

^{13}C CP/MAS NMR Study of Cross-linked Poly(vinylpyrrolidone) on Surface of Cerium Oxide Nanoparticles

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The highly dispersed property of poly(vinylpyrrolidone) (PVP)-coated cerium oxide nanoparticles can be retained for a long time in polar solvents. In this ^{13}C CP/MAS NMR study, it is revealed that the surface PVP forms cross-linked structures during the synthesis of the nanoparticles.

Highly dispersed metal oxide nanoparticles have attracted much attention as interesting functional materials. Recently, many researchers have investigated the preparation of such nanoparticles.^{1–7} One method of preparing highly dispersed metal oxide nanoparticles is to coat the surface with organic polymers.^{4–7} Cerium oxide possesses the property of high ultraviolet absorbance.^{1,8} Therefore, the sol of cerium oxide nanoparticles is expected to be applied to several fields such as cosmetics and optics. However, it is necessary to prepare highly dispersed metal oxide nanoparticles with long-term stability. We have previously reported a one-step procedure for synthesizing highly dispersive poly(vinylpyrrolidone) (PVP)-coated cerium oxide nanoparticles by a reflux method.⁹ Spherical nanoparticles are obtained with a narrow size distribution, and their size can be controlled by the molecular weight of the PVP. The coated PVP possesses high affinity to polar solvents, such as ethylene glycol, ethanol, and water. The PVP-coated CeO_2 nanoparticles, therefore, possess good dispersibility in polar solvents. Interestingly, the suspension of PVP-coated CeO_2 nanoparticles in ethylene glycol exhibited no precipitation over several weeks. This result indicates that the coated PVP on cerium oxide nanoparticles is stable, i.e., it does not dissolve in the solvent, although pristine PVP dissolves in ethylene glycol.

In the present study, we have carried out a structural characterization of PVP coated on CeO_2 nanoparticles to clarify why the coated PVP is stable in polar solvents.

The PVP-coated CeO_2 nanoparticles were synthesized in accordance with our previous report:⁹ 1) we heated cerium(III) nitrate hexahydrate (Kojundo) in PVP (Sigma-Aldrich) dissolved in ethylene glycol (Wako) at 190 °C. The average molecular weight of the PVP is 4350 [calibrated with poly(ethylene glycol)]; 2) we removed the unreacted materials by centrifugation followed by washing with water and ethanol; 3) we dried the nanoparticles at 80 °C. The resulting nanoparticle powder was used as an NMR sample. Solid-state ^{13}C CP/MAS NMR spectroscopic analyses were carried out with a JEOL EX-400WB spectrometer operating at 100 MHz using cross-polarization with the magic angle spinning (CP/MAS) technique. The spinning speed of the rotor was 6 kHz. The chemical shift is referred to hexamethylbenzene (17.3 ppm). In the NMR analyses, PVP and polyvinyl polypyrrolidone (PVPP, Nacalai) were also analyzed. PVPP is a highly cross-linked PVP.

Figure 1a shows the ^{13}C CP/MAS NMR spectra of PVP-

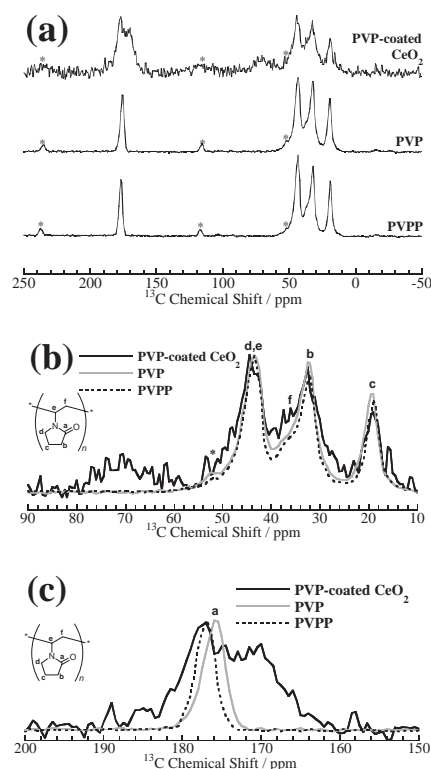


Figure 1. ^{13}C CP/MAS NMR spectra of PVP-coated CeO_2 nanoparticles, PVP, and PVPP. The intensities of all the spectra are normalized. Asterisks denote spinning sidebands. Labels a–f denote the peaks assigned to PVP: (a) all regions, (b) enlarged region of 10–90 ppm, and (c) enlarged region of 150–200 ppm.

