Applied Catalysis A: General 343 (2008) 125–133

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Preferential CO oxidation in hydrogen-rich stream over Pt catalysts modified with alkali metals

Part II. Catalyst characterization and role of alkali metals

Hisanori Tanaka [a], Masatoshi Kuriyama [a], Yoichi Ishida [a], Shin-ichi Ito [a], Takeshi Kubota [b], Toshihiro Miyao [c], Shuichi Naito [c], Keiichi Tomishige [a,*], Kimio Kunimori [a]

[a] Institute of Materials Science, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan
[b] Department of Material Science, Shimane University, Matsue 690-8504, Japan
[c] Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama, Kanagawa 221-8686, Japan

ARTICLE INFO

Article history:
Received 16 January 2008
Received in revised form 10 March 2008
Accepted 26 March 2008
Available online 30 March 2008

Keywords:
Preferential CO oxidation
Platinum
Alkali metals
Potassium
OH group
FTIR
X-ray absorption fine structure

ABSTRACT

The addition of alkali metals over Pt/Al_2O_3 has both promoting and negative effects on the catalytic performance in the preferential CO oxidation in H_2-rich stream (PROX), therefore there is an optimum amount of alkali metal. The Pt/Al_2O_3 catalysts modified with Na, K, Rb and Cs were characterized by means of transmission electron microscopy (TEM), extended X-ray absorption fine structure (EXAFS), X-ray absorption near-edge structure (XANES), and Fourier transform infrared spectroscopy (FTIR). The results show that the addition of larger amount of alkali metals with stronger basicity causes the aggregation of Pt metal particles. The Pt particles on Pt/Al_2O_3 modified with alkali metals are more electron-deficient than those on Pt/Al_2O_3, and this weakens the strength of CO adsorption on Pt/Al_2O_3 modified with alkali metals, which is related to the enhancement of turnover frequency of the PROX. In addition, *in situ* FTIR observation suggests that the coadsorbed species originating from H_2 and O_2 (e.g., the OH species) under the PROX condition, which promote the CO oxidation, can be found on highly active catalysts.

1. Introduction

Alkali metals are often used as additives to promote the catalytic activity and/or the selectivity of supported metal catalysts in some catalytic reactions. Recent studies indicate that introduction of alkali metals to supported metal catalysts is effective for the preferential oxidation of CO by O_2 in H_2-rich stream (PROX) [1–9]. Our group has reported that addition of potassium enhanced the catalytic performance of Rh/SiO_2 and Rh/USY [1,2]. In both cases, there was an optimum additive amount of potassium. The promoting effect of potassium is the enhancement of Rh dispersion on Rh/SiO_2, and it is the enhancement of turnover frequency of the PROX on Rh/USY. On both Rh catalysts, a negative effect of potassium can be due to covering of the surface of Rh metal particles with potassium species. In addition, the microstructure of $K–Rh/SiO_2$ was dependent on the method of catalyst preparation, and the relation between the catalytic performance in the PROX and the microstructure has been discussed [3].

Our group has also reported that Pt/Al_2O_3 modified with potassium is effective to the PROX, and the additive effect of potassium has been discussed [4–6]. Furthermore, the effect of alkali metals (Li, Na, K, Rb, Cs) on the PROX reaction over the Pt catalysts supported on Al_2O_3 has been investigated, and it is found that the catalytic performance is strongly affected by the basic strength and the additive amount of alkali metals [9]. In this work, the catalysts were characterized by transmission electron microscopy (TEM), extended X-ray absorption fine structure (EXAFS), X-ray absorption near-edge structure (XANES), and Fourier transform infrared spectroscopy (FTIR). The promoting and negative effects of the alkali metal addition on the catalytic performance are discussed on the basis of the catalyst characterization results.

