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Preferential CO oxidation on Ru/Al$_2$O$_3$ catalyst: An investigation by considering the simultaneously involved methanation

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Abstract

The CO removal with preferential CO oxidation (PROX) over an industrial 0.5% Ru/Al$_2$O$_3$ catalyst from simulated reformates was examined and evaluated through considering its simultaneously involved oxidation and methanation reactions. It was found that the CO removal was fully due to the preferential oxidation of CO until 383 K. Over this temperature, the simultaneous CO methanation was started to make a contribution, which compensated for the decrease in the removal due to the decreased selectivity of PROX at higher temperatures. This consequently kept the effluent CO content as well as the overall selectivity estimated as the ratio of the removed CO amount over the sum of the consumed O$_2$ and formed CH$_4$ amounts from apparently increasing with raising reaction temperature from 383 to 443 K when the CO$_2$ methanation was yet not fully started. At these temperatures the tested catalyst enabled the initial CO content of up to 1.0 vol.% to be removed to several tens of ppm at an overall selectivity of about 0.4 from simulated reformates containing 70 vol.% H$_2$, 30 vol.% CO$_2$ and with steam of up to 0.45 (volume) of dry gas. Varying space velocity in less than 9000 h^{-1} did not much change the stated overall selectivity. From the viewpoint of CO removal the article thus concluded that the methanation activity of the tested Ru/Al$_2$O$_3$ greatly extended its working temperatures for PROX, demonstrating actually a feasible way to formulate PROX catalysts that enable broad windows of suitable working temperatures.
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Keywords: Selective CO oxidation (PROX); Methanation; Polymer electrolyte fuel cell (PEFC); Hydrogen purification; Ru catalyst

1. Introduction

Running the polymer electrolyte fuel cell (PEFC) on reformates of various hydrocarbon fuels requires a gas cleanup facility to remove CO in the hydrogen-rich reformate to several tens of ppm (i.e. 10s ppm), preferably to less than 10 ppm [1–3]. In theory, there are several physio-chemical methods, which can be employed for the facility to remove CO or to separate H$_2$ from the other gas components (e.g., CO$_2$, CO, etc.). These include the pressure swing adsorption (PSA [4]), Pd-membrane diffusion [5–7], CO methanation (both non-competitive [8] and selective [6–8]), electrolytic CO oxidation [9] and preferential CO oxidation [4–7,10]. As for the

use in PEFC systems, the suitable and presently technique-possible method may be only the preferential CO oxidation (PROX) [3,5,11], resulting in the extensive studies in last decade on it in both catalyst development [5,12] and reactor design [7,13,14]. The early report about PROX can date back to the 1960s [15]. Then, Oh and Sinkevitch [16] evaluated the catalytic suitability of a variety of alumina-supported metallic materials (Pt, Pd, Rh, Ru, Co/Cu, Ni/Co/Fe, Ag, Cr, Fe and Mn). Succeeding that work, many studies were carried out to formulate high-efficient and high-selective catalysts for PROX with different noble (including Au and Ag) and base metals [5,12]. In practices, however, the common catalyst formulations are still based on Pt-group elements, for their high reliability in applying to various other catalytic reactions [4–7,12–14]. The favorite use of the Pt-family catalysts for PROX is also due to the reaction temperatures of these cata-

lysts for PROX, which are generally from 373 to 473 K and just fit in with the working temperatures of the upstream WGS reactor (∼473 K) and downstream PEFC stack (∼253 K).

Of the five elements in Pt-group metals, the catalysts formulated with Pt (particularly Pt/Al_2O_3) have been most extensively tested [4,16–20]. The CO conversion over the catalysts, however, is highly sensitive to reaction temperature so that there is usually a narrow range (e.g., <20 K) of suitable temperatures for operation [14,17–19]. Changing formulations of the catalysts may widen their working temperature windows, but the available examinations are limited to laboratory scales [21,22]. On the other hand, the Ru-based catalysts, especially Ru/Al_2O_3, are also commonly available, while they have been shown to be more efficient for oxidizing CO than the other catalysts based on Pt, Pd, Rh and Co (under normal pressure conditions [23]). In fact, Ru/Al_2O_3 was already demonstrated to enable the better CO removal performance than Pt/Al_2O_3 in a few works [16,24–27]. This may be why the Ru-based catalysts, including Pt-Ru alloy catalysts, are widely used in the presently existing practical PROX reactors and processes [13,14,25,28,29].

