Bis(2-pyridinecarboxylato)vanadium(IV) in NaY Zeolite Cages: Synthesis and Spectroscopic Properties

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Encapsulated vanadium(IV) picolinato complex was synthesized by treatment of VO^{2+}-NaY zeolite with molten picolinic acid. The structure of the 'ship-in-a-bottle' species was determined by EXAFS, XANES, ESR, IR and UV-vis spectroscopies. It was suggested by XPS and XRD that the complex was located in the zeolite cage. $VO(pic)_2$-NaY has been shown to retain solution like activity in oxidation of alkanes, alcohols and benzene with hydrogen peroxide.

Heterogenization of metal complex catalysts through entrapment in supercages of faujasites has been extensively studied in the last decade. 'Ship-in-a-bottle' complex catalysts which have been subject of detailed studies showed solution-like activity for the electrophilic oxygen transfer like alkene epoxidation.[1-3] On the other hand, few publications were concerned with radical-based hydrocarbon hydroxylation using zeolite-encapsulated complexes. Therefore heterogenization of metal complexes with enhanced homolytic reactivity such as vanadium complexes with pyridine- and pyrazine carboxylic acids is currently of scientific interest.[4] Here we report synthesis of $VO(pic)_2$ (pic: picolinate, i.e., 2-pyridinecarboxylate anion) encapsulated in Y-zeolite supercages and its spectroscopic properties in comparison with the impregnated complex located mainly on the external surface of the zeolite.

VO^{2+} ion exchange of zeolite NaY (Towa Co. HSZ-320NAA, Lot. 3001) was carried out according to a standard procedure (4 h/room temperature, N_2 atmosphere, 0.03 mol l^{-1} $VOSO_4$).[5] This sample was dried (230 °C/2 h in vacuo), treated with excess of molten picolinic acid (picH) at 160 °C/6 h (N_2 atmosphere) and Soxhlet-extracted with pyridine for 60 h. Finally, the sample was heated for 10 h at 140 °C in a He flow to remove adsorbed pyridine.

Detail characterization was performed to elucidate structure and location of the vanadium species (Table 1.). ESR spectra of the synthesized sample showed disappearance of VO^{2+}-NaY signal and appearance of a new signal with parameters identical to the impregnated $VO(pic)_2$-NaY ($g_{||}$= 1.945, $g_{\perp}$= 1.990, $A_{||}$= 179.6G, $A_{\perp}$= 64.6G). IR spectra of the synthesized sample exhibited a strong band at ~1389 cm^{-1} and doublet bands at 1440-1490 cm^{-1}, which are characteristic of picolinate species.[6] The band ~1530 cm^{-1} for freshly synthesized $VO(pic)_2$-NaY which is attributable to picolinic acid disappeared completely after the Soxhlet extraction. Diffuse reflectance spectra for $VO(pic)_2$-NaY consisted of bands at 740, 560, and 365 nm, assigned to the electronic transitions $b_2 \rightarrow e^*$, $b_2 \rightarrow b_1^*$, and $b_2 \rightarrow 1a_1^*$, respectively, which resembled the bands for VO^{2+}-picolinic acid in solution.[7]

Figure 1 shows vanadium K-edge XANES of impregnated and synthesized $VO(pic)_2$-NaY samples as well as of reference compounds $VO(pic)_2*H_2O$ and $VO(pic)_2(py)$. The pre-edge and edge features in position and intensity were almost the same for the impregnated and synthesized $VO(pic)_2$-NaY samples and similar to those of $VO(pic)_2*H_2O$. The pre-edge peak position ~4.0 eV higher than that for vanadium foil indicates an oxidation state of V(IV), consistent with the peak position determined for vanadyl complexes. Comparison of the XANES of the synthesized sample with the corresponding data for well-defined vanadium compounds reveals square pyramidal or distorted

Table 1. Spectroscopic characterization for the vanadium species

	$VO(pic)_2$-NaY synthesized	$VO(pic)_2$-NaY impregnated	$VO(pic)_2*H_2O$ crystalline	$VO(pic)_2$ in solution
FTIR (ν/ cm^{-1})	1573	1570	1568	—
	1480	1478	1480	
	1454	1449	1450	
	1389	1389	1389	
	1299	1297	1297	
UV-vis (λ/ nm)	742, 559, 365	742	718, 557, 368	730, 560, 365
	$VO(pic)_2$-NaY synthesized	$VO(pic)_2$-NaY impregnated	VO^{2+}-NaY	NaY
ESR $g_{||}$	1.945	1.944	1.933	—
$g_{\perp}$	1.990	1.991	1.995	
$A_{||}$	179.6G	179.3G	191.0G	
$A_{\perp}$	64.6G	64.7G	69.6G	
XFA V/Si	0.036	0.039	0.072	—
XPS V/Si	0.002	0.023	0.019	—
XRD[a]	1 /0.60 /0.09	1 /0.37 /0.53	1 /0.34 /0.41	1 /0.42 /0.58

[a] $I_{331}/ I_{311}/ I_{220}$ ratio.

