Differences in Thermal Decomposition Behavior of Platinum Salt on Silica and Alumina Characterized by X-ray Absorption Spectroscopy

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Abstract: The thermal decomposition behavior of supported $PtCl_6^{2-}$ salt on silica and alumina under air was investigated with XANES/EXAFS techniques using a laboratory-type spectrometer. The platinum species were reduced to form atomic platinum specie upon elevating temperature until 573 K accompanied with elimination of coordinated Cl atoms. The atomic species aggregated to form metallic particle on silica whereas re-oxidation occurred on alumina above 623 K. The cation-vacant site on γ-alumina would capture the isolated Pt atoms, and the adjacent oxygen atoms would decrease occupancy of Pt 5d orbital.

Keywords: supported platinum salt, decomposition behavior, XAFS

1. Introduction

Supported platinum catalysts are widely utilized for practical use such as automobile exhaust gas, hydrogenation/dehydrogenation, reforming, and electrode catalysts for PEFC. It is well known that preparation procedure would influence on the catalytic performance and the physical properties pf platinum particles remarkably [1], but relatively few studies have been reported on formation of platinum particles in the initial step of catalyst preparation [2-7]. In the present study, transformation of platinum salt on silica and γ-alumina upon calcination and was investigated by in-situ XAFS spectroscopic technique.

2. Experimental

Catalyst samples were prepared by impregnation of silica (JRC-SIO-9A) or γ-alumina (JRC-ALO-8) with aqueous solution of H_2PtCl_6 or $Pt(NH_3)_4Cl_2$ at 353 K, followed by drying at 383 K. The loading amounts were 2 wt% as Pt. The in-situ Pt L-edge XAFS spectra were recorded using a laboratory–type spectrometer R-XAS Looper (Rigaku) in a transmission mode under 50 ml/min of air or He stream up to 773 K. The parameters for in-situ XANES/EXAFS measurements were described elsewhere [8]. Oxidation states of supported platinum species was evaluated with the d-orbital occupancy by analyzing L2,3 XANES spectra according to the manner reported by Mansour et al. [9].

3. Results and discussion

The decomposition behavior of supported H_2PtCl_6 species was first examined under air. The Pt L3 edge XANES spectra gave an intense peak so-called whiteline due to transition of 2p electron to unoccupied 5d-orbital. The whiteline intensity of silica-supported species gradually decreased with increasing treatment temperature. The intensity for an alumina-supported sample decreased until 573 K whereas increased above 623 K. Figure 1 shows changing of unoccupied d-orbital upon thermal treatment under air stream analyzed using the corresponding Pt L2 and L3 edge XANES spectra. As mentioned above, supported $H_2Pt^{VI}Cl_6$ species were gradually reduced until 573 K on both silica and

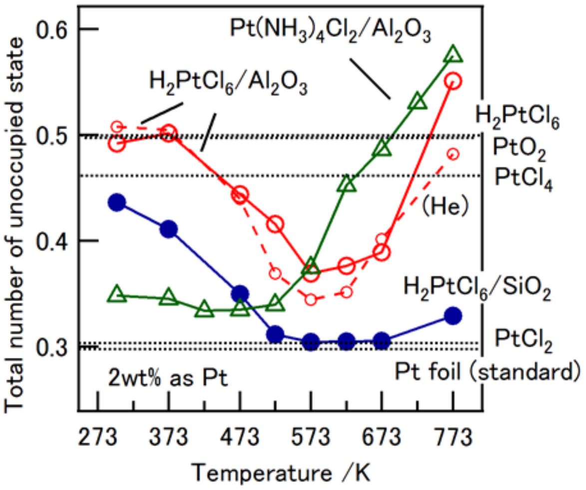

Figure 1. Effect of calcination temperature on states of unoccupied d-orbitals of supported Pt species under air.

alumina. Further increment of calcination temperature up to 773 K little influenced on the oxidation states on silica; however, re-oxidation proceeded on alumina. This reduction-reoxidation behavior for H_2PtCl_6/Al_2O_3 samples was confirmed under He stream as well. $Pt^{II}(NH_3)_4Cl_2$ of cationic precursor was also re-oxidized on alumina above 523 K.

Figure 2 shows Pt L3 edge EXAFS spectra of supported H_2PtCl_6 salt after thermal treatment under air and the radial structure functions. The curve-fitting analyses revealed that the number of coordinated Cl atoms for supported H_2PtCl_6 species decreased upon calcination until 573 K. Formation of Pt-Pt pair proceeded on silica after calcination at 773 K. In contrast, Pt-O and Pt-(O)-Al pairs were detected on H_2PtCl_6/Al_2O_3 calcined at 773 K whereas no Pt-Pt pairs were confirmed. The possible scheme of decomposition behavior was illustrated in Figure 3. The isolated Pt species formed on both supports at around 573 K under air and/or He stream accompanied by elimination of chlorine atoms. The isolated species would aggregate to form Pt particle on the surface of silica above 573 K, whereas cation-vacant site on γ-alumina captures the isolated Pt atoms. The adjacent oxygen atoms would cause re-oxidation.

