Preferential CO oxidation promoted by the presence of H_2 over K–Pt/Al_2O_3

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Received (in Cambridge, UK) 28th October 2004, Accepted 5th January 2005
First published as an Advance Article on the web 26th January 2005
DOI: 10.1039/b416565a

In preferential CO oxidation in H_2-rich gas, K–Pt/Al_2O_3 (K/Pt = 10) was very effective in decreasing CO concentration below 10 ppm in the 375–410 K range, and the turnover frequency of the K–Pt/Al_2O_3 was 20 times as high as that of Pt/Al_2O_3 at 353 K; furthermore, the activity of CO oxidation was promoted drastically by the presence of H_2.

Polymer electrolyte fuel cells (PEFC) can generate electricity without polluting the environment, however, they demand high-purity hydrogen as fuel. Especially when hydrogen is produced by reforming of methanol and hydrocarbons, the gas always contains some amount of CO, which poisons for the fuel cell. Therefore, the hydrogen production system must be equipped with a CO removal system. Although the CO concentration can be decreased *via* water gas shift reaction, the stream produced usually contains about ~1–2 vol% CO. The performance of PEFC with the conventional Pt catalyst seriously decreased with a poisoning of only 10 ppm of CO.[1,2] Regarding the CO poisoning, it has been reported that the PtRu alloy has higher resistance (100 ppm) than Pt catalyst.[3] However, in any case, stringent removal of CO is necessary, and one promising method is preferential oxidation of CO in H_2-rich gas with air. Supported noble metals, such as Pt,[4–8] Pd, Rh[9,10] have been reported. We report that a K-promoted Pt/Al_2O_3 catalyst is highly efficient for CO removal down to 10 ppm level by preferential CO oxidation in H_2-rich gas compared to Pt/Al_2O_3. It is also mentioned that the presence of H_2 promoted drastically CO oxidation over K–Pt/Al_2O_3.

Al_2O_3 (JRC-ALO-4 from Japan Reference Catalyst (JRC); BET surface area, 170 $m^2\ g^{-1}$) was used as a support material; it was calcined at 873 K for 3 h under atmosphere. Pt/Al_2O_3 catalyst was prepared by impregnation of Al_2O_3 support with an aqueous solution of $Pt(NO_2)_2(NH_3)_2$. The sample was dried at 383 K for 12 h, and then calcined in air at 773 K for 3 h. The loading amount of Pt was 2 wt.%. Potassium-promoted Pt/Al_2O_3 catalyst (denoted as K–Pt/Al_2O_3) was prepared by impregnation with an aqueous solution of $Pt(NO_2)_2(NH_3)_2$, followed by drying at 383 K for 12 h, and then impregnation of an aqueous solution of KNO_3. After these procedures, the calcination was carried out in air at 773 K for 3 h. Potassium loading is denoted as the molar ratio of K/Pt in parentheses. These catalysts were reduced with hydrogen at 773 K for 1 h in a catalyst bed reactor just before the activity test.

CO oxidation in H_2-rich gas was carried out in a fixed-bed flow reaction system at atmospheric pressure using 100 mg of the catalyst at the total flow rate of 100 $cm^3\ min^{-1}$ (STP) (GHSV = 30 000 h^{-1}). The feed stream contained 0.2 vol% CO, 0.2 vol% O_2 and 75 vol% H_2 (He balanced). The effluent gas was analyzed using an on-line gas chromatograph (GC) system equipped with a TCD detector. In addition, the concentration at ppm level of CO in the effluent gas was determined using FID-GC equipped with a methanator. The activity was evaluated on the basis of CO and O_2 conversions, which can be calculated on the basis of CO and O_2 concentrations in the reactant gas and the effluent gas. The selectivity of CO oxidation is defined as the ratio of O_2 consumption for the CO oxidation to total O_2 consumption. In addition, we also measured the catalyst bed temperature directly using a thermocouple. No temperature increase was observed at all during the reaction. Therefore under these reaction conditions, the thermal effect, which is due to exothermic reaction of CO and H_2 oxidation, can be neglected. The catalysts were characterized by H_2 and CO adsorption measurements and by transmission electron microscope observation. The amounts of irreversible adsorption of H_2 (H/Pt) and CO (CO/Pt) were measured at room temperature in a vacuum system (sample weight: 0.15 g, dead volume: 65 cm^3) by the volumetric method.[10]