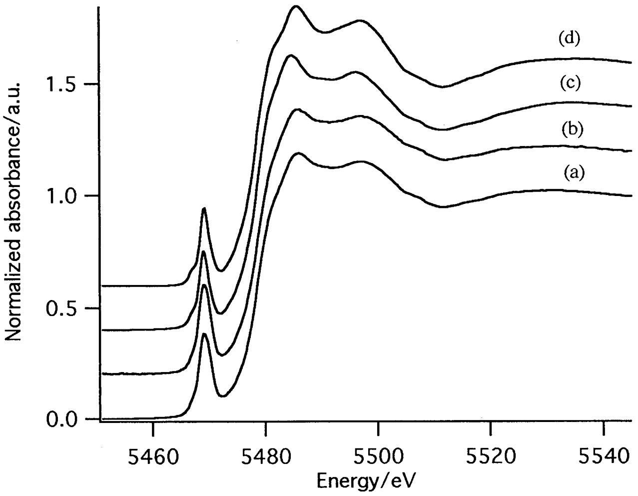

Figure 1. Vanadium K-edge XANES of (a) $VO(pic)_2$-NaY impregnated, (b) $VO(pic)_2$-NaY synthesized, (c) $VO(pic)_2*H_2O$, and (d) $VO(pic)_2(py)$.

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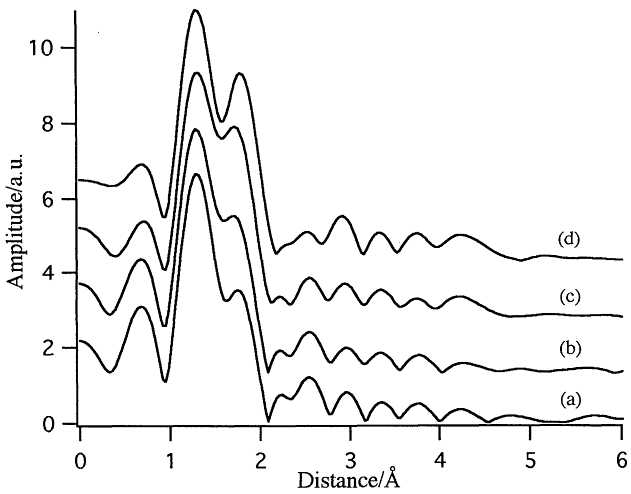

Figure 2. k^3-weighted Fourier transforms of EXAFS data for (a) $VO(pic)_2$-NaY impregnated, (b) $VO(pic)_2$-NaY synthesized, (c) $VO(pic)_2*H_2O$, and (d) $VO(pic)_2(py)$.

octahedral coordination around vanadium.[8] This is also in an agreement with the ESR data.[9]

The Fourier transforms of EXAFS data for vanadium picolinate species are shown in Figure 2. Noticeable difference in spectra between the reference compounds and the $VO(pic)_2$-NaY sample concerns with change in the second shell and can be explained by coordination of a zeolite hydroxy group in an axial position to the vanadium complex as well as distortion of the complex in the supercage.

Contrary to the structure of V-sites the location of the complex strongly depended on the preparation procedure. The diameter of the $VO(pic)_2$ complex is too large to effectively penetrate through the zeolite-cage free-aperture (~0.74 nm), but it is small enough to be accommodated once the complex is formed in the large cavity (internal diameter ~1.3 nm). Flexible ligand technique allowed us to prepare the 'ship-in-a-bottle' $VO(pic)_2$ complex which was not removed by Soxhlet extraction with pyridine for 60 h. The intrazeolitic location of $VO(pic)_2$ was also examined by XRD and XPS. Portions of X-ray powder diffraction patterns showed no appreciable loss in zeolite crystallinity for either impregnated or synthesized sample compared to the NaY. No additional feature due to bulk crystalline vanadium compounds was detected. It has been reported that an empirically derived relationship exists between the relative intensity of the 331, 311, and 220 XRD peaks and the cation location in faujasite-type zeolites.[10] Little change occurred in the relative intensities of the 331, 311, and 220 peaks upon impregnation of NaY with $VO(pic)_2*H_2O$ and after VO^{2+}-ion exchange, as shown in Table 1. Retention of random location of sodium ions in the zeolite is thus assumed. However, analysis of the pattern for the synthesized $VO(pic)_2$-NaY indicates that the encapsulated complex formation was accompanied by a significant cation redistribution. We presume that the large $VO(pic)_2$ complexes displaced the sodium ions from their random positions in supercages.

The information on the location of the complex can also be obtained from a combination of X-ray photoelectron spectroscopy (XPS) and X-ray fluorescence analysis (XFA). Comparison of the signal intensities of the V $2p_{3/2}$ lines for the synthesized $VO(pic)_2$-NaY sample and the impregnated sample indicates that the latter had a higher surface concentration of the complex than the former despite the similar vanadium loading of the two samples. The XPS intensity was also referred to that for Si 2p in the zeolite lattice. Comparison of the surface (XPS) and bulk (XFA) concentration ratios listed in Table 1 for the impregnated and synthesized $VO(pic)_2$-NaY samples indicates that the impregnated sample definitely possesses higher external surface content of the V complex. This allowed a more reliable confirmation of the intrazeolitic location of the entrapped complex.

The 'ship-in-a-bottle' vanadium complex detaches from the zeolite when treated with 30% H_2O_2 solution. Therefore, the catalytic oxidations were carried out under anhydrous conditions at room temperature to suppress the leaching. Cyclohexane, cyclohexanol and benzene were oxidized by urea hydrogen peroxide adduct in acetonitrile to cyclohexyl hydroperoxide, cyclohexanone, and phenol, respectively. Thus, the encapsulated vanadium picolinate complex retained the solution-like activity.

In conclusion, the vanadium picolinate 'ship-in-a-bottle' complex was synthesized inside NaY and its structure and location were characterized. This complex shows the solution-like activity. Presently schematic data collection on the catalytic activity of the synthesized sample for selective oxidation reactions is in progress.

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