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ESR Microscopic Imaging on the Spatial Distribution of Paramagnetic Reactive Centers on Catalysts

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An ESR microscopic imaging on the V^{4+} and Mo^{5+} ions Dispersed in the tablets of silica and zeolite carriers was carried out. Distributions of these ions on the surfaces and the cross sections of the catalyst tablets were observed. These results may be a useful information about proper shapes, sizes, and operating conditions of the catalyst particles.

In heterogeneous catalysis various paramagnetic ions are used as working sites of catalytic reactions. EPR spectroscopy on these paramagnetic ions has been widely applied to the research on the structures of the working sites so far.1) During catalytic reactions the paramagnetic sites occasionally change their valency, then the EPR signals reflect these changes. It seems to be of much interest to observe the spatial distribution of the working site in the catalyst tablets or pellets, which are practically used in the reactors of chemical plants or even in automobiles, because the appropriate shape and size, proper preparation, poisoning effect, and life time of catalyst particles could be established on the basis of the informations about the distributions of the working sites. ESR microscopic imaging has been so far successfully applied to the investigations in the fields of geochemistry,2) radiation damage of high polymers,3) and the lattice imperfection in crystals.4) In the present letter we report the first example of an application of ESR imaging to catalysis. Preliminary results on the spatial distributions of Mo^{5+} and V^{4+} ions in the catalyst tablets of silica or zeolite carrier are presented.

In the solution of 1.0 g of $H_3PMo_{12}O_{40}$ (Japan New Metal Co. Ltd.) with 10 cm^3 of water, 5.0 g of silica (Wakogell-Q63) was added, then the mixture was ground thoroughly. The dried powder of the mixture was pressed in a mold to be a tablet of 20 mm in diameter. The tablet was reduced in the stream of the N_2-H_2 mixture at 450 °C for 4 h (Sample A). 0.89 g of NH_4VO_3 was dissolved in 10 cm^3 water, and mixed together with 5 g of zeolite powder (Wako F-9). The mixture was processed in the same procedure as sample A, and was reduced in the stream of propane at 480 °C for 1 h (Sample B). Thus, the VO_3^- ion held on zeolite decomposed into the paramagnetic vanadium ion in the tetravalent state.

The instrument used in ESR imaging was a JEOL FE-1X spectrometer equipped with a microwave resonant cavity of TE_{102} mode, which was specially designed for microscopy with a pin-hole of 2 mm diameter at the top of the cavity. The sample was placed on the pin-hole and finely translated by a precision moving-stage, which was driven by a data acquisition system of NEC PC9801 VX microcomputer. Details of the apparatus are described in the previous articles.2,3)

The ESR of the Mo^{5+} ion supported on silica has been so far observed in the course of reduction.5) A broad ESR signal of the Mo^{5+} ion with g-factor of 1.907 in sample A is shown in Fig. 1a. An ESR imaging on the upper surface of sample A was done by sitting on the center of the ESR signal of Mo^{5+} in the course of reduction. The stream of reducing gas mixture H_2-N_2 was blown onto the lower surface of the tablet and passed around its outer edge to the upper surface. As seen in Fig. 1b the Mo^{5+} concentration on the upper surface decreases concentrically toward the center of the upper surface. During the reduction of the tablet, its right side edge touched to the inner wall of the