2. Experimental

2.1. Catalyst preparation

The Pt/Al_2O_3 catalysts with and without the modification of potassium were prepared by the same method reported in our

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[*] Corresponding author. Tel.: +81 29 853 5030; fax: +81 29 853 5030.
E-mail address: tomi@tulip.sannet.ne.jp (K. Tomishige).

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doi:10.1016/j.apcata.2008.03.029

previous report [6]. The Pt/Al_2O_3 catalysts modified with sodium, rubidium and cesium were prepared in a similar way to Pt/Al_2O_3 modified with potassium, and a different point is that precursors of sodium, rubidium and cesium were $NaNO_3$, $RbNO_3$ and $CsNO_3$, respectively. The loading amount of Pt was 2 wt%. The loading amount of alkali metals is described in the molar ratio to Pt (M/Pt), and the ratio was 3 and 10 in the present study. The modified Pt/Al_2O_3 catalysts are denoted as M–Pt/Al_2O_3, and M/Pt is shown in parenthesis like K–Pt/Al_2O_3 (10). All the M–Pt/Al_2O_3 catalysts were calcined at 773 K for 1 h. As a reference, Pt/Al_2O_3 catalysts calcined at higher temperatures (823, 873, and 1073 K) were also prepared, and they were described with the calcination temperature in an angle bracket, for example, Pt/Al_2O_3 [773]. The catalysts were reduced with hydrogen at 773 K for 1 h as a pretreatment for the activity test and catalyst characterization.

2.2. Catalyst characterization

2.2.1. TEM observation

Transmission electron microscope (TEM) images were taken by means of JEM-2010F (JEOL) equipment operated at 200 kV. The catalysts were reduced by H_2 pretreatment at 773 K for 1 h in a fixed-bed reactor. Samples were dispersed in 2-propanol using supersonic waves, and they were put on Cu grids for TEM observation under air atmosphere. Average metal particle size (d) is calculated by $d = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$ (n_i: number of pieces; d_i: particle size) [10].

2.2.2. EXAFS and XANES

Pt L_3-edge extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectra were measured at the BL-12C station of the Photon Factory at the High Energy Accelerator Research Organization (Proposal No. 2005G041). The storage ring was operated at 2.5 GeV. A Si(1 1 1) single crystal was used to obtain a monochromatic X-ray beam. The monochromator was detuned to 60% maximum intensity to avoid higher harmonics in the X-ray beam. Two ion chambers filled with Ar and 15% Ar diluted N_2 for Pt L_3-edge EXAFS and XANES were used, respectively, as detectors of I and I_0. The samples for the measurement were prepared by pressing 200 mg of catalyst powder to disks. The thickness of the samples was chosen to be 0.6–0.7 mm (10 mmØ) to give an edge jump of 0.7. The samples were pretreated with H_2 at 773 K for 1 h. After the pretreatment, we transferred the samples to the measurement cell without exposing the disk to air, using a glove box filled with nitrogen. EXAFS and XANES data were collected in a transmission mode at room temperature. For EXAFS analysis, the oscillation was first extracted from the EXAFS data by a spline smoothing method [11]. The oscillation was normalized by the edge height around 50 eV. The Fourier transformation of the k^3-weighted EXAFS oscillation from k space to r space was performed over the range 30–160 nm^{-1} to obtain a radial distribution function. The inversely Fourier filtered data were analyzed by a common curve-fitting method [12,13]. For the curve-fitting analysis, the empirical phase shift and amplitude functions for Pt–Pt, Pt–O bonds were extracted from the data for Pt foil and $Na_2Pt(OH)_6$, respectively. Analysis of EXAFS data was performed using the "REX2000" program (Version: 2.3.3; Rigaku Corp.). In the analysis of XANES spectra, the normalized spectra were obtained by subtracting the pre-edge background from the raw data with a modified Victoreen's equation and normalizing them by the edge height [14–17].