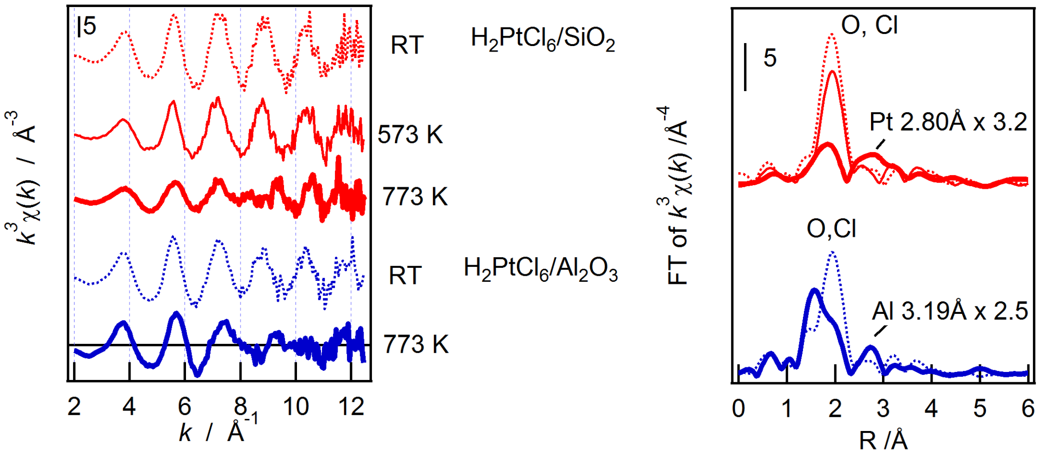

Figure 2. Pt L3 edge EXAFS spectra of supported H_2PtCl_6 species after thermal treatment under air and the Fourier transforms.

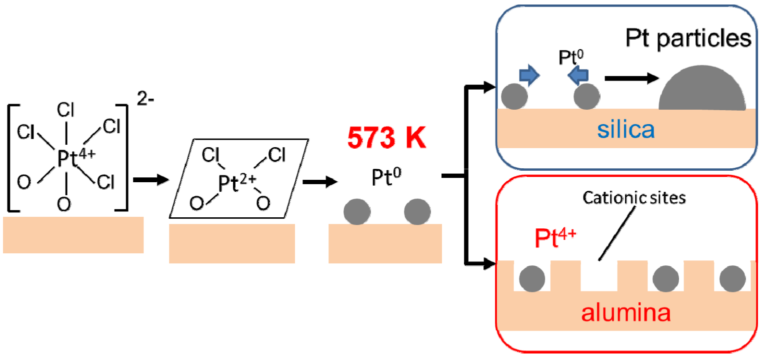

Figure 3. Possible scheme of decomposition behavior of supported chloroplatinate species on SiO_2 and Al_2O_3.

References

1. H. Matsuhashi, S. Nishiyama, H. Miura, K. Eguchi, K. Hasegawa, Y. Iizuka, A. Igarashi, N. Katada, J. Kobayashi, T. Kubota, T. Mori, K. Nakai, N. Okazaki, M. Sugioka, T. Umeki, Y. Yazawa, D. Lu, Appl. Catal. A, 272 (2004) 329.
2. M. K. Oudenhuijzen, P. J. Kooyman, B. Tappel, J. A. van Bokhoven, D. C. Koningsberger, J. Catal., 205 (2002) 135.
3. A. Goguet, D. Schweich, J. P. Candy, J. Catal., 220 (2003) 280.
4. J. T. Miller, M. Schreier, A. J. Kropf, J. R. Regalbuto, J. Catal., 225 (2004) 203.
5. P. J. Chupas, K. W. Chapman, G. Jennings, P. L. Lee, C. P. Grey, J. Am. Chem. Soc., 129 (2007) 13822.
6. S. Kaneko, M. Izuka, A. Takahashi, M. Ohshima, H. Kurokawa, H. Miura, Appl. Catal. A, 427 (2012) 85.
7. T. Shishido, H. Nasu, L. Deng, K. Teramura, T. Tanaka, J. Phys., Conf. Ser., 430 (2013) 012060.
8. T. Yamamoto, A. Yukumoto, Bunseki Kagaku, 62 (2013) 555.
9. A. N. Mansour, J. W. Cook Jr, D. E. Sayers, J. Phys. Chem., 88 (1984) 2330.