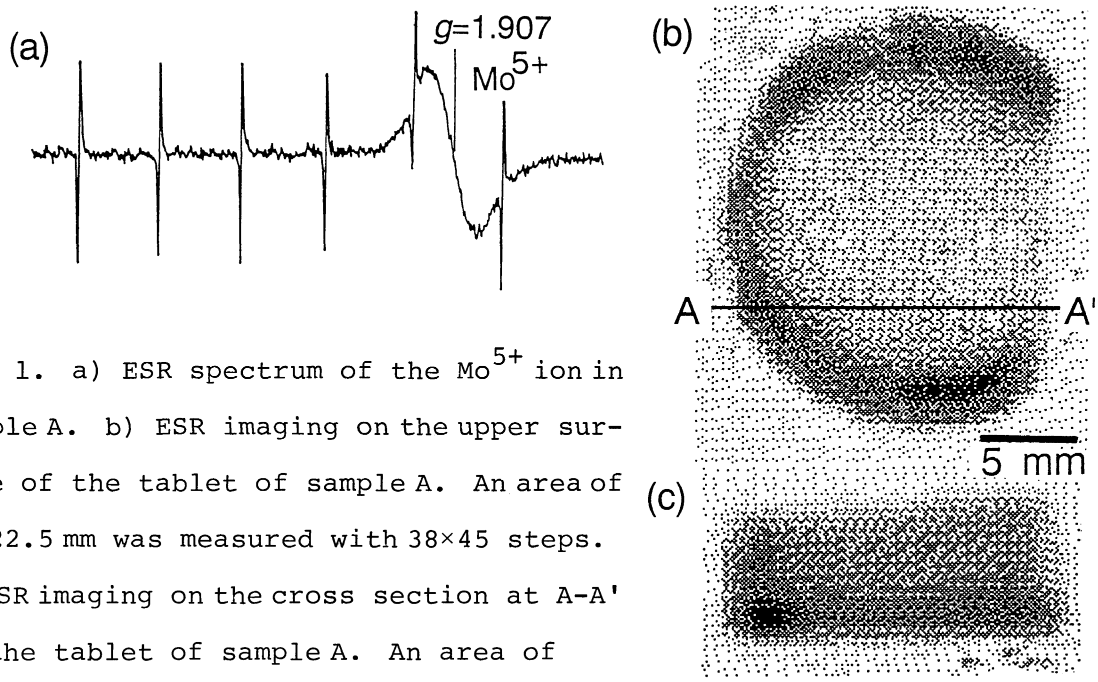

Fig. 1. a) ESR spectrum of the Mo^{5+} ion in sample A. b) ESR imaging on the upper surface of the tablet of sample A. An area of 19×22.5 mm was measured with 38×45 steps. c) ESR imaging on the cross section at A-A' of the tablet of sample A. An area of 10×18.5 mm was measured with 20×37 steps.

reactor, thus the poor supply of the reducing gas in this region resulted in the much lower concentration of the Mo^{5+} ion at the right side edge. Another imaging on the cross section of sample A at A-A' (Fig. 1b) shows that on the lower surface and the edge of upper surface the concentrations of Mo^{5+} are relatively high and gradually decreases from the surface inward.

As shown in Figs. 2a and 2b for sample B a signal with g-factor of 2.0036, which is ascribable to the carbon radical formed by the decomposition of the reducing gas on the surface of catalyst, superposed on the center of hfs for the V^{4+} ion.

The imaging on the individual species separately was difficult on this sample due to the small difference between g-factors of both ions. An ESR imaging for sample B is shown in Fig. 2c, and the ESR signal may arise from the carbon radical and the V^{4+} ion. This is consistent with the visual inspection on the surface of the tablet which was covered in place by the black color of carbon and the V^{4+} ion. In case that more than two paramagnetic species exist in a system, ESR imaging on the individual species separately may be possible, when the differences among g-factors of the species

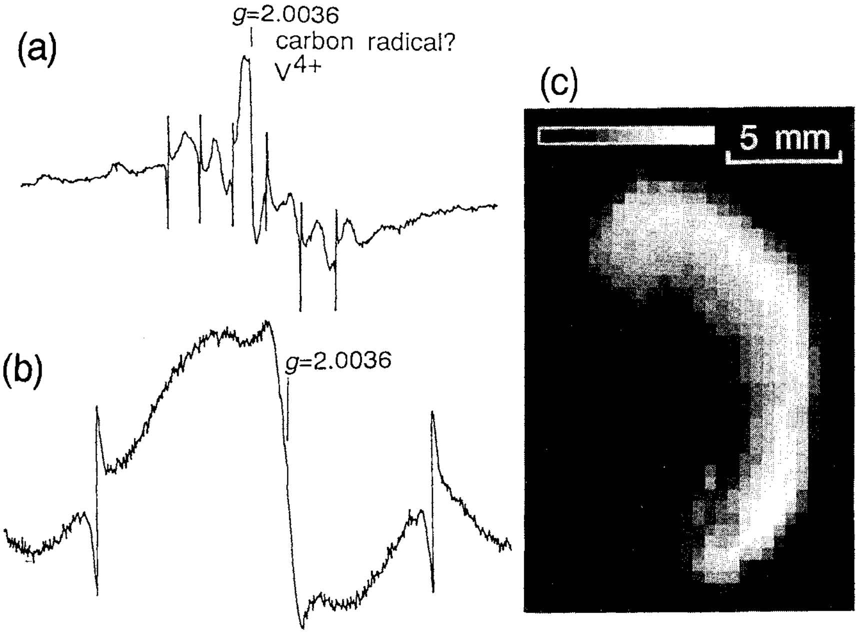

Fig. 2. a) ESR spectrum of the V^{4+} ion in sample B. b) The central part of spectrum a. c) ESR imaging of the upper surface of the tablet. An area of 14× 20 mm was measured with 28×40 steps.

to each other are large enough. Reduction of the linewidth at low temperature also favors the ESR imaging on the individual species.

The sectional view of the distribution of paramagnetic species was shown to be very useful, then three-dimensional imaging$^{6)}$ should become of much more importance in the future application of this technique. The authors would like to thank to Prof. Toshinobu Imanaka, Dr. Yasuaki Okamoto, and Ms. Yuriko Nitta of Osaka University for their assistance in the preparation of catalyst tablets.

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