Mordenite-Supported Noble Metal Catalysts for Selective Oxidation of Carbon Monoxide in a Reformed Gas

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Selective oxidation of carbon monoxide in high excess of H_2 was examined on noble metal catalysts (Pt, Ru, Pd, Co, and Pt-Ru) supported on mordenite. Pt-Ru/mordenite exhibited fairly high selectivity over a wide flow rate condition even at 150 °C. Thus, it seems to be a promising catalyst for polymer electrolyte fuel cells operated with reformed gas.

Polymer electrolyte fuel cells (PEFCs) are attracting much attention as power sources in electric vehicles and residential power sources. It is desirable to operate the PEFC with reformed gas from liquid fuels or natural gas. However, a conventional Pt anode catalyst operating with reformed gases seriously poisoned by a small amount of carbon monoxide.[1] We showed that the Pt electrocatalyst is poisoned by the presence of only 10 ppm CO,[2] whereas the content of CO in reformates is about 1% in general. There are two essential developments to solve the CO poisoning problem for PEFCs: one is to develop catalysts reducing the CO content in feed streams to a certain level (e.g., 10 ppm) and second is to increase CO tolerance of the anode against the residual 100 ppm-level CO.[3–6] A simple and effective method for the reduction of CO content is a selective oxidation of CO in fuels.[7–11]

$$CO + 1/2 \, O_2 \rightarrow CO_2 \qquad (1)$$
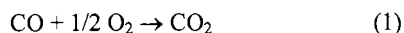
Alumina has been used conventionally as a support for catalysts such as Pt or Au. But these catalysts are not so selective for the oxidation of CO. They require an additional approximately 2% of O_2 for the oxidation of 1% CO in H_2 fuels,[7] although the needed stoichiometric amount of O_2 is only 0.5%. The excess O_2 causes H_2 combustion leading to fuel efficiency loss.

$$H_2 + 1/2 \, O_2 \rightarrow H_2O \qquad (2)$$
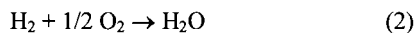
Furthermore, the addition of excess O_2 involves a risk of incident explosion. Therefore, it is necessary to develop more selective catalysts than the conventional ones for PEFCs.

We have proposed Pt catalysts supported on zeolites with different sizes of the molecular cages for the selective oxidation of CO, taking an advantage of the specific condensation property of the cages for CO as well as O_2[12,13] We found that the selectivity is affected by the supporting materials and decreases in the following order: A-type zeolite > mordenite > X-type zeolite > Al_2O_3. Pt supported on mordenite showed the highest conversion from CO to CO_2 among the catalysts examined and had almost similar selectivity to that of A-type zeolite.[13]

The present study attempts to develop further active and selective catalysts for the preferential oxidation of CO by examining various metals (Pt, Ru, Pd, Co, and Pt-Ru) supported on mordenite.

Pt, Ru, Pd, Co, and Pt-Ru (2:1, weight ratio) catalysts were supported on mordenite [$Na_8(Al_8Si_{40}O_{96})\cdot24H_2O$] by using conventional ion-exchange method.[12–14] They are denoted as Pt/M, Ru/M, Pd/M, Co/M, and Pt-Ru/M, respectively. A conventional Pt catalyst supported on Al_2O_3 (Pt/Al_2O_3) was also prepared as a reference catalyst.[14,15] The catalytic oxidation of CO was carried out in a conventional flow reactor. The reaction mixture consisted of 1.0% CO, 0.5% O_2, and H_2 balance. On-line gas chromatograph with TCD detectors was used to measure the catalytic activity.[16] Steady-state conversion at a constant temperature and flow rate was collected after ca. 6 h, and only stable data are reported here. Thus, 100% carbon balance was achieved under all reaction conditions.

XRD patterns of all the zeolite catalysts showed peaks assigned to mordenite but no peak for supported metals. This indicates that the particle size of the metals may be smaller than 1 nm and supported in the mordenite cage. In contrast to this result, the size of Pt particles of Pt/Al_2O_3 was found to be 7 nm.

Table 1 summarizes the results of CO oxidation on various catalysts at 200 and 150 °C. At 200 °C, Pt/M (No. 4, Table 1), Ru/M (No. 2), and Pt-Ru/M (No. 1) catalysts showed a higher conversion and selectivity for the CO oxidation than a conventional Pt/Al_2O_3 catalyst (No. 7). Note that in spite of a low catalyst loading of 0.025 g the Ru/M and Pt-Ru/M catalysts showed a higher CO conversion than Pt/M and Pt/Al_2O_3 with 0.100 g loading; Pt/M with 0.025 g Pt loading (No. 3) showed fairly low CO conversion. Among the various catalysts examined at 200 °C, Ru/M (No. 2) showed the highest CO conversion and selectivity of approximately 100%, i.e., only CO is oxidized selectively with the stoichiometric amount of O_2.