Fig. 1 shows the reaction temperature dependence of the performance of CO oxidation in H_2-rich gas over K–Pt/Al_2O_3 catalysts. The CO conversion over unpromoted Pt/Al_2O_3 catalyst was much lower than those over K–Pt/Al_2O_3 catalysts. The selectivity of CO oxidation was in the range of 10–30% over Pt/Al_2O_3, and this indicates that the oxidation of CO is less preferential than H_2 oxidation. On the other hand, the addition of K to Pt/Al_2O_3 enhanced the CO conversion and selectivity of CO oxidation dramatically. The additive effect of potassium was greatly dependent on the amount of additive, and the optimum amount was K/Pt = 10. In addition, the CO concentration in the effluent gas over K–Pt/Al_2O_3 (K/Pt = 10) is also shown in Fig. 1(a). It is interesting that CO concentration was maintained below 10 ppm in the 375 K–410 K range. Especially from the practical view of hydrogen production for PEFC, this result can be important. In our experiments, the feeding ratio of CO to O_2 was 1/1, and this corresponds to the twice of the stoichiometric O_2 amount. This is related to about 50% of CO oxidation selectivity. The stoichiometric condition ($CO/O_2 = 2$) can be ideal in terms that the loss of H_2 by oxidation and higher efficiency. However, the CO conversion and the selectivity of CO oxidation over K–Pt/Al_2O_3 (K/Pt = 10) under the stoichiometric feeding conditions (0.2 vol% CO, 0.1 vol% O_2 and 75 vol% H_2 balanced with He) were 58.0% and 57.6% at 388 K, and the CO concentration in the effluent gas is not so low as that shown in Fig. 1. This result indicates that our feeding ratio ($CO/O_2 = 1$) is necessary to decrease the CO concentration in the effluent gas to the suitable level.

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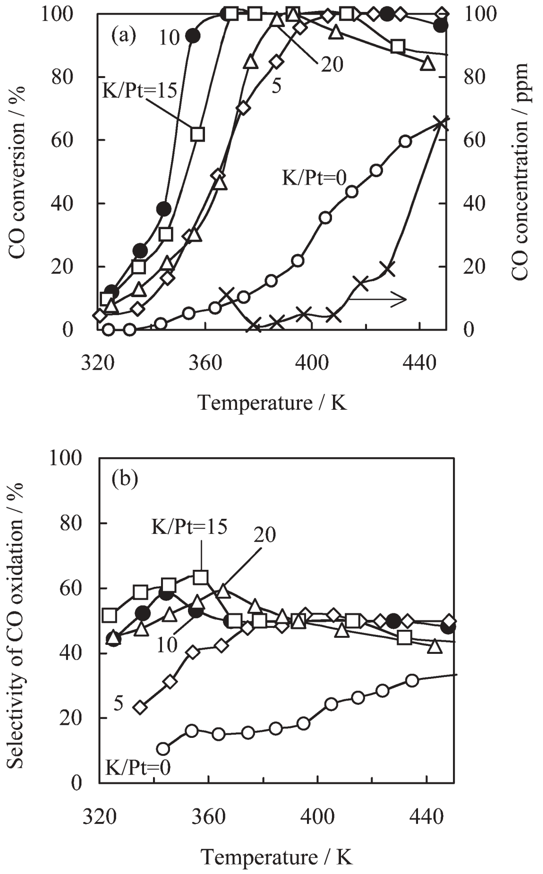

Fig. 1 Reaction temperature dependence of (a) CO conversion and (b) selectivity of CO oxidation in CO oxidation in H_2-rich gas over K–Pt/Al_2O_3 catalysts (K/Pt = 0, 5, 10, 15 and 20). CO concentration in the effluent gas over K–Pt/Al_2O_3 (K/Pt = 10) (×). Reaction conditions: 0.2 vol% CO, 0.2 vol% O_2 and 75 vol% H_2 (He balance).

