

Monometallic and Bimetallic Pt- and Ru-Based Catalysts for Selective Oxidation of CO in Excess Hydrogen

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Abstract

Selective oxidation of CO in excess hydrogen and in the presence of CO₂ and H₂O has been studied over monometallic Pt, Ru and bimetallic Pt–Ru supported on porous carbonaceous material catalysts. The catalysts provided CO conversion $\geq 98\%$ and seem to be promising for efficient single-step removal of CO from hydrogen-rich streams containing CO₂ and H₂O.

1. INTRODUCTION

Hydrogen fuelled polymer electrolyte membrane fuel cells (PEMFC) have been recognized as a promising energy source for replacement of internal combustion engines in automobiles and other transportation systems. However, problematic storing of H₂ onboard a vehicle and a lack of hydrogen refueling infrastructure put forward an idea to combine PEMFC with onboard catalytic reformer that converts a common hydrocarbon fuel into hydrogen-rich gas [1–3].

Such reformer approach for PEMFC vehicles is currently based on steam reforming or autothermal reforming of hydrocarbon fuels and water-gas shift reaction processes. The product stream from the reformer typically contains 40–75 % vol. H₂, 20–25 % vol. CO₂, a few % vol. H₂O, N₂ (if air is an oxidant) and 0.5–2 % vol. CO. However, PEMFCs are intolerant to such streams, because CO easily poisons PEMFC anode. Thus, before PEMFC feeding, the content of carbon monoxide in the stream (reformed gas) must be reduced to 10–100 ppm. Selective or preferential oxidation of CO with oxygen (air) is considered now as the

primary choice for the removal of carbon monoxide from hydrogen-rich streams.

Reported catalysts for this reaction are based predominantly on alumina-supported noble metals (Pt, Ru, Rh, Pd) [4–8] and zeolite-supported platinum [7, 9, 10]. It has been shown [4–6, 10] that Pt- and Ru-based catalysts are the most active towards selective oxidation of CO and successfully operate in the temperature range of 150–200 °C. Besides, in ref. [10] mordenite-supported bimetallic Pt–Ru (2 : 1 mass ratio) catalyst has been proposed for selective oxidation of CO. This catalyst composed of bimetallic Pt–Ru particles appeared to be more active than mordenite-supported monometallic Pt and Ru catalysts. However, all these catalysts demonstrate low selectivity of CO oxidation (~30–40 %) and require considerable excess of oxygen in order to provide efficient cleanup of hydrogen-rich stream from CO.

In this work the catalytic properties of Ru, Pt and Pt–Ru supported on Sibunit (a special hydrophobic porous carbonaceous material [11]) towards selective oxidation of CO in excess hydrogen have been studied as a function of temperature and composition of Pt–Ru bimetallic catalysts. The reaction was examined us-

ing a simulated reformed gas (containing H₂, CO, CO₂ and H₂O steam) at atmospheric pressure. The catalytic performance of monometallic Pt and Ru catalysts for selective CO oxidation has been compared to that of bimetallic Pt–Ru catalysts.

2. EXPERIMENTAL

2.1. Catalysts

Monometallic Pt, Ru, and bimetallic Pt–Ru catalysts (hereinafter Pt/C, Ru/C, Pt–Ru/C) were prepared using Sibunit as a support. Sibunit consisted of spherical granules of size ~1–2 mm and had pore volume 0.3 cm³/g and the BET surface area (*S*_{BET}) 300 m²/g.

The Pt/C catalyst was prepared by adsorbing cluster [Pt₃(CO)₆]₅²⁻ on Sibunit from water-acetone solution [12]. The sample obtained was dried at 120 °C in air. The Pt content was 0.5 % mass.

The Ru/C catalyst was prepared using RuOHCl₃ as the metal precursor. Sibunit granules were poured with hot acidified aqueous solutions of RuOHCl₃ and heated under agitation on water bath until complete evaporation of the solvent. The sample obtained was dried at 100 °C in air and then reduced by hydrogen at 400 °C. The Ru content was 0.5 % mass.

XPS studies of Pt/C and Ru/C catalysts proved the presence of metallic Pt and Ru on Sibunit surface. According to TEM, the catalysts contained metal particles of size 20–30 Å.

