BL-9A/2020G080

Effect of H_2 plasma irradiation on surface structure of a Cu/α-Al_2O_3(0001) model catalyst studied by *in situ* PTRF-XAFS technique

Satoru TAKAKUSAGI*, Haoran XU, Bang LU, Shuai LIU and Kiyotaka ASAKURA
Hokkaido University, Sapporo, 001-0021, Japan

1 Introduction

Recently, plasma catalysis has attracted much attention because the plasma can activate the reactant gases and significantly improve the performance of many catalytic reactions, including ammonia synthesis, CO_2 hydrogenation, CH_4 activation and the water-gas shift reactions.[1-2] The enhancement in the reaction performance results from synergy between the plasma and the catalyst surface. However, the mechanisms of the plasma catalysis are complex, and the plasma-catalyst interactions are not fully understood because *in situ* characterization techniques are limited. In this study, *in situ* polarization-dependent total reflection fluorescence (PTRF)-XAFS technique for plasma catalysis has been developed and the effect of H_2 plasma on surface structure of a Cu/α-Al_2O_3(0001) model catalyst was examined.

2 Experiment

Cu/α-Al_2O_3(0001) surface was prepared by vacuum deposition of Cu onto an α-Al_2O_3(0001) surface in a separate UHV chamber. The Cu coverage was estimated to be 1.0 ML by the XPS measurements, where 1ML was defined as surface Al density (5.1×10^{14} /cm^2). The sample was transferred to the compact vacuum chamber, termed an *operando* PTRF-XAFS cell which was recently developed by our group.[3] The electron cyclotron resonance (ECR) plasma source (Sairem) was attached to the cell to carry out the *in situ* XAFS measurements in the presence of plasma (Fig. 1). The Cu K-edge PTRF-XAFS measurements were conducted after fixing the cell to the 6-axis goniometer and optimizing the total-reflection conditions for incident X-rays using the goniometer.

3 Results and Discussion

Figs. 2(a) and (b) show the Cu K-edge *in situ* PTRF-XANES spectra of the Cu/α-Al_2O_3(0001) surface measured at 473 K under H_2 flow and H_2 plasma, respectively. In Fig.2(a), no polarization dependence was found, indicating that the Cu species had a spherical shape. Preliminary curve fitting analysis of the EXAFS spectra suggested the presence of Cu-Cu interaction (0.252±0.002 nm) and its coordination number was ~7 both for *s*- and *p*-polarizations. On the other hand, polarization dependence was found in Fig.2 (b), showing that the H_2 plasma irradiation modified the structure of the Cu species. The EXAFS analysis revealed that the coordination numbers of Cu-Cu (0.253±0.002 nm) were 9.8±0.8 and 7.6±0.7 for *s*- and *p*-polarizations, respectively. Thus, the H_2 plasma treatment might induce lateral growth of the Cu atoms and promote formation of the flat-shaped Cu nanoparticles. The XPS measurements of the Cu/α-Al_2O_3(0001) surface showed that the amount of the Cu atoms decreased probably due to the etching reaction[4] and density of surface hydroxy groups on the α-Al_2O_3(0001) surface increased after exposure to the H_2 plasma. These may be origins of formation of the flat-shaped Cu nanoparticles observed in the PTRF-XAFS results

Our results suggested that the role of the plasma is not only activation of the reactant gases but also modification of the catalyst structure, which may be the origins of the enhanced catalytic performance in the plasma catalysis.

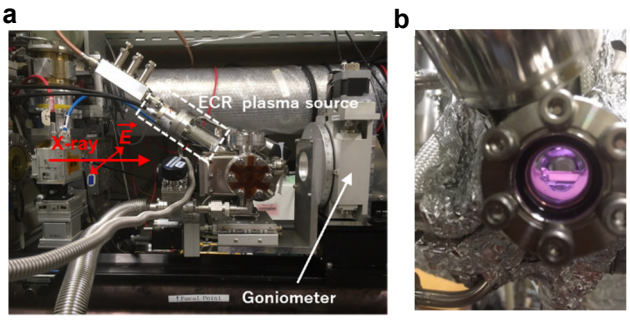

Fig. 1: (a) *in situ* PTRF-XAFS technique for plasma catalysis. (b) H_2 plasma (10 W). H_2: 1.9 mL min^{-1}, 1 Pa.

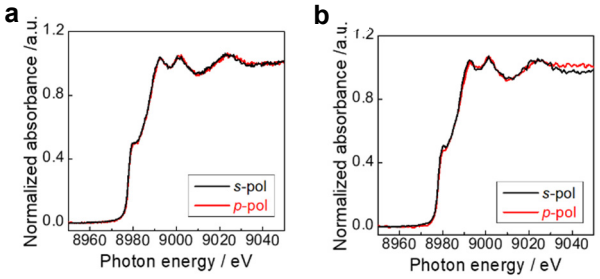

Fig. 2: Cu K-edge PTRF-EXAFS spectra of the Cu/α-Al_2O_3(0001) surface measured at 473 K under (a) H_2 flow and (b) H_2 plasma (10 W). H_2: 1.9 mL min^{-1}, 1 Pa.

Acknowledgement

We thank the PF staffs for their kind technical support.

References

[1] L. Shuang *et al.*, *ACS. Catal.* **10**, 2855 (2020).
[2] A. Bogaerts *et al.*, *J. Phys. D* **53**, 443001 (2020).
[3] B. Lu *et al.*, *J. Phys. Chem. C* **125**, 12424 (2021).
[4] F. Wu et al., *J. Electrochem. Soc*. **159**, H121 (2011).

* takakusa@cat.hokudai.ac.jp