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Low-Temperature Copper Intercalation in Sodium Vanadium Oxibronze: Preparation and Characterization

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The vanadium oxibronze α'-NaV_2O_5 reacts with $CuCl_2$ in water at 373 K affording a new compound, $Cu_{0.5}V_2O_5(H_2O)_{0.5}$, which has a high surface area for such an unsupported phase. The overall process is described as the replacement of two sodium ions by one copper ion and one water molecule. Structural and chemical investigations by visible and IR spectroscopy, X-ray powder diffraction, thermal analyses, and oxidation studies are described. It is suggested that the metastable structure of $Cu_{0.5}V_2O_5(H_2O)_{0.5}$ is reminiscent of the lamellar character of the precursor phase α'-NaV_2O_5. Heat treatment under inert atmosphere first leads to amorphization *via* dehydration with an activation energy of 110 kJ mol^{-1}, then to the β'-$Cu_{0.5}V_2O_5$ phase formation at 973 K. The oxidizing properties *vs* hydrogen and carbon monoxide are compared with those of related compounds. For carbon monoxide oxidation, the temperature of carbon dioxide formation follows the order V_2O_5 > α'-NaV_2O_5 > β'-$Cu_{0.5}V_2O_5$ > CuO/V_2O_5 > $Cu_{0.5}V_2O_5$. Therefore the presence of copper involves a greater lability of the oxygen atoms of the V_2O_5 lattice. This effect is enhanced with the new compound $Cu_{0.5}V_2O_5$. Preliminary results in the catalytic decomposition of 2-propanol show that $Cu_{0.5}V_2O_5$ is selective for the oxidative dehydrogenation route whereas the other compounds are also active for dehydration.

Introduction

Catalysts comprising vanadium pentoxide as the basic component have long been known for promoting oxidation reactions of organic compounds.[1-6] The selectivity and activity are closely related to the oxidation state of vanadium ions and are enhanced by the presence of an average oxidation state in the range +4 to +4.6.[2,4,7-11] To our knowledge, few studies have been carried out using vanadium oxibronzes, although they contain vanadium ions in oxidation states +4 and +5 with various stoichiometries according to the nature and the number of the cations incorporated in the vanadium pentoxide matrix.[12-15] One of the reasons is the preparation conditions which involve conventional powder processing at high temperature, generally above 823 K, therefore affording materials with low surface areas, a drawback for catalytic applications.[16-20] Moreover large amounts of such materials are not easily obtained through a one-batch synthesis at the laboratory scale.

Our interest in vanadium oxibronzes containing copper ions has been focused on the development of new preparation procedures at temperatures generally lower than 373 K.[21] Such mild conditions enable metastable structures to be produced with high surface areas and enhanced catalytic properties. More specifically, it can be expected that the lamellar structure of the parent compound V_2O_5 will be retained.[22,23] This paper describes the incorporation of copper ions in the V_2O_5 matrix under mild conditions. The precursor chosen was α'-NaV_2O_5 which affords, like V_2O_5, an orthorhombic phase. The sheets are constituted of VO_5 square pyramids, sharing edges and corners, parallel

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to the *b* axis with sodium ions between.[17] The new copper-containing compound was characterized by thermogravimetry (TG), differential thermal analysis (DTA), visible and IR spectroscopy, X-ray powder diffraction (XRD) and temperature-programmed reduction (TPR). Its catalytic activity in the oxidation of carbon monoxide has also been measured as well as in the decomposition of 2-propanol and compared to that of V_2O_5, α'-NaV_2O_5, CuO supported on V_2O_5, and β'-$Cu_{0.5}V_2O_5$. The latter compound exhibits a monoclinic phase in which the sheets are constituted of oxygen polyhedra with a common atom giving rise to true tunnels where copper atoms occupy a toric section in a wide oxygen trigonal bipyramid.[24,25]

Experimental Section

α'-NaV_2O_5 and β'-$Cu_{0.5}V_2O_5$ were prepared from vanadium pentoxide (Merck) and sodium oxalate (copper oxalate) according to ref 20.