Pt dispersions estimated from the adsorption amounts of H_2 and CO are listed in Table 1. In the case of Pt/Al_2O_3, the dispersion can be determined to be about 0.5, which corresponds to the particle size 2 nm based on the previous report.[11] The adsorption amounts of H_2 and CO decreased with increasing the additive amount of potassium. On the other hand, we also measured XRD patterns of reduced K–Pt/Al_2O_3 catalysts, and the peak assigned to Pt metal was not observed at all on all the K–Pt/Al_2O_3 catalysts. This indicates that the size of Pt metal particles is below 3 nm on all the catalysts. Average particle size of Pt over K–Pt/Al_2O_3 (K/Pt = 10) was determined to be 2.0 nm by TEM observation, and this suggests that the dispersion can be 0.55, and this is larger than the estimation from the adsorption measurements. From this difference, it is suggested that the surface of Pt metal particles are covered with potassium compound. Similar behavior was also observed on K–Rh/USY catalysts.[12] TOF(turnover frequency) values of CO_2 formation in H_2-rich gas are also listed in Table 1. In this case, TOF was determined on the basis of CO adsorption. It is possible that CO is adsorbed on potassium oxide to give carbonate species. CO is mainly adsorbed on Pt surface atoms compared to potassium ions, and this is confirmed by FTIR observation of CO adsorption over K–Pt/Al_2O_3. This indicates that potassium oxide is minor species on the catalyst, and it is expected that potassium species is present as potassium carbonate. In addition, CO was not adsorbed on potassium carbonate as reported previously.[13] TOF increased drastically with increasing the additive amount of potassium in the range of K/Pt = 5–10. On the other hand, by more addition, TOF decreased, and the optimum was observed at K/Pt = 10. Especially, it should be noted that the TOF of K–Pt/Al_2O_3 (K/Pt = 10) was 20 times higher than that of Pt/Al_2O_3 in terms of CO conversion. This indicates that the addition of potassium to Pt/Al_2O_3 dramatically promotes the preferential oxidation of CO in H_2-rich gas.

Table 1 Pt dispersion and TOF of CO oxidation in H_2-rich gas over K–Pt/Al_2O_3

	TEM	Adsorption[a]		10^3TOF/s^{-1}
K–Pt/Al_2O_3K/Pt	Particle size/nm	H/Pt	CO/Pt	CO_2 formation[b]
0	—	0.70	0.52	1.5
5	—	0.45	0.41	11
10	2.0	0.38	0.40	33
15	—	0.25	0.30	29
20	—	0.19	0.27	16

[a] Irreversible adsorption amount. [b] TOF of CO_2 formation at 353 K is calculated on the basis of CO/Pt. Reaction conditions are the same in Fig. 1.

Fig. 2 shows the reaction temperature dependence of catalyst performance in CO oxidation (CO + O_2) and preferential oxidation of CO (CO + O_2 + H_2) over K–Pt/Al_2O_3 (K/Pt = 0 and 10). In the CO oxidation (CO + O_2) without the presence of H_2, K–Pt/Al_2O_3 exhibited higher CO oxidation activity than Pt/Al_2O_3. Furthermore, in the case of Pt/Al_2O_3, from the comparison between CO + O_2 and CO + O_2 + H_2 reactions, the addition of H_2 promoted CO oxidation in the temperature range below 413 K, however, at higher temperature, the presence of H_2 drastically inhibited CO oxidation. This is because oxidation of H_2 is more preferential than CO oxidation. On the other hand, regarding K–Pt/Al_2O_3 (K/Pt = 10), the presence of H_2 promoted CO oxidation drastically. The promoting effect of the H_2 presence on K–Pt/Al_2O_3 was much more significant than that on Pt/Al_2O_3.

