactions [17,18]. Thermodynamically, CO production rates are suppressed at low reforming temperatures. The low CO production obtained over Pt–Ni catalysts eliminates the need for two successive shift reactors and brings about one feasible solution to high volume requirement of FP by merging the two steps of the WGS reaction process [19] resulting in a unique medium temperature WGS stage.

Following the confirmation of the catalytically active and steam tolerant site formation upon Re addition to Au/CeO_2 catalyst [11], our group has started to study the Au–Re system in a multidirectional way. The currently ongoing studies by our group aim shed a light on the enhancement of water activation by Au–Re bimetallic system in WGS reaction both experimentally through the use of FTIR-DRIFT-MS and theoretically through quantum mechanical studies on Au–Re surface alloys. Current study summarizes the results of the studies aiming to determine the reaction orders and activation energy of WGS reaction over Au–Re/CeO_2. Kinetic studies conducted for realistic reformate streams including not only the reactants but also the products of forward WGS reaction are not as common as studies performed with a mixture of pure CO and steam. For this reason, experiments were conducted at conditions close to the ones likely to be encountered in a FP.

2. Experimental

Ceria support was prepared by homogenous precipitation of cerium nitrate using Na_2CO_3. 1%Au–0.5%Re/CeO_2 (weight %) catalyst was prepared by Re impregnation on to ceria support followed by deposition precipitation of Au. The details of the preparation procedure and catalyst characterization have been reported elsewhere [11].

The kinetic tests were carried out in 4 mm ID tubular differential reactors, and catalyst particles were pretreated in situ by reduction under 5% H_2 flow at 200 °C. The catalyst bed was fixed in stainless steel (SS) reactor by silane treated glasswool and blank tests confirmed that SS reactor and the silane treated glasswool were inert under the reaction conditions. The height of the catalyst bed was ca. 0.6 cm. The temperature of the catalyst bed was controlled (±0.1 °C) via a programmable temperature controller (Eurotherm 3216P). Experiments were performed under differential conditions at atmospheric pressure where reactants and products were mixed with balance N_2 to keep a constant total flow rate (100 ml min^{-1}) at 300 °C. The tests for activation energy calculations were also conducted at 280 and 325 °C. With the intention of keeping conversions at low values, small amounts of catalyst (10 or 15 mg) were diluted with δ-Al_2O_3 (45–60 mesh size), which was proven to be inert by blank tests, were put into the reactor such that the total bed weighed 150 mg. The Al_2O_3 particle sizes range were chosen to minimize mass transfer limitations based on a separate preliminary experiment [20]. In order to eliminate axial dispersion, the $D_{tube}/D_{particle} > 10$ and $L_{bed}/D_{particle} > 50$ criteria were also satisfied [21]. Further details of the experiment system have been reported elsewhere [11].

Table 1
Feed stream compositions and corresponding initial rates of different experimental sets.

Experiment no	Percentage in feed stream				Reaction rate (μmol g^{-1} s^{-1})	R^2	$(1-\beta)$
	CO	H_2O	CO_2	H_2			
1a–1b	10	35	10	20	99.12	0.9942	0.9853
2a–2b	7.5	35	10	20	73.52	0.9641	0.9804
3a–3b	5	35	10	20	60.41	0.8992	0.9705
4a–4b	10	32	10	20	88.17	0.9969	0.9839
5a–5b	10	29	10	20	66.42	0.9932	0.9822
6a–6b	10	38	10	20	119.9	0.9500	0.9864
7a–7b	10	35	12	20	91.50	0.9139	0.9823
8a–8b	10	35	14	20	89.18	0.9953	0.9794
9a–9b	10	35	8	20	107.4	0.9220	0.9882
10a–10b	10	35	10	24	91.04	0.9990	0.9823
11a–11b	10	35	10	22	92.70	1.0000	0.9838
12a–12b	10	35	10	16	115.7	0.8847	0.9882

A base experiment was selected prior to the design of the experimental sets. Then, the kinetic tests have been performed at least for 3 different partial pressures of each species for two different W/F values. Reaction orders were evaluated (Eq. 1) using reaction rates calculated from conversion versus residence time data (Eq. 3). The data were fitted to a linear equation (validated by R^2 values given in Table 1) indicating that the experiments were performed in the kinetically controlled region where no mass and heat transfer limitations were present. The β values were usually of the order of 0.01–0.03 indicating that the reaction was carried out far from equilibrium.

$$-r_{CO} = \frac{dx_{CO}}{d(W_{cat}/F_{CO})}. \quad (3)$$

3. Results and discussion

Table 1 summarizes reactant and product concentrations in the feed stream of WGS reaction. The concentrations, given in mole percent, can be converted into partial pressures very easily since the total pressure was ca. 1 atm. 12-pairs of experiments were performed with 10 and 15 mg catalysts each (denoted as Run a, Run b; respectively). The reaction rates were calculated from slopes of the conversion versus

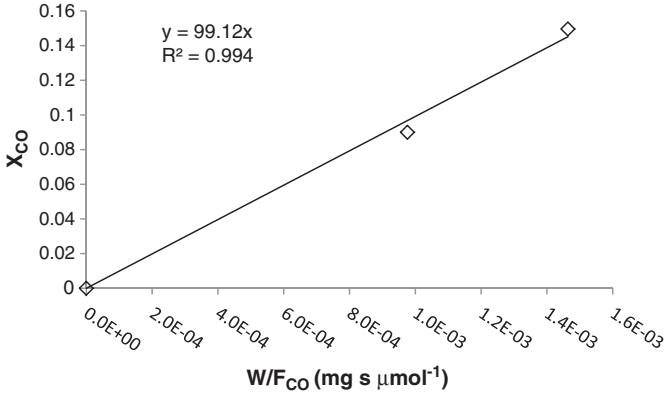

Fig. 1. CO conversion levels for different residence times at Run1a–1b conditions.