The incorporation of copper ions into α'-NaV_2O_5 was performed as follows. To α'-NaV_2O_5 (4 g, 19.5 mmol) in 150 mL of degassed distilled water was added $CuCl_2{\cdot}2H_2O$ (3.33 g, 19.5 mmol). The suspension then was refluxed under argon for 2 weeks and filtered, and the resulting solid washed with distilled water until the chloride test with $AgNO_3$ was negative. Finally the solid was dried under vacuum for 12 h at room temperature. The reaction was followed by taking aliquots (1 mL) of the solution for recording the copper concentration changes by visible spectroscopy on a Cary 219 instrument. At the same time aliquots (30 mg) of the solid were also examined by IR and XRD. The IR spectra were recorded on a Perkin-Elmer 983 spectrometer coupled with a 3600 data station, the samples being dispersed in Nujol and settled between NaCl windows. The X-ray powder patterns were recorded at room temperature and in ambient air using an XRD 3000TT Seifert diffractometer equipped with a back graphite monochromator (Cu Kα_1, λ = 0.154 059(8) nm).

Supported copper oxide on vanadium pentoxide (2.9 wt % CuO) was prepared by impregnation with $CuCl_2$ followed by calcination for 12 h at 753 K.

The surface areas of the solids were determined by nitrogen adsorption at 77 K by using the BET method. Elemental analyses were performed at the Service Central d'Analyses du CNRS, Solaize.

Thermogravimetric and thermal analyses were respectively performed on a TG85 Setaram thermobalance and on a M5 Setaram analyzer, both under a constant flow of helium (33 mL min^{-1}) with a 3 K min^{-1} heating rate.

Temperature-programmed reductions were performed with 50 mg of the sample under a constant flow (50 mL min^{-1}) of hydrogen or carbon monoxide using a procedure described previously.[26] The heating rate was fixed at 7 K min^{-1} under hydrogen and 2 K min^{-1} under carbon monoxide. The formation of water or carbon dioxide was monitored with the katharometer detector of an Intersmat 120 MB chromatograph. The experimental error in the temperatures, T_m, corresponding to the maxima of the desorption peaks was ±5 K.

The catalytic activity for carbon monoxide oxidation was carried out in a fixed-bed reactor at atmospheric pressure with a mixture of CO, O_2, and N_2 (balance gas) in the ratio 1:2.5:10. The contact time expressed as the ratio of the sample weight to the mass flow of CO was fixed at a value of 7 min. The extent of the reaction was determined by gas chromatography analysis with an Intersmat 120 MB instrument using a Carbosphere column (L = 3.0 m, ϕ = $^1/_8$ in., 80–100 mesh) fitted with a katharometer detector.

For the catalytic decomposition of 2-propanol, the same reactor was used with a mixture of 2-propanol, O_2, and N_2 (balance gas) in the ratio 1:8:31; the contact time was fixed at 16.9 min. Product analysis was performed by gas chromatography with an Intersmat 120 FL instrument using a 10% Carbowax 20M/Gas Chrom Q column (L = 2.0 m, ϕ = 1/8 in., 100–200 mesh) fitted with a flame ionization detector.

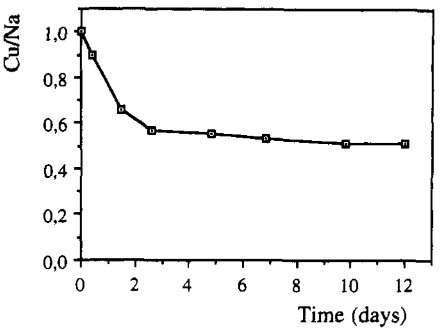

Figure 1. Time evolution of the concentration of soluble $[Cu(H_2O)_6]^{2+}$ ions normalized to the initial ratio Cu/Na.

Results and Discussion

Reaction of $CuCl_2$ with α'-NaV_2O_5 in Water. The reaction in refluxed water (1:1 stoichiometry) was followed by monitoring the disappearance with time of $[Cu(H_2O)_6]^{2+}$ ions in solution by visible spectroscopy (λ = 790 nm). Figure 1 reports this variation which is normalized to the initial ratio Cu/Na.

Nearly half of the initial copper ions present in solution disappeared within two days. During this period swelling of the solid was observed. After 6 days a plateau was attained. The maximum amount of copper ions incorporated in the solid corresponds to a Cu/Na ratio of 0.5. The elemental analysis of the solid obtained after 10 days of reaction showed a stoichiometry Cu/2V = 0.5 with no chloride and sodium ions left after washing. Hence the incorporation of copper in the V_2O_5 matrix is achieved through an ion exchange Cu^{2+}–Na^+. Two sodium ions are replaced by one copper ion.