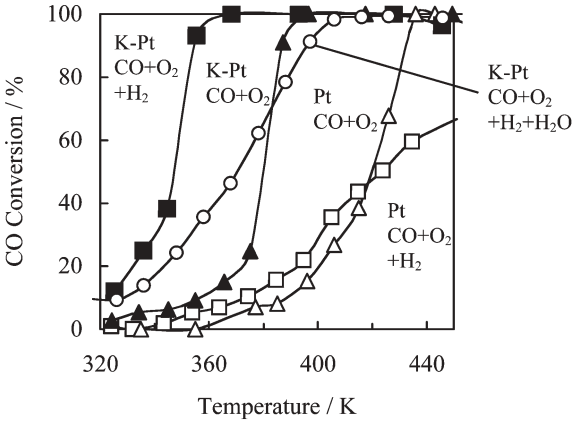

Fig. 2 Reaction temperature dependence of CO conversion in CO oxidation (without H_2) and preferential oxidation of CO over K–Pt/Al_2O_3 (K/Pt = 0 and 10). K/Pt = 0 (□,△), K/Pt = 10 (■,▲,○). Reaction conditions: 0.2 vol% CO, 0.2 vol% O_2 and 75 vol% H_2 balanced with He (□,■), 0.2 vol% CO and 0.2 vol% O_2 balanced with He (△,▲), 0.2 vol% CO, 0.2 vol% O_2, 75 vol% H_2 and 5 vol% H_2O balanced with He (○).

From the observed behavior, it is thought that the additive effect of potassium on preferential oxidation of CO has two aspects: one is the effect on the $CO + O_2$ oxidation and the other is the effect of H_2 presence. According to the previous report,[14,15] the promoting effect of alkali ion on the O_2 adsorption can be explained by changing the binding energies of adsorbed oxygen, and it can promote CO oxidation. On the other hand, the effect of H_2 presence on CO oxidation can not be explained by water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$), which is induced by the H_2O production from H_2 oxidation. This is because Pt/Al_2O_3 and $K–Pt/Al_2O_3$ exhibited very low activity of water gas shift reaction. One interpretation can be due to the role of the hydroxyl group (OH), which can be formed from H_2 and O_2. It has been reported that the OH group can promote CO oxidation on Pt (111).[15,16] In fact, the effect of H_2 presence on CO oxidation over Pt/Al_2O_3 was observed in low temperature range, although it was not so significant. In contrast, the effect over $K–Pt/Al_2O_3$ was much more remarkable. At present, it is thought that the coverage of OH group can be increased over $K–Pt/Al_2O_3$ due to the interaction with potassium species, which covers Pt metal surface. Another possibility is that H_2O_2, which can be formed from the reaction between H_2 and O_2, can promote the preferential CO oxidation. Promoting mechanism of H_2 presence over $K–Pt/Al_2O_3$ is not clear at present, and further investigation is necessary for the elucidation of this mechanism. In terms of practical case, the effect of the presence of steam in the reactant gas is important. In fact, under our basic feeding conditions (0.2 vol% CO, 0.2 vol% O_2 and 75 vol% H_2 balanced with He) as shown in Fig. 1, about 0.1% steam was formed when CO and O_2 conversions are almost 100%. Under these conditions, $K–Pt/Al_2O_3$ was very stable. This suggests that the effect of low steam pressure is small. In addition, we investigated the effect of higher steam pressure (5 vol% H_2O), and the result is also shown in Fig. 2. The addition of 5 vol% steam to $CO + O_2 + H_2$ decreased the CO conversion level over $K–Pt/Al_2O_3$ ($K/Pt = 10$). The temperature, where CO conversion reached 90%, became 40 K higher by the addition of steam. This indicates that high concentration of steam can decrease the catalytic activity of preferential oxidation of CO. On the other hand, this poisoning effect of steam was reversible, and the high activity was completely reproduced in the reaction when the steam addition stopped. This indicates that the catalyst structure was very stable even after exposing to steam. Although the details are not shown here, the additive effect of steam is small in $CO + H_2 + O_2$ over Pt/Al_2O_3. The important point is that the effect of potassium is very remarkable even under the presence of steam with high pressure.

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