2.2.3. FTIR measurements

FTIR spectra were recorded with a Nicolet Magna 550 spectrometer equipped with a MCT detector (resolution: 4 cm^{-1}) in a transmission mode, using an *in situ* IR quartz cell with CaF_2 windows. All samples for the IR measurement were pressed into self-supporting wafers with a diameter of 20 mm and a weight of about 150 mg. The sample disk was transferred to the IR cell connected to the closed circulating vacuum systems for the observation of CO desorption profile when the sample temperature increases. The IR cell was connected to the flow systems for the observation during the preferential CO oxidation in hydrogen-rich stream. In the former case, the sample was reduced with H_2 at 773 K for 1 h in 30 ml min^{-1} H_2 at the flow system as a pretreatment. In the experiments for the CO desorption profile, the sample after the pretreatment was cooled down to room temperature, and then it was exposed to 2.7 kPa CO for 15 min and evacuated. The spectra were obtained in the range of 313–433 K. In the experiments under the preferential CO oxidation reaction in hydrogen-rich stream, the sample was cooled down to 313 K after the pretreatment, and the reactant gases ($CO + O_2 + H_2$) were introduced to the IR cell using the flow system. Temperature dependence of FTIR spectra during the reaction was measured for 15 min at each temperature. FTIR spectra of adsorbed species were obtained by subtracting the background spectra at the same temperature. The total flowing rate in the reactant gases was adjusted to GHSV = 30,000 h^{-1}, which was used for the activity tests in the fixed bed reactor.

3. Results and discussion

3.1. TEM observation

Fig. 1 shows TEM images of Pt/Al_2O_3 [773], K–Pt/Al_2O_3 (3 and 10) and Cs–Pt/Al_2O_3 (3 and 10). The average particle sizes of Pt/Al_2O_3 [773] and K–Pt/Al_2O_3 (3) were smaller than those of other three catalysts, and they were determined to be 0.5 ± 0.1 and 0.6 ± 0.1 nm, respectively, which are supported by high dispersion on the basis of CO adsorption (CO/Pt = 0.52, 0.46). Average particle size of K–Pt/Al_2O_3 (10) was determined to be 2.0 ± 0.3 nm. Those of Cs–Pt/Al_2O_3 (3 and 10) were estimated to be 1.7 ± 0.2 and 3.8 ± 0.3 nm, respectively. From the comparison, it is found that the modification by larger amount of alkali metals with stronger basicity increased the average particle size of Pt.

3.2. EXAFS and XANES

Fig. 2 shows the result of Pt L_3-edge EXAFS analysis of the catalysts. Curve fitting results are listed in Table 1. The Pt–Pt and Pt–O bonds were required for the curve fitting of Pt/Al_2O_3 [773] and [823], although the contribution of the Pt–O bond was rather small. This suggests that highly dispersed Pt metal particles interact with the surface of the Al_2O_3 support. The coordination numbers of the Pt–Pt bond on Pt/Al_2O_3 increased monotonously with increasing calcination temperature. This behavior corresponds to the aggregation by the calcination at higher temperature. In the case of the M–Pt/Al_2O_3 (3) (M = Na, K, Rb, Cs), the Pt–Pt and Pt–O bonds were necessary. The coordination number of the Pt–Pt bond on M–Pt/Al_2O_3 (3) was a little larger than that on Pt/Al_2O_3 [773], which is consistent with the TEM results. On the other hand, the spectra of M–Pt/Al_2O_3 (10) were fitted by only the Pt–Pt bond, and the coordination number increased more remarkably by the addition of alkali metals with stronger basicity.

Fig. 3 shows Pt L_3-edge XANES spectra of the catalysts, and Table 2 gives the results of XANES analysis. The white line intensity of Pt L_3-edge is known to be an informative indication of the electron state of Pt; the larger white line is due to the greater electron vacancy in d-orbital [18]. As reported previously, a relative electron deficiency of the Pt species can be determined based on the white line intensity [14–17]. For the Pt/Al_2O_3