Bimetallic Pt–Ru/C catalysts were prepared by the following procedure. First, the Pt/C catalysts containing 0.4, 0.3, 0.2 and 0.1 % mass Pt were prepared as described previously. Then the samples obtained were poured with hot acidified aqueous solution of RuOHCl₃, heated under agitation on water bath until complete evaporation of the solvent, dried at 100 °C in air and then reduced by hydrogen at 400 °C. The procedure resulted in Pt–Ru/C catalysts with total content of noble metals equal to 0.5 % mass and the following content of individual metals expressed as, % mass: Pt(0.4)–Ru(0.1); Pt(0.3)–Ru(0.2); Pt(0.2)–Ru(0.3); Pt(0.1)–Ru(0.4)

All prepared catalysts consisted of spherical granules of size 1–2 mm, contained 0.5 %

mass of noble metals and had the same pore volume and *S*_{BET} as the initial Sibunit support.

2.2. Catalytic activity measurements

The reaction of selective oxidation of CO in excess hydrogen was carried out in a fixed-bed continuous-flow quartz reactor (i.d. 8 mm) at temperatures of 25–200 °C under atmospheric pressure. The bed was made of 0.6 g of a catalyst mixed with 2 g of inert quartz powder and fixed by quartz wool. No catalyst pretreatment was applied.

The catalyst activities in the reaction of selective oxidation of CO in excess hydrogen were measured using reaction mixture of composition: 1 % vol. CO + 1.5 % vol. O₂ + 20 % vol. CO₂ + 3 % vol. H₂O + H₂ (balance). The total flow rate of the reaction mixture (WHSV) in all experiments was equal to 12 000 cm³/(g h).

The inlet and outlet gas mixtures were analyzed on-line by two gas chromatographs “Tsvet-530” (Russia) using Molecular Sieves and Porapak columns. Detection limit of CO, CO₂ and CH₄ was ~10⁻⁴ % vol. (or ~1 ppm); detection limit of O₂, H₂O was not worse than 2 · 10⁻³ % vol.

The conversions of CO (*X*_{CO}) and O₂ (*X*_O) as well as the selectivity (*S*_{CO}) of CO oxidation in excess hydrogen were calculated by equations:

$$X_{\text{CO}}, \% = \frac{[\text{CO}]_0 - [\text{CO}]}{[\text{CO}]_0} 100$$

$$X_{\text{O}_2}, \% = \frac{[\text{O}_2]_0 - [\text{O}_2]}{[\text{O}_2]_0} 100$$

$$S_{\text{CO}}, \% = \frac{0.5([\text{CO}]_0 - [\text{CO}])}{[\text{O}_2]_0 - [\text{O}_2]} 100$$

where [CO]₀ and [O₂]₀ are the inlet concentrations, [CO] and [O₂] are the outlet concentrations.

3. RESULTS AND DISCUSSION

3.1. CO oxidation on monometallic Ru/C and Pt/C catalysts

Figure 1 presents the temperature dependencies of CO conversion and CO selectivity at selective CO oxidation in excess hydrogen over 0.5 % mass Pt/C and 0.5 % mass Ru/C. Note

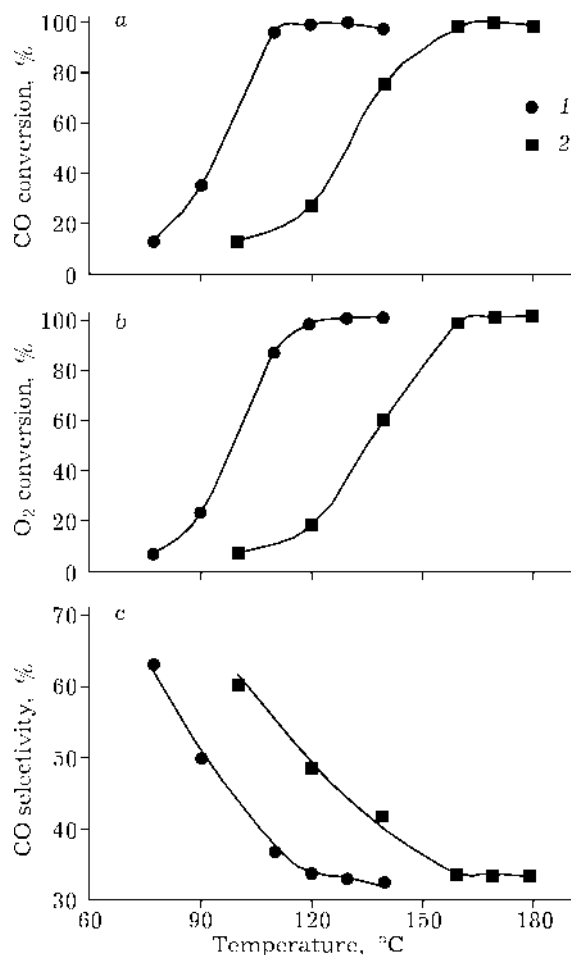


Fig. 1. Effect of temperature on CO conversion (a), O₂ conversion (b) and CO selectivity (c) at selective CO oxidation over 0.5 % mass Ru/C (1) and 0.5 % mass Pt/C (2).

that in contrast to Pt/C, the products of selective CO oxidation over Ru/C contained ≤ 30 ppm of CH₄ (not shown in Fig. 1).

