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XAFS evidence on redox-nature of palladium in Pd-$Mg_3V_2O_3$ catalysts

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Introduction

It is known that *pyro*-$Mg_2V_2O_7$ and *ortho*-$Mg_3V_2O_8$ show the highest and lowest catalytic activity for the oxidative dehydrogenation of propane among magnesium vanadates, respectively. However, in our recent study [1], it has been found out that *ortho*-$Mg_3V_2O_8$ is more stable than *pyro*-$Mg_2V_2O_7$ for the redox involving abstraction-insertion of the lattice oxygen. Thus it is necessary that the activity of $Mg_3V_2O_8$ should be improved by enhancing the mobility of the lattice oxygen. In the present study, palladium cation (Pd^{2+}) was incorporated into $Mg_3V_2O_8$ in order to enhance the activity and redox nature of palladium species in the catalyst was analyzed by XAFS.

Experimental

Magnesium *ortho*-vanadates doped with Pd^{2+}, which are described as X%Pd-ortho-MgVO, were prepared from $Mg(OH)_2$, $Pd(NO_3)_2$ and NH_4VO_3. Fixed-bed continuous flow reactor operated at atmospheric pressure was employed for the catalytic activity tests. The standard reaction conditions were as follows: W=0.5 g, T=723 K, P(C_3H_8)=14.4 kPa and P(O_2)=4.1 kPa diluted with helium, and F=30 ml min^{-1}. X-ray absorption fine structure (XAFS) near Pd K-edge was measured (6.5 GeV) with a storage ring current of approximately 400 mA at the High Energy Research Organization. The X-rays were monochromatized with Si(311) at NW-10A station. The absorption spectra were observed using ionization chambers in a transmission mode.

Results and Discussion

The catalytic activities for the oxidative dehydrogenation of propane on 5%Pd-ortho-MgVO were measured for 6 h on-stream. At rather shorter time-on-stream (0.75 h), the conversion of propane and the selectivity to propylene on 5%Pd-ortho-MgVO were 11.8 % and 61.4 %, respectively. With the incorporation of Pd^{2+} into $Mg_3V_2O_8$, the remarkable improvement of the yield of C_3H_6 from 3.0 % on $Mg_3V_2O_8$ to 7.2 % on 5%Pd-ortho-MgVO was observed. Furthermore, it was found out that the catalytic activity on 5%Pd-ortho-MgVO was greater than that on $Mg_2V_2O_7$ (C_3H_6 yield=6.1 %), which is the most active catalyst among magnesium vanadates.

Unfortunately, the conversion of C_3H_8 and the selectivity to C_3H_6 on 5%Pd-ortho-MgVO decreased to 6.7 and 33.6 %, respectively, with progressing time-on-stream. However re-oxidation with oxygen (25 ml min^{-1}) for 1 h at 723 K of the deactivated 5%Pd-ortho-MgVO resulted in the regeneration of the activity similar to that on fresh 5%Pd-ortho-MgVO.

In order to check the redox nature of Pd species in 5%Pd-ortho-MgVO during the reaction and re-oxidation, XAFS were employed and Fourier transformation of XAFS of 5%Pd-ortho-MgVO ((A) before reaction, (B) after the reaction and (C) after the re-oxidation) was described in Fig. 1.

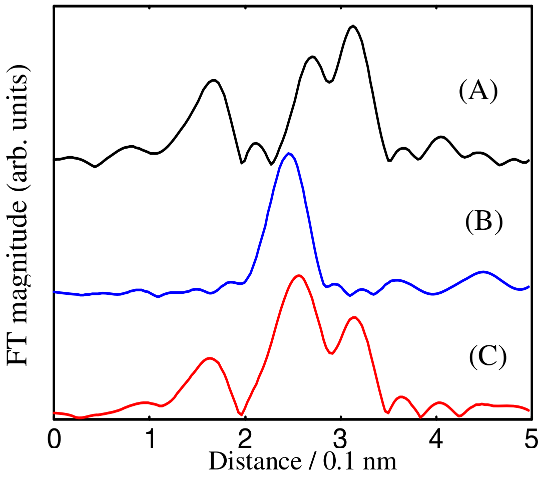

Fig. 1 Fourier transformation of XAFS for 5% Pd-ortho-MgVO.

Fig. 1 reveals that Pd species in 5%Pd-ortho-MgVO before the reaction, after the reaction, and after the re-oxidation was Pd^{2+}, Pd^0 and a mixture of Pd^{2+} and Pd^0, respectively, indicating that redox cycle with Pd species proceeds favorably during the reaction to enhance the catalytic activity.

Reference

[1] S. Sugiyama et al., J. Ceramic Soc. Jpn., 115, 667 (2007).

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