However, the public information about the PROX performance of Ru catalysts is very limit, compared to the prolific reports about Pt catalysts. An early study of Brown and Green [15] on an industrial 0.5% Ru/Al_2O_3 showed that the required O_2-to-CO atomic ratio (O/CO ratio) increases with increasing the initial CO content and it must be higher than 3.5 (v/v) for oxidizing 0.5 vol.% CO down to 10 ppm in a hydrogenous gas containing about 60 vol.% H_2, 20 vol.% CO_2 and 20 vol.% N_2. The suitable temperatures were said to be 395–435 K. With a N_2-base gas containing 0.85 vol.% H_2, 900 ppm CO and 800 ppm O_2, Oh and Sinkevitch [16] realized CO removals of up to 100% at temperatures between 375 and 575 K on a commercial 0.5% Ru/Al_2O_3. Compared to the narrower temperature range of Brown and Green [15], the wider working temperature window in the latter case would be a result of its lower H_2 content in the treated gas. The recently available data about PROX over Ru-based catalysts are limited to a few literature reports [13,14,24–33]. Most of the works dealt with the formulation and characterization of the catalysts prepared for their own specified PROX reactors or fuel processors [13,14,25–29] or just for laboratory tests [30–33]. Hence, the documented results are less systematic and less general, even divergent. While Abdo et al. [30] reported viable PROX-suitable temperatures from 343 to 433 K for their impregnated Ru (0.5–3.0 wt.%) on a porous alumina, Utaka et al. [33] identified a temperature window between 513 and 573 K over their own 2% Ru/Al_2O_3 formulation. Over a 5% Ru/γ-Al_2O_3 reduced in pure H_2 at 423 K, Han et al. [26,27] preferred the working temperatures below 423 K so that the simultaneous CO and CO_2 methanations can be completely avoided. Different O/CO ratios varying from 3.0 (v/v) [14,32] to 6.0 (v/v) [28–30] were also demonstrated to be necessary for oxidizing CO down to lower than 100 ppm in simulated reformates containing 0.5–1.0 vol.% CO. Therefore, we are indeed lacking systematic characteri-

zation of the PROX performance of Ru catalysts, especially of the commercially available Ru catalysts that would be most possibly used for practical PROX reactors.

Moreover, the Ru catalysts are also highly active to CO and CO_2 methanations [34–36]. The aforementioned literatures, however, disregarded this or simply treated it as a minor point. The CO methanation may positively affect the CO abatement with PROX over Ru catalysts [25,37,38], although it is generally treated as an undesired side reaction [24–27,33]. Thus, without considering the simultaneous CH_4 formation with PROX one may never fully understand the causes for the better CO removal performance of Ru catalysts. Recently, Han et al. [26,27] revealed that the methanations of CO and CO_2 with PROX on a 5% Ru/Al_2O_3 in methanol reformate are negligible at temperatures below 423 K, causing their insistence on operating the PROX over the catalyst at temperatures not over 423 K. However, it is questionable if the methanation of CO is truly deadly undesirable for PROX.

The present article tested the PROX over an industrial 0.5% Ru/Al_2O_3 catalyst, under an intention of examining and further evaluating its CO removal performance with consideration of the simultaneously involved oxidation and methanation reactions. Succeeding experimental measurements of both the CO removal and CH_4 formation with PROX over the catalyst, the further evaluation of the acquired CO removal in terms of an overall selectivity and its accompanied H_2 loss clarified how the methanation activity of the catalyst affected the CO removal efficiency and effectiveness (i.e. selectivity). It was shown that the simultaneously involved CO methanation much broadened the catalyst's suitable temperature window for PROX in the view of removing CO, whereas its induced additional H_2 loss was not significant at the suitable temperatures that assured as well the preferential methanation of CO. Consequently, the article concluded that a highly active catalyst for PROX is better to have a high activity for methanation in order to selectively removing CO in a wide temperature window.

2. Experimental

2.1. Catalyst and reactant gases

The adopted 0.5% Ru/Al_2O_3 catalyst was characterized in Table 1, which was from N.E. Chemcat Corporation and had a cylindrical-pellet shape in size of Ø 3.2 mm × 3.5 mm. Its average bulk density and BET surface area were 950 kg m^{-3} and 92.9 m^2 g^{-1}, respectively. The catalyst contained mesopores in sizes of 3.2–38.5 nm, but most pores had diameters around 6.8 nm (by N_2 adsorption/desorption at 77 K in BELSORP28, Bel Japan). The Ru dispersion of the original catalyst determined from CO adsorption was about 60%.

All tested reformates were based on a H_2-to-CO_2 volumetric ratio (dry-base) of about 70/30 (fluctuated in ±1.0) and their CO contents varied from 0.1 to 1.0 vol.%. Pure O_2 was additionally added as the oxidant according to the desired