

X-ray induced polymerization of Si resin and reduction of Pt catalysts

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Introduction

Pt catalysts are important for hydrosilylation reactions. We have studied the structure of Pt catalysts during the reaction and extended our work to the retardation effects of bismaleate which are important for the control of the solidification of the silicon resin. During the work we found that the X-ray radiation-induced the polymerisation reaction accompanied by the reduction of Pt catalysts. In order to carry out the structural analysis of the Pt catalysts, we first revealed the origin of the observed X-ray irradiation effect on the structure of Pt catalysts.

Experimental

The EXAFS measurements were carried out at BL9A.

The sample including Pt catalyst, bismaleate, vinylpolydimethylsiloxane and polydimethylsiloxane. Bismaleate is a retardor of the reaction. In order to see the structural change of the Pt catalysts during the reaction we varied the reaction times and temperatures and we followed the structure change of Pt in the reaction processes.

Results and Discussion

Fig. 1 shows the XANES of Pt L₃ edge soon after the X-ray irradiation (A) and 2 hours after the continuous measurement (B). The spectra changes with the exposure time to X-ray. The analysis of EXAFS indicated the agglomeration of Pt to form Pt clusters. At the same time, the resin was hardened at the irradiated spots. Thus the X-ray irradiation induced the polymerization reaction. There are two possibilities for the radiation effect. One is the excitation of Pt L₃ edge which initiates the catalytic reaction of polymerization. The other is the radical reaction formed from the solvent or reactants by the irradiation of X-ray. To confirm this point, we carried out the EXAFS measurement at 11400 eV a little lower energy than the Pt L₃ edge for 2 hours. Fig. 1C shows the XANES spectra, indicating the reduction of Pt occurred together with the polymerization reaction. Thus the latter possibility is more plausible.

In order to reduce the polymerization reaction, we carried out the experiment at lower temperature than 70 K. However, we could not inhibit the reaction. Thus the activation energy for the polymerization reaction induced by X-ray is very low. This can be rationalized by the hot atom formation by the high energy X-ray. Thus we carried out the XAFS measurements with a short time and accumulated the data by changing the position with every scan. Finally we obtained the data at the initial stage. The Pt-C bond was found at 0.220 nm as shown in Fig.2.

Further analysis is now going on and we will try to determine the interaction between retardor and Pt catalyst.

This work has revealed that focused and intense X-ray may change the sample and we have to be more careful about the radiation damage.

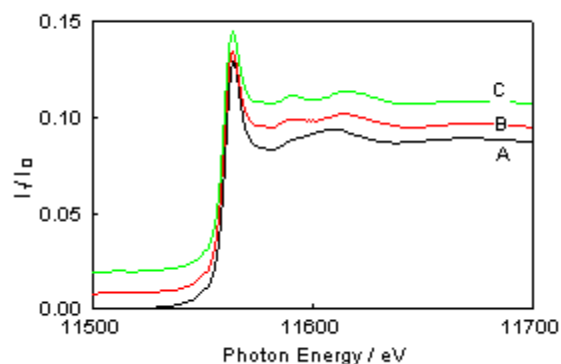


Fig.1 Radiation damage of Pt complex just after the irradiation (A), 2 hours after the continuous measurements (B), and 2 hours after the X-ray irradiation with 11 KeV less than Pt L3 edge (C).

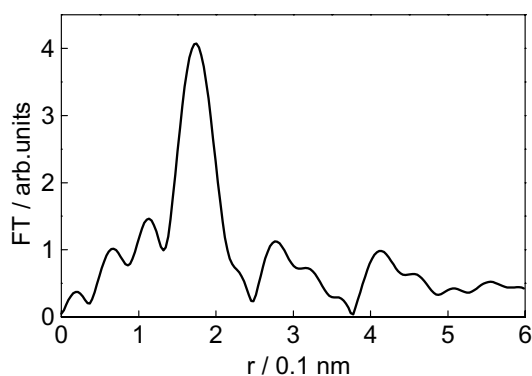


Fig. 2 Fourier transformation of the Pt catalyst soon after the reaction.

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