coated CeO_2 nanoparticles, PVP, and PVPP. The intensities of all the spectra in Figure 1 are normalized. The spectrum of PVP exhibits sharp peaks at approximately 178, 45, 33, and 19 ppm. All the resonance peaks of PVP are assigned by referring to previous reports on ^{13}C NMR measurements.^{10–12} PVPP has a cross-linked structure of PVP in which the side-chain pyrrolidone ring opens and reamidates to other pyrrolidone groups. Therefore, PVPP has almost the same spectrum as PVP, as shown in Figure 1a. In the case of PVP-coated CeO_2 nanoparticles, the spectrum exhibits peaks with lower intensity than those for PVP and PVPP because approximately 80% of each nanoparticle comprises CeO_2 and the organic components comprise only approximately 20%. However, all the PVP-related peaks appear in the spectrum of PVP-coated CeO_2 nanoparticles.

Figure 1b shows the enlarged spectra in the region of 10–90 ppm. In this region, the NMR spectrum of the PVP-coated CeO_2 nanoparticles is different from those of PVP and PVPP.

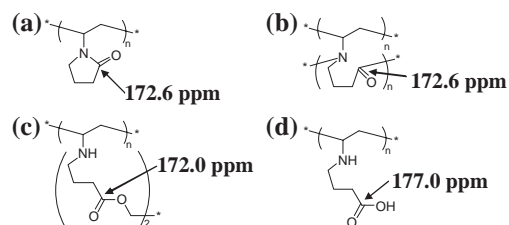
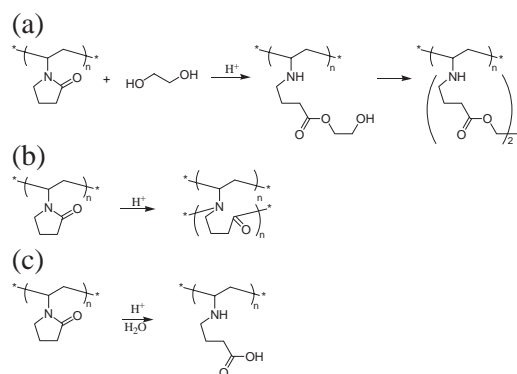


Figure 2. Calculated chemical shifts of carbonyl carbons in pyrrolidone groups: (a) PVP, (b) PVPP, (c) PVP with open pyrrolidone ring after reaction with ethylene glycol, and (d) PVP with open pyrrolidone ring after hydrolysis.

The spectrum of PVP-coated CeO_2 has a broad peak centered at approximately 70 ppm. This indicates that the ethylene glycol molecules from the solution were incorporated into the organic components of the PVP-coated CeO_2 nanoparticles during their synthesis.^{13,14} The carbonyl carbon peaks of all the spectra are enlarged in Figure 1c. The carbonyl carbon peak of PVPP has a slightly higher chemical shift than that of PVP, although other peaks of PVPP exhibit almost the same chemical shift as those of PVP. This may be due to the cross-linking of pyrrolidone groups. The carbonyl carbon peak of the PVP-coated CeO_2 nanoparticles is also different from those of PVP and PVPP. The peak of the PVP-coated CeO_2 nanoparticles is broad, and is thought to be formed by the overlapping of several peaks. The broad peak covers not only the carbonyl carbon peaks of PVP and PVPP but also exhibits lower and higher chemical shifts than those of PVP and PVPP, respectively.

Figure 2 shows the calculated chemical shift of carbonyl carbons in pyrrolidone groups with various chemical structures. The calculated values are obtained by ChemDraw. The actual chemical shifts of carbonyl carbons in PVP and PVPP are slightly different from calculated values, as shown in Figures 2a and 2b. In the program it is considered that the carbonyl carbons in amide groups of both the pyrrolidone ring (PVP) and the cross-linkage (PVPP) are under the same conditions. Although the calculated values do not perfectly match the actual values, they could be used to elucidate the components of the broad peaks from the PVP-coated CeO_2 nanoparticles. Parts of the amide groups in the pyrrolidone groups may cause chemical reactions during the synthesis of PVP-coated CeO_2 nanoparticles. The pyrrolidone rings are thought to open at the amide groups, and then esterification with the ethylene glycol because the broad peak from the methylene carbons of the ethylene glycol groups appears in the spectrum of the PVP-coated CeO_2 nanoparticles, as shown in Figure 1b. In this case, the calculated chemical shift of the carbonyl carbon is lower, as shown in Figure 2c. In the case that the pyrrolidone ring opens and a carboxylic group is formed by hydrolysis, the calculated chemical shift of the carbonyl carbon is higher, as shown in Figure 2d.

