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Effect of metal content and calcination–hydration on the environment of V in zeolites prepared by impregnation of SiBEA with $V^{IV}OSO_4$ solution

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Dedicated to the late Dr. D. Barthomeuf.

Abstract

The presence of different V^V species in VSiBEA zeolite prepared by impregnation in air of dealuminated BEA zeolite with aqueous $V^{IV}OSO_4$ solution is evidenced by diffuse reflectance UV–Visible and photoluminescence spectroscopies. The former technique shows that in as prepared VSiBEA with 0.26 and 0.68 wt%, V is present as lattice mononuclear tetrahedral species. In calcined-hydrated VSiBEA whatever the V content (0.26 and 0.68 wt%) and in as prepared VSiBEA with 1.36 V wt%, V is present both as lattice mononuclear tetrahedral and extra-lattice octahedral species. However, only photoluminescence spectroscopy is able to clearly distinguish three kinds of distorted lattice mononuclear tetrahedral V^V species, whose relative amounts depend on V content and calcination–hydration treatments. Moreover, FT-IR demonstrates that the presence of V in dealuminated BEA zeolite generates Brønsted and Lewis acidic sites whose amounts increase with V content.

Keywords: SiBEA zeolite; Vanadium; $VOSO_4$; Diffuse reflectance UV–Visible; Photoluminescence; Brønsted and Lewis acidic sites

1. Introduction

Microporous zeolites containing transitions metal ions with redox properties represent an interesting class of materials for selective oxidation reactions [1,2]. The ordered structure of these materials [3,4] offers a suitable matrix able to isolate and stabilize transition metal ions in tetrahedral coordination [2,5–8]. Recently, we have shown [9] that catalytically active vanadium species are dispersed in SiBEA zeolite by impregnation with aqueous NH_4VO_3 solution, used as V^V precursor. Vanadium was incorporated as lattice tetrahedral V^V species.

A similar post-synthesis method has been used [10] to introduce V in dealuminated BEA zeolite from an aqueous $VOSO_4$ solution, used as V^{IV} precursor. On the basis of XRD, IR, UV–Visible and ^{51}V NMR data, it was shown that V is incorporated in VSiBEA as lattice tetrahedral V^V species whatever the atmosphere (air or Ar) used for impregnation. However, despite the combined deployment of different techniques, it was difficult to conclude whether there was a single type or a mixture of different types of tetrahedral V species.

In this paper, we use photoluminescence spectroscopy to identify tetrahedral V species in VSiBEA prepared by impregnation in air of SiBEA zeolite with aqueous $VOSO_4$ solution. Due to the high sensitivity of this technique to the local environment of a luminescent center, three different kinds of mononuclear tetrahedral V species have been

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distinguished in VSiBEA zeolite whose relative amounts depend on V content and on calcination/hydration treatments. Using DR UV–Visible spectroscopy, we show that calcination and hydration of a VSiBEA lead not only to changes of the symmetry of the mononuclear tetrahedral V species but also to formation of octahedral ones. Moreover, FT-IR shows that introduction of V in SiBEA zeolite generates Brønsted and Lewis acidic sites whose amounts increase with V content.

2. Experimental

2.1. Materials

The TEABEA sample with a framework Si/Al ratio of 11 was provided in its tetraethylammonium (TEA) templated form by RIPP (China). It was dealuminated by treatment in a 13 mol L^{-1} HNO_3 solution for 4 h at 353 K, as already described [9,11,12]. The dealuminated zeolite, noted SiBEA, thus obtained (Si/Al > 1300) was recovered by centrifugation, washed with distilled water and dried overnight at 353 K.

Following a method described earlier [10], 2 g of SiBEA were impregnated in air with an excess of aqueous $V^{IV}OSO_4$ solution of 3.2×10^{-2} mol L^{-1}. The volume of $VOSO_4$ solution was varied from 3.75 to 11 ml. The suspension was stirred several hours in air (pH = 2.4) at 353 K up to evaporation of all water. Then the solid was washed three times with distilled water and dried in air at 353 K overnight. Three VSiBEA samples were prepared with 0.26, 0.68 and 1.36 V wt% and labeled $V_{0.26}$SiBEA, $V_{0.68}$SiBEA and $V_{1.36}$SiBEA. The solids $V_{0.26}$SiBEA and $V_{0.68}$SiBEA are white while $V_{1.36}$SiBEA is light yellow.