Table 1. The activity and selectivity for CO oxidation on various catalysts.

| No.	Catalyst	CO conv. / %	O_2 conv. / %	O_2(CO) / %
	200 °C			
1	Pt-Ru/M [a]	80.4	100.0	80.4
2	Ru/M [a]	100.0	100.0	100.0
3	Pt/M [a]	16.1	23.3	69.1
4	Pt/M [b]	79.2	91.6	86.5
5	Pd/M [b]	20.8	100.0	20.8
6	Co/M [b]	50.8	80.5	63.1
7	Pt/Al_2O_3 [b]	51.0	100.0	51.0
	150 °C			
8	Pt-Ru/M [a]	89.7	100.0	89.7
9	Ru/M [a]	57.0	58.0	98.7
10	Pt/M [b]	7.0	9.8	71.4

CO 1.0%, O_2 0.5%, H_2 balance, gas flow rate = 50 cm³ min⁻¹.
a: The amount of catalyst was 0.025 g. b: The amount of catalyst was 0.100 g.
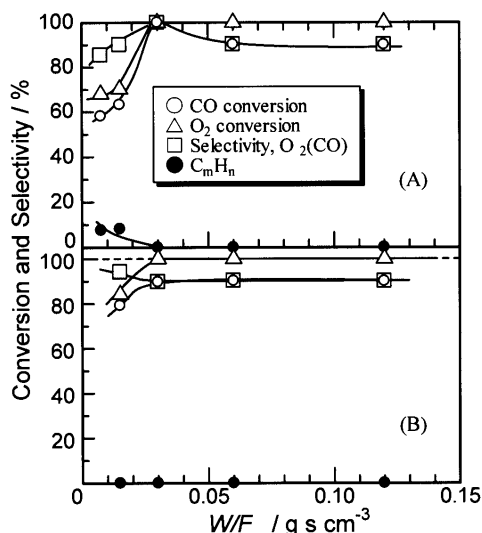
Figure 1. Changes of CO conversion, O_2 conversion, selectivity $O_2(CO)$, and C_mH_n formation on (A) Ru/M at 200 °C and (B) Pt-Ru/M at 150 °C as a function of W/F. The amount of catalyst was 0.025 g. CO 1.0%, O_2 0.5%, H_2 balance.

Figure 1A shows changes of the CO conversion, the O_2 conversion, and the selectivity index $O_2(CO)$ of Ru/M at 200 °C as a function of W/F. W and F are the weight of the catalyst and the total flow rate of the reactant gas, respectively. It is clear that the excellent performances of Ru/M can be obtained only at $W/F = 0.03$ g s cm^{-3}. Using lower W/F (a larger flow rate against the given amount of catalysts), hydrocarbons (C_mH_n) were formed by a hydrogenation reaction of CO.

$$m \; CO + n/2 \; H_2 \rightarrow C_mH_n \qquad (3)$$
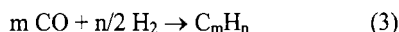
On the other hand, when W/F is increased, the CO conversion decreases. That is probably due to a lack of O_2 for CO oxidation or due to the following reverse-shift reaction, resulting from a depletion of O_2.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (4)$$
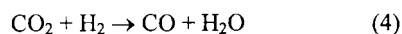
It was also found that CO conversion and O_2 conversion on Ru/M decreased considerably by lowering the reaction temperature to 150 °C (see Table 1). Therefore, there is room for the improvement of Ru/M catalyst performance.

On the other hand, we have found that any side reactions did not occur on Pt/M at 150 to 350 °C, unlike Ru/M.[13] However, as shown in Table 1, both conversions, CO and O_2, are fairly low on Pt/M at 150 °C (No. 10). Then, Ru alloyed with Pt (Pt/Ru = 2, weight ratio) was supported on mordenite, attempting to improve both the conversions and the selectivity.[17] Figure 1B shows the changes of the CO conversion, the O_2 conversion, and the selectivity on Pt-Ru/M at 150 °C. In a wide W/F range, the CO conversion on Pt-Ru/M showed a high value of ca. 90% and was almost constant. Furthermore, unfavorable side reactions were suppressed and $O_2(CO)$ was kept at about 90% over the whole W/F range which was examined.

The excellent catalytic properties of Pt-Ru/M may be explained by the so-called "bi-functional mechanism": CO mol-ecules adsorbed on Pt sites are oxidized by adjacent oxygen atoms adsorbed on Ru sites.[3] If the surface sites are covered preferentially with either CO or oxygen, the CO oxidation can occur and suppress the side reactions.

In conclusion, the Pt-Ru/mordenite is a promising catalyst for the preferential oxidation of CO in reformed gases to an acceptable CO content for PEFCs.

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14 The obtained powders were pelletized, crushed, and then sieved to 100–200 mesh. Before usage, they were heat-treated in a reactor in an O_2 flow at 500 °C for 0.5 h and then in a H_2 flow at 500 °C for 1 h. Metal loadings on the mordenite determined by ICP were 6 wt% for Pt/M, Ru/M, Pd/M, Co/M, and Pt/Al$_2$O$_3$ and (4 wt% Pt + 2 wt% Ru) for Pt-Ru/M, respectively.
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16 The lower limit of CO detection was 20 ppm in this work. The CO conversion was calculated based on the CO_2 formation, and the O_2 conversion based on the O_2 consumption. The selectivity index $O_2(CO)$ is defined as the fraction of oxygen that is used for the oxidation of CO to CO_2, $O_2(CO) = \{0.5 \times [CO_2]/([O_2]_0 - [O_2])\} \times 100\%$, where $[O_2]_0$ is the inlet O_2 concentration and $[O_2]$ is the O_2 concentration after reaction. The CO conversion into hydrocarbon was estimated from the carbon balance.
17 We don't have a direct proof of Pt–Ru alloy formation in the mordenite cage. But we have confirmed that bulk Pt–Ru alloy is formed when heating Pt and Ru reagents on mordenite surface in H_2 at > 300 °C. Our preliminary EXAFS study also suggests a possibility of such an alloy particle formation in the mordenite cage.