Scheme 1 shows the proposed chemical reactions of PVP on the surface of CeO_2 particles. The reaction solution contains water due to the dissolution of cerium(III) nitrate hexahydrate. During the synthesis of PVP-coated CeO_2 nanoparticles, nitrogen dioxide is generated; thus, the reaction solution becomes acidic. Therefore, the conditions for the reactions in Scheme 1 to occur are satisfied. The dissolved PVP is deposited onto the surface of the CeO_2 nanoparticles when they are formed, indicating that a heterogeneous field is a necessary condition for the



Scheme 1. Proposed chemical reactions of pyrrolidone group in PVP on the surface of CeO_2 nanoparticles: (a) formation of cross-linked structure due to reaction with ethylene glycol, (b) formation of cross-linked structures due to opening of pyrrolidone ring and reamidation, and (c) opening of pyrrolidone ring by hydrolysis.

reaction of PVP. Therefore, the coated polymer layer of the PVP-coated CeO_2 nanoparticles is expected to have several structures, i.e., cross-linked structure with ethylene glycol (Scheme 1a), cross-linked structures generated by reamidation (Scheme 1b), and the hydrolysis of the amide group (Scheme 1c), and a nonreacted structure. These structures are consistent with the results of the ^{13}C CP/MAS NMR spectra shown in Figures 1b and 1c.

In conclusion, it is revealed that the PVP on the surface of CeO_2 nanoparticles forms cross-linked structures during the synthesis of PVP-coated CeO_2 nanoparticles. The rigidity of the structures is thought to ensure the stability of PVP on the surface of the CeO_2 particles, i.e., it does not dissociate from CeO_2 particles and is insoluble in polar solvents.

References

- 1 J.-S. Lee, J.-S. Lee, S.-C. Choi, *Mater. Lett.* **2005**, *59*, 395.
- 2 J. Yu, V. S. Murthy, R. K. Rana, M. S. Wong, *Chem. Commun.* **2006**, 1097.
- 3 X. Fan, L. Lin, P. B. Messersmith, *Compos. Sci. Technol.* **2006**, *66*, 1198.
- 4 S. Wang, G. Shi, *Mater. Chem. Phys.* **2007**, *102*, 255.
- 5 A. Petri-Fink, B. Steitz, A. Finka, J. Salaklang, H. Hofmann, *Eur. J. Pharm. Biopharm.* **2008**, *68*, 129.
- 6 A. H. Latham, M. E. Williams, *Acc. Chem. Res.* **2008**, *41*, 411.
- 7 C. Ho, J. C. Yu, T. Kwong, A. C. Mak, S. Lai, *Chem. Mater.* **2005**, *17*, 4514.
- 8 R. Li, S. Yabe, M. Yamashita, S. Momose, S. Yoshida, S. Yin, T. Sato, *Solid State Ionics* **2002**, *151*, 235.
- 9 N. Izu, I. Matsubara, T. Itoh, W. Shin, M. Nishibori, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 761.
- 10 A. Asano, T. Kurotu, *J. Mol. Struct.* **1998**, *441*, 129.
- 11 C. Lau, Y. Mi, *Polymer* **2002**, *43*, 823.
- 12 T. Watanabe, S. Hasegawa, N. Wakiyama, A. Kusai, M. Senna, *Int. J. Pharm.* **2003**, *250*, 283.
- 13 Y. Miwa, Y. Takahashi, Y. Kitano, H. Ishida, *J. Mol. Struct.* **1998**, *441*, 295.
- 14 U. Skogsberg, C. Meyer, J. Rehbein, G. Fischer, S. Schauff, N. Welsch, K. Albert, A. J. Hall, B. Sellergren, *Polymer* **2007**, *48*, 229.