$V_{0.26}$SiBEA, $V_{0.68}$SiBEA, and $V_{1.36}$SiBEA samples were further calcined (50 K/h) at 773 K for 2 h in flowing oxygen (7.2 L h^{-1}) and then outgassed at this temperature for 0.5 h. The samples thus obtained are white and denoted C-$V_{0.26}$SiBEA, C-$V_{0.68}$SiBEA and C-$V_{1.36}$SiBEA, respectively. These samples are then cooled to room temperature and hydrated at 298 K in room atmosphere for 30 h and labeled Hyd-C-$V_{0.26}$SiBEA, Hyd-C-$V_{0.68}$SiBEA and Hyd-C-$V_{1.36}$SiBEA, where C stands for calcined and Hyd for hydrated. The color of these samples is yellow.

2.2. Techniques

Diffuse reflectance UV–Visible (DR UV–Visible) spectra were recorded on a Cary spectrometer 5E equipped with an integrator and a double monochromator. The parent V-free materials were used as references.

Photoluminescence spectra were recorded at 77 K with a Spex Fluorolog II Jobin-Yvon spectrofluorimeter (equipped with 460 W Xe lamp as excitation source, and color filters to eliminate scattered light) with UV photons with energies above 250 nm. Before measurements, samples were placed in a quartz cell with window and furnace sections connected to a vacuum line and outgassed at 353 or 473 K for 2 h at 10^{-3} Pa. Emission spectra were recorded using 250 nm excitation light and an emission band-pass of 4.5 nm.

Transmission FT-IR spectra were recorded at room temperature on a Bruker IFS 66 V spectrometer, with a resolution of 2 cm^{-1} on self-supported wafers. Previous to measurements, the wafers were dehydrated under flowing oxygen (7.2 L h^{-1}, 8 h) at 573 K (heating rate of 100 K h^{-1}) then evacuated for 6 h at the same temperature. Gaseous pyridine was directly contacted with the dehydrated wafers by opening a connection between the cell and an independent compartment containing liquid pyridine. Physisorbed pyridine was eliminated by evacuating the cell at 298 and 423 K for 1 h each time.

3. Results and discussion

As shown earlier [10], upon impregnation of V^{IV} precursor on SiBEA zeolite in air, SiO–H groups are consumed as revealed by the progressive disappearance of the corresponding IR band at 3520 cm^{-1}. Its intensity decreases as the vanadium amount introduced increases.

3.1. DR UV–Visible

The nature and environment of V species in $V_{0.26}$SiBEA, $V_{0.68}$SiBEA, $V_{1.36}$SiBEA, C-$V_{0.68}$SiBEA and Hyd-C-$V_{0.68}$SiBEA were studied by DR UV–Visible spectroscopy (Fig. 1).

The spectra of $V_{0.26}$SiBEA, $V_{0.68}$SiBEA and $V_{1.36}$SiBEA exhibit two bands at 263 and 339 nm. Due to the absence of d–d transitions in the range 600–800 nm expected for V^{IV} ions [13,14] and of any V^{IV} EPR signal, these bands involve only V^{V} ions and are assigned to lattice mononuclear tetrahedral V^{V} species and attributed to $\pi(t_2) \rightarrow d(e)$ and $\pi(t_1) \rightarrow d(e)$ oxygen–tetrahedral V^{5+} charge transfer (CT) transitions involving bridging (V–O–Si) and terminal (V=O) oxygen, respectively, in line with earlier results [7,16]. For $V_{1.36}$SiBEA, a band near 410 nm (Fig. 1c) can be assigned to extra-lattice mononuclear V^{V} species and attributed to oxygen–octahedral V^{5+} charge transfer (CT) transition, in line with earlier data [7]. The formation of such V^{V} species was observed earlier for VSiBEA materials prepared by impregnation of SiBEA support with V^{V} precursor (aqueous NH_4VO_3 solution) [16]. As previously reported [17,18], these extra-lattice V^{V} species are less active in oxidative dehydrogenation (ODH) of alkanes than lattice V^{V} species due to their higher electron-acceptor character (higher Lewis acidity) [16].

Calcination of $V_{0.26}$SiBEA, $V_{0.68}$SiBEA and $V_{1.36}$SiBEA at 773 K for 2 h in flowing oxygen induces a strong shift of the bands to shorter wavelength. This is shown in Fig. 1d for C-$V_{0.68}$SiBEA with the broad band probably around 230 nm and with a shoulder at 275 nm. The DR UV–Visible spectra of Hyd-C-$V_{0.26}$SiBEA, Hyd-C-$V_{0.68}$SiBEA and Hyd-C-$V_{1.36}$SiBEA, samples hydrated in moist air, exhibit two bands at 263 and 375 nm, as shown for Hyd-C-