Concomitantly to the analysis of the solution, the solid was examined by IR and X-ray powder diffraction. The XRD spectra of samples taken from the reaction medium, washed with distilled water and further dried under vacuum at 393 K showed that after 2 days the characteristic lines of α'-NaV_2O_5 were strongly decreased while new diffraction lines appeared and increased for 7 days and remained unchanged up to 2 weeks. However, the more intense diffraction lines (h,k,0) of α'-NaV_2O_5 were still present. This result indicates that only the *c* parameter representing the interlayer distance of the lamellar structure of α'-NaV_2O_5 was modified during the reaction.[17] The IR study of the solid showed that after 3 days of reaction, modification of the bands in the range 1200–400 cm^{-1} was occurring. Moreover new bands relevant to the presence of water in the structure appeared at 3600, 3480, 3420, and 1620 cm^{-1} (Figure 2). Therefore the composition of the final product from the reaction of $CuCl_2$ with α'-NaV_2O_5 corresponds to $Cu_{0.5}V_2O_5{\cdot}x(H_2O)$.

Thermogravimetric Analysis. The presence of water detected by IR was quantified by TG on the final product, and DTA analysis was performed (Figure 3).

The DTA curve (Figure 3a) exhibits three endothermic peaks at 383, 523, and 961 K. The last peak is not accompanied by a weight loss in the TG experiment (Figure 3b) and has a profile characteristic of a phase transition. The other two peaks correspond to weight losses due to two types of water. The first type has an activation energy

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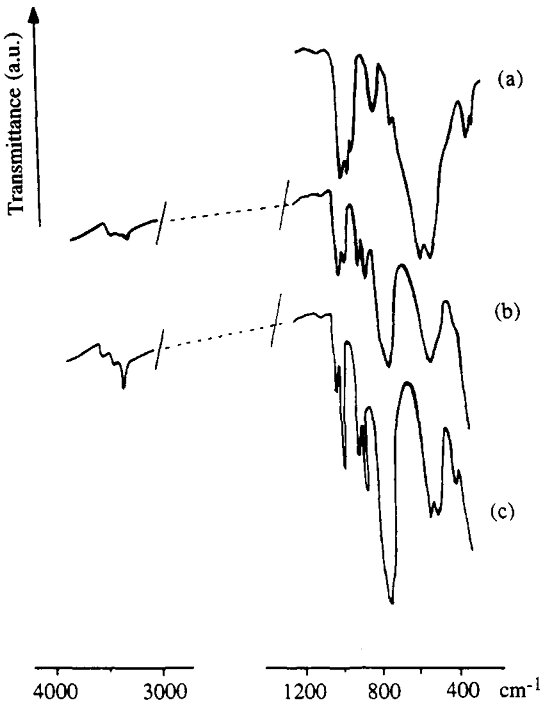

Figure 2. IR spectra (a) α'-NaV_2O_5, (b) taken after 3 days of reaction, and (c) after 15 days.

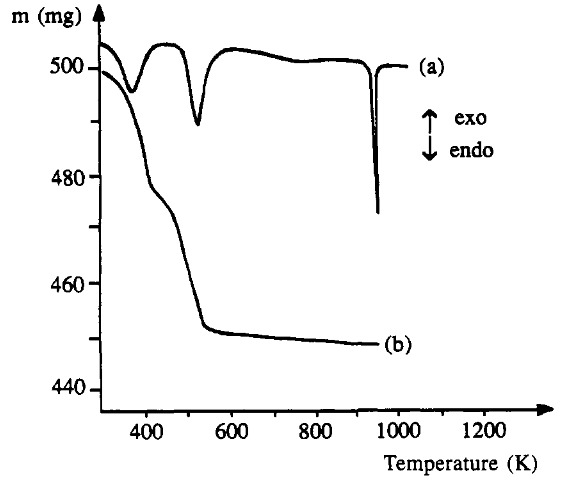

Figure 3. TG and DTA of $Cu_{0.5}V_2O_5{\cdot}x(H_2O)$ under helium at 3 K min^{-1} heating rate: (a) DTA; (b) TG.

for desorption of 48 ± 5 kJ mol^{-1}. This value is in agreement with those already reported for dehydration of the V_2O_5 surface.[27] The second type of water has a higher activation energy for desorption: 110 kJ mol^{-1}, and a 1:1 H_2O to Cu stoichiometry was determined after a pretreatment of 2 h at 383 K. Therefore, this strongly held water is a component of the structure leading to the formula $Cu_{0.5}V_2O_5(H_2O)_{0.5}$. As shown by an XPS study, these water molecules do not appear to be coordinated to the copper ions.[28