The principal observations with respect to CO removal from hydrogen-rich stream were as follows. For both catalysts, the CO conversion first increased and then slightly decreased with increasing temperature. The O₂ conversion increased with increasing temperature and attained 100 %. Compared to Pt/C, the temperature dependencies of the CO and O₂ conversions for Ru/C demonstrated a 30–40 °C shift towards the lower temperature region. The CO selectivity monotonically decreased from 60–65 % to ~33 % with increasing temperature for both catalysts.

For Pt/C, the maximum CO conversion equal 98.5 % was attained at 170 °C. For Ru/C,

the maximum CO conversion equal 98.3 % was attained at 120 °C. Respective outlet CO concentrations ranged within 150–170 ppm. It should be noted that the outlet CO concentrations could be decreased two–three-fold by means of a 10–20 % increase of the inlet O₂ concentration (*i. e.*, by increasing O₂/CO ratio from 1.5 to 1.65–1.8).

Analysis of the above data suggests a conclusion that, compared to Pt/C, Ru/C is more active for selective oxidation of CO in excess hydrogen. Similar trend has been reported previously for alumina- and mordenite-supported Pt and Ru catalysts [4, 5, 10].

3.2. CO oxidation on bimetallic Pt–Ru/C catalysts

The reaction of selective CO oxidation in excess hydrogen was studied over the following bimetallic catalysts: (0.1 Pt – 0.4 Ru)/C; (0.2 Pt – 0.3 Ru)/C; (0.3 Pt – 0.2 Ru)/C; (0.4 Pt – 0.1 Ru)/C. The maximum CO conversion for these catalysts was equal to ≥ 98 %. For (0.1 Pt – 0.4 Ru)/C and (0.2 Pt – 0.3 Ru)/C, the reaction products contained ~10–20 ppm of CH₄, while in experiments with (0.3 Pt – 0.2 Ru)/C and (0.4 Pt – 0.1 Ru)/C no CH₄ was observed. The temperature dependencies of CO and O₂ conversions, and of CO selectivity at selective CO oxidation over all bimetallic catalysts were similar to each other and to respective dependencies for monometallic Pt and Ru catalysts (see Fig. 1). The results obtained suggest a conclusion that the activity of bimetallic catalysts decreases with decreasing Ru content.

As an example, Fig. 2 demonstrates the temperature dependencies of X_{CO} , X_{O_2} and S_{CO} at selective CO oxidation over (0.2 Pt – 0.3 Ru)/C and (0.4 Pt – 0.1 Ru)/C. It is seen that the CO conversion increased with increasing temperature and attained 98.5 % at 125 °C for (0.2 Pt – 0.3 Ru)/C and 98.3 % at 150 °C for (0.4 Pt – 0.1 Ru)/C. At higher temperatures, the CO conversion slowly decreased for both catalysts. The O₂ conversion increased with increasing temperature and attained 100 %. For both catalysts, the CO selectivity monotonically decreased from 50–55 % to ~33 % with increasing temperature. Compared to (0.4 Pt – 0.1 Ru)/C,

