Physical Chemistry Chemical Physics

Electronic Supplementary Information

Paramagnetic dioxovanadium(IV) molecules inside the channels of zeolite BEA – EPR screen of VO$_2$ reactivity toward small gas-phase molecules

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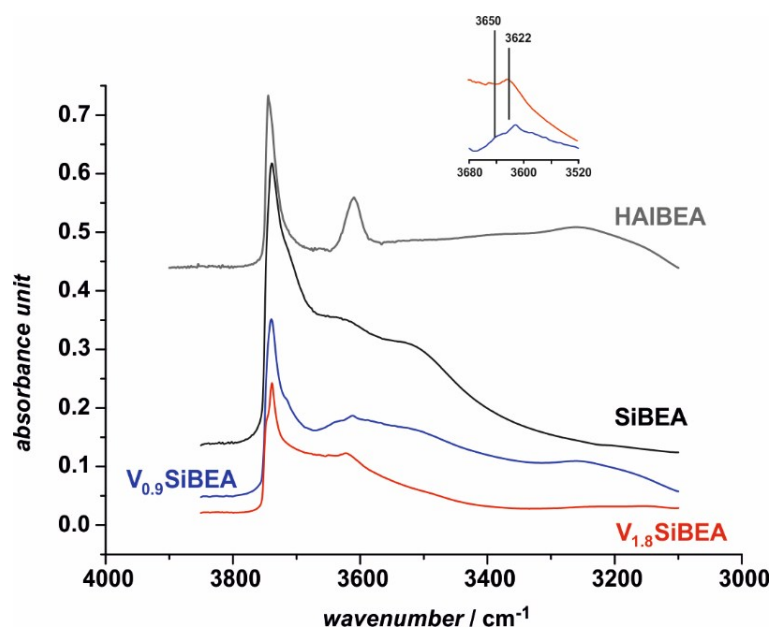E-mail: pietrzyk@chemia.uj.edu.pl

Figure 1S. IR spectra of native HAlBEA zeolite sample, dealuminated SiBEA, and vanadium-loaded samples V$_{0.9}$SiBEA and V$_{1.8}$SiBEA.
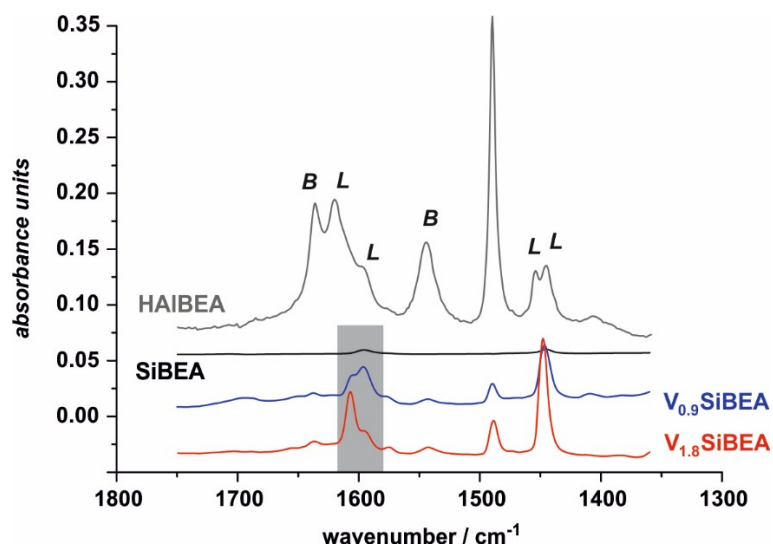
Figure 2S. IR spectra of pyridine adsorption on native HAlBEA zeolite sample, dealuminated SiBEA, and vanadium-loaded samples $V_{0.9}$SiBEA and $V_{1.8}$SiBEA. *B* – bands due to Broensted centers, *L* – bands due to Lewis centers. Highlighted is the spectral region characteristic of vanadium-Py adducts (1607 and 1596 cm^{-1}).

Table 1S. Concentration of Brønsted and Lewis centers calculated based on IR measurements of pyridine adsorption.

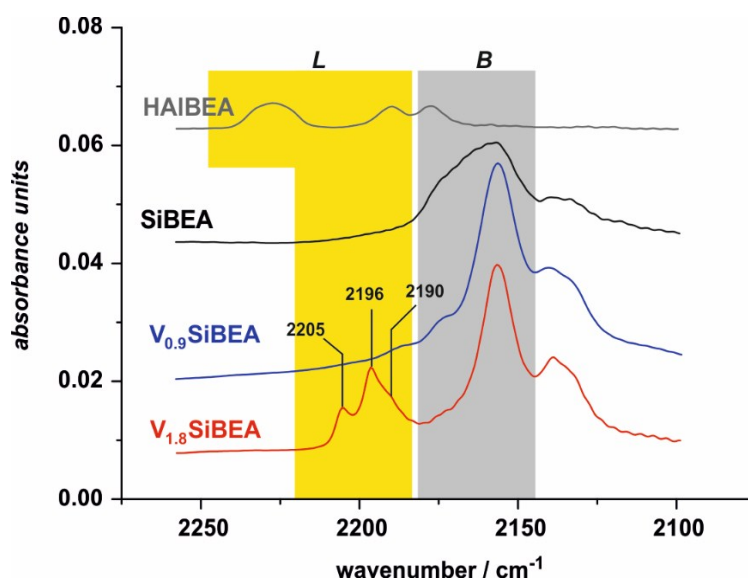| sample	Brønsted centers μmol/g	Lewis centers μmol/g
HBEA	350	320
SiBEA	0	10,2
$V_{0.9}$SiBEA	36	159
$V_{1.8}$SiBEA	37	346

Figure 3S. IR spectra of CO adsorption on native HAlBEA zeolite sample, dealuminated SiBEA, and vanadium-loaded samples $V_{0.9}SiBEA$ and $V_{1.8}SiBEA$. *B* – bands due to Broensted centers, *L* – bands due to Lewis centers. Specific bands due to V–CO adducts are designated at 2205, 2196, and 2190 cm^{-1}.

Table 2S. Spin-Hamiltonian parameters of monooxo VO^{2+} and dioxo VO_2 species and oxygen adducts obtained after reaction with N_2O and O_2 molecules in zeolite SiBEA.

species	g_{xx}	g_{yy}	g_{zz}	$\|A_{xx}\|/$ mT	$\|A_{yy}\|/$ mT	$\|A_{zz}\|/$ mT
VO^{2+}/SiBEA [a]	1.986	1.990	1.931	7.4	8.3	20.5
VO_2/SiBEA [b]	1.803	1.942	1.968	26.9	32.8	31.8
O^--VO_2^+/SiBEA	2.0202	2.0173	2.0284	1.65	1.58	1.49
O_2^--VO_2^+/SiBEA [c]	2.0054	2.0113	2.0239	0.54	0.68	0.98

[a] absolute signs of *A* tensor taken from previous DFT calculations (ref. 11) are as follows:
 [–7.4; –8.3; –20.5] / mT

[b] absolute signs of *A* tensor taken from previous DFT calculations (ref. 11) are as follows:
 [+26.9; +32.8; +31.8] / mT

[c] EPR spectrum of monoclinic symmetry with non-coincidence angle α = 16° in the *yz* plane, g_{xx} and A_{xx} axes are coincident. Taking into account available literature (e.g. J. Phys. Chem. 1988, 92, 1541) for similar superoxo species (Co(III)–O_2^-), one assumes that all signs should be negative resulting in the following *A* tensor: [–0.54; –0.68; –0.98].