

Relationship between the Catalytic Activity for the Oxidative Dehydrogenation on Te-Pd/SiO₂ and the Te-Properties Estimated Using Fluorescent XAFS for Te-K Edge

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1 Introduction

In our laboratories, Pd catalysts doped with a heavy metal supported on silica have attracted attention, particularly for industrial application. Although there are various results for XAFS studies on Pd-species [1-3], rather few reports on XAFS information on the heavy metal have been published. In our beam time, we have measured fluorescent XAFS for Te-K edge of Pd/SiO₂ doped with Te (Te-Pd/SiO₂) and finally obtained reliable results from the fluorescent XAFS of Te-K edge. In the present report, we wish to report the correlation between the catalytic activity for the oxidative dehydrogenation on Te-Pd/SiO₂ and the Te-properties obtained using the fluorescent XAFS.

2 Experiment

Two kinds of Te-Pd/SiO₂ were prepared as follows. One catalyst was prepared using telluric acid and the others using metallic tellurium. When telluric acid was employed, the acid (0.054 g; Wako Pure Chemical Industries) was dissolved in a distilled water (10.0 g). In this aqueous solution, 2.185 g of aqueous Pd(NO₃)₂ (23 wt%, N.E. Chemcat) was added and diluted using distilled water up to 20 g of the aqueous solution. In using metallic tellurium, 10.0 g of an aqueous solution consisting of metallic tellurium (Wako) and HNO₃ was used instead of the aqueous telluric acid solution. Into those aqueous solution consisting of H₆TeO₆ or Te, SiO₂ (surface area: 450 m²/g) was added, evaporated, and dried in air at 473 K for 3 h. The precursor of the catalyst thus obtained was reduced using 37% formalin at 343 K for 2 h. After the reduction, the catalyst was filtrated, washed and dried. The catalysts thus prepared from H₆TeO₆ and Te, respectively, were referred to as Te-Pd/SiO₂ (A) and Te-Pd/SiO₂ (M), respectively. Analysis of fluorescent XAFS near the Te-K edge was carried out at the High Energy Accelerator Research Organization with a storage ring current of 400 mA (6.5 GeV). The X-rays were monochromatized with Si(311) at an NW-10A station. The absorption spectra were observed using ionization chambers in the fluorescent mode, Lytle detector and indium filter. The photon energy was scanned in the range of 31,311–32,911 eV for the Te-K edge.

3 Results and Discussion

Figure 1 showed XANES spectra of Te-Pd/SiO₂ (A) and Te-Pd/SiO₂ (M) together with the reference samples; TeO₂ and metallic Te. As shown in the spectra for TeO₂ and metallic Te, absorption edges were detected at essentially identical absorption energy, while the shape in the white line obtained from TeO₂ was evidently different from that from metallic Te. Based on this information on the shape of the white line, XANES spectra of Te-Pd/SiO₂ (A) and Te-Pd/SiO₂ (M) were analyzed qualitatively. The absorption edges of Te-Pd/SiO₂ (A) and Te-Pd/SiO₂ (M) were almost same while the intensity of top of the signal due to Te-Pd/SiO₂ (M) was weaker than that due to Te-Pd/SiO₂ (A), indicating that the nature of Te-Pd/SiO₂ (M) is more similar to that of metallic Te rather than TeO₂, comparing to Te-Pd/SiO₂ (A). It is of interest to note that the shapes and the absorption edges of Te-Pd/SiO₂ (A) and Te-Pd/SiO₂ (M) were evidently different from metallic Te although those supported catalysts were previously reduced using formalin.

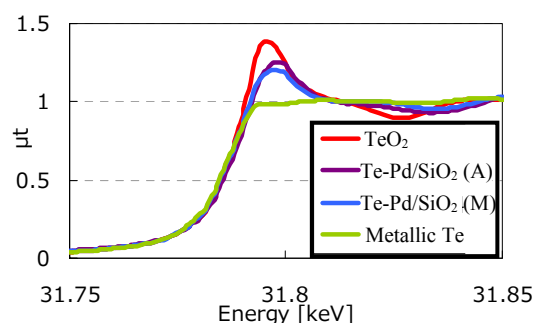


Figure 1. Te-K edge XANES spectra of various Te-contained samples.

The yield for the oxidative dehydrogenation on Te-Pd/SiO₂ (M) was 7% greater than that on Te-Pd/SiO₂ (A). Therefore it can be confirmed that Te-Pd/SiO₂ (M), in which Te was not completely reduced but more reduced than Te-Pd/SiO₂ (A), is an excellent catalyst for the oxidative dehydrogenation.

References

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