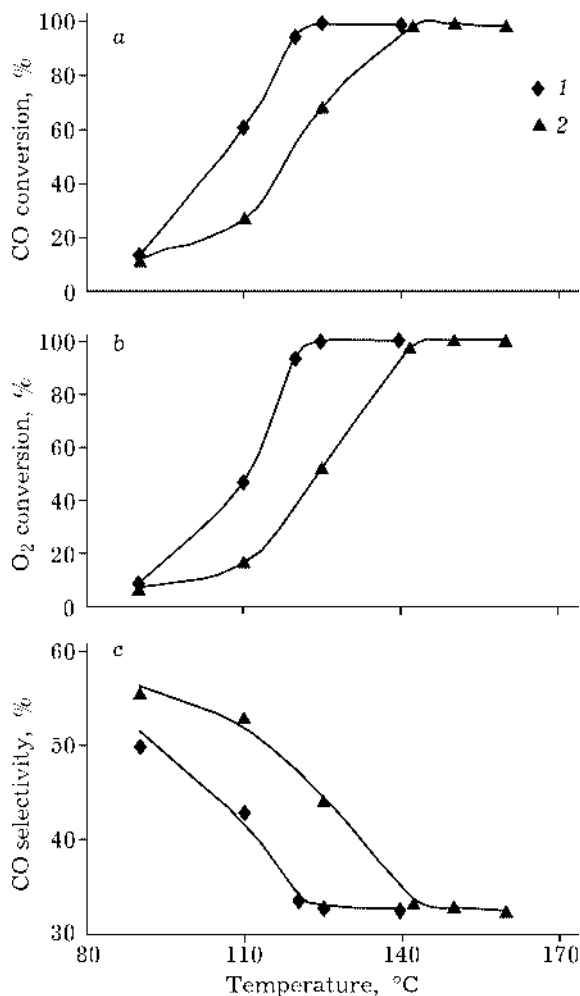


Fig. 2. Effect of temperature on CO conversion (a), O₂ conversion (b) and CO selectivity (c) at selective CO oxidation over (0.3 % mass Ru–0.2 % mass Pt)/C (1) and (0.1 % mass Ru–0.4 % mass Pt)/C (2).

the temperature dependencies of X_{CO} and X_{O_2} for (0.2 Pt – 0.3 Ru)/C demonstrated a 15–20 °C shift towards the lower temperature region. This means that, compared to (0.4 Pt – 0.1 Ru)/C, (0.2 Pt – 0.3 Ru)/C is more active for selective CO oxidation in excess hydrogen.

3.3. Comparison of CO oxidation activity of monometallic and bimetallic catalysts

It has been shown in ref. [10] that mordenite-supported bimetallic Pt–Ru catalysts demonstrated higher activity towards selective oxidation of CO than both monometallic Pt and Ru mordenite-supported catalysts. The authors attributed this fact to the formation of bimetallic Pt–Ru particles (or alloy) in mordenite cages.

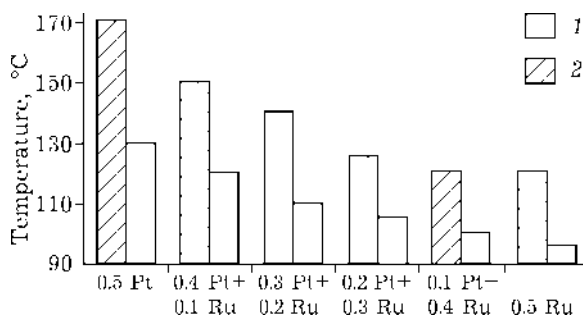


Fig. 3. Temperatures at which CO conversions of 50 (1) and 98 % (2) were attained at selective CO oxidation in hydrogen excess over Pt–Ru/C catalysts.

Figure 3 compares catalytic activities of Pt/C, Ru/C and Pt–Ru/C in the reaction of selective CO oxidation in hydrogen excess. As a measure of the catalyst's activity, we selected the temperatures T_{50} and T_{98} at which CO conversions of 50 % and 98 % were attained. It is seen that both T_{50} and T_{98} monotonically decreased with increasing Ru content in the catalysts. Moreover, the maximum T_{50} and T_{98} were observed for Pt/C catalyst, the minimum – for Ru/C. That is, Pt/C showed the lowest catalytic activity, while Ru/C – the highest activity. Bimetallic Pt–Ru/C catalysts were more active than Pt/C and less active than Ru/C; their activity monotonically increased with increasing Ru content. The most likely explanation for these results is that the used procedure to prepare Pt–Ru/C catalysts (see Section 2.1) led to the formation of separate monometallic Pt and Ru particles. In particular, the formation of monometallic Pt and Ru particles was observed also in the case of Pt–Ru/SiO₂ catalysts when they were prepared by impregnating Pt/SiO₂ with aqueous solution containing [Ru(NH₃)₆]Cl₃ or RuCl₃ [13].

It should be stressed finally problematic comparison of the performance of Pt/C, Ru/C and Pt–Ru/C catalysts towards selective CO oxidation with other noble-metal based catalysts reported in literature owing to various reaction conditions used in different works. Nevertheless, under the used experimental conditions Pt/C, Ru/C and Pt–Ru/C provided CO conversion ≥ 98 % and therefore seem to be promising catalysts for efficient single-step removal of CO from hydrogen-rich streams containing CO₂ and H₂O.

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