

Analyses of Preferential Oxidation of Carbon Monoxide in a Reformed Gas over Pt and Pt-Alloy Catalysts Supported on Zeolites

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It is desirable to operate polymer electrolyte fuel cells (PEFCs) with reformed gas from liquid fuels or natural gas. There are two essential developments to solve the CO poisoning problem for PEFC anode: 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. A simple and effective method for the reduction of CO content is preferential oxidation of CO in fuels.

We have proposed Pt catalysts supported on zeolites with different sizes of the molecular cages, expecting an advantage of the specific adsorption property of the cages for CO as well as O₂.^{1,2} We found that the selectivity is affected by the supporting materials and decreases in the following order: A-type zeolite > mordenite > X-type zeolite > Al₂O₃. Pt supported on mordenite showed the highest conversion from CO to CO₂ and had almost similar selectivity to that of A-type zeolite. Recently, we found that Pt-Ru or Pt-Fe/mordenite exhibited fairly high selectivity even at 150°C.³⁻⁵

In this paper, we will report the preferential CO oxidation properties on Pt, Ru, Pt-Ru, and Pt-Fe/mordenite and the reaction mechanism studied by FTIR, TPD, and quartz crystal microbalance (QCM) methods to find a clue for further active and selective catalysts.

Pt, Ru, Pt-Ru (2:1, weight ratio), and Pt-Fe (2:1, weight ratio) catalysts were supported on mordenite [Na₈(Al₈Si₄₀O₉₆)·24H₂O] (6 wt% metal loading).¹⁻⁵ They are denoted as Pt/M, Ru/M, Pt-Ru/M, and Pt-Fe/M, respectively. XRD patterns of all the catalysts showed peaks assigned to mordenite but no peak for metals. This indicates that the particle size of the metals may be smaller than 1 nm and supported in the mordenite cage.

Table 1 summarizes the results of CO oxidation on various catalysts at 150°C. In spite of a low catalyst loading of 0.025 g, the Pt-Fe/M, Pt-Ru/M, Ru/M catalysts showed a higher CO conversion than Pt/M with 0.100 g loading. Among the various catalysts examined, Pt-Fe/M showed the highest CO conversion and selectivity of approximately 100%, *i.e.*, only CO is oxidized selectively with the stoichiometric amount of O₂.

In order to analyze how such good catalytic properties

Table 1. The activity and selectivity for CO oxidation on various catalysts at 150°C.

Catalyst	CO conv. / %	O ₂ conv. / %	O ₂ (CO) / %
Pt-Fe/M	99.6	100.0	99.6
Pt-Ru/M	89.7	100.0	89.7
Ru/M	57.0	58.0	98.7
Pt/M	7.0	9.8	71.4

CO 1.0%, O₂ 0.5%, H₂ balance, gas flow rate = 50 cm³ min⁻¹. The amount of catalyst was 0.025 g except Pt/M (0.100g). The selectivity index O₂(CO) is defined as O₂(CO) = {0.5×[CO₂]/([O₂]₀ - [O₂])} × 100%, where [O₂]₀ is the inlet O₂ concentration and [O₂] is the O₂ concentration after reaction.

of Pt-Fe/M did appear, FTIR measurements were carried out. Figure 1 shows IR spectra of adsorbed CO on Pt-Fe/M, Pt-Ru/M, and Pt/M under the steady state in (1% CO+ 1% O₂)/H₂ balance. An absorption band at 2080 cm⁻¹ assigned to the linearly bound CO (CO_L) was observed during the CO oxidation reaction on Pt/M at 200°C. The CO_L band was also seen on Pt-Ru/M and Pt-Fe/M in 1% CO (without O₂)/H₂, but it disappeared in (1% CO+ 1% O₂)/H₂, indicating that the adsorbed CO was oxidized rapidly at 200°C on both alloy catalysts.

It was found that such differences were more marked at a low temperature of 30°C. When Pt-Fe/M, Pt-Ru/M, and Pt/M were exposed to 1% CO/H₂ gas, the CO_L band was also observed. The steady-state absorbance for CO_L decreased in the order, Pt > Pt-Ru > Pt-Fe. After purging N₂ gas, the CO_L absorbance was almost unchanged on Pt/M and Pt-Ru/M, whereas it decreased appreciably on Pt-Fe/M by desorption of CO. Surprisingly, even at 30°C, the CO_L band on Pt-Fe/M disappeared by the complete oxidation after exposing it to pure O₂ for 5 min, consisting well with the result of TPD analysis. The CO_L on Pt-Ru/M also disappeared at 30°C after exposing it to O₂ for 10 min, but that on Pt/M hardly occurred, as judged by the very low CO conversion even at 150°C (see Table 1).

We can clearly understand the above results as follows. Because the pure Pt surface is fully covered with strongly adsorbed CO molecules at low temperature (< 150°C), there are no free sites for dissociative adsorption of oxygen, *i.e.*, oxygen is the limiting reactant for the oxidation of CO. Excellent catalytic properties of Pt-Fe/M and Pt-Ru/M can be well explained by so-called "bi-functional mechanism, *i.e.*, the different surface sites are covered preferentially with either CO or oxygen, the CO oxidation can occur rapidly among them. Particularly, weakly adsorbed CO on Pt-Fe can be oxidized easily.

References

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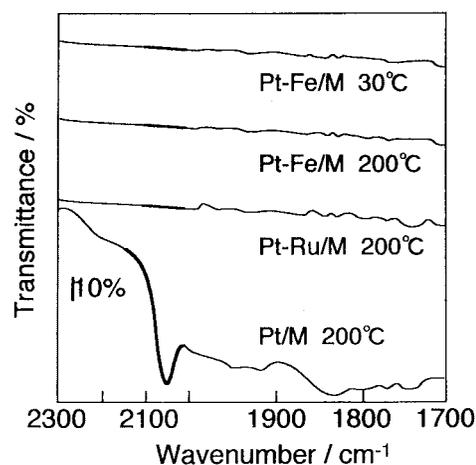


Figure 1. IR spectra of adsorbed CO on Pt-Fe/M, Pt-Ru/M, and Pt/M in (1% CO+ 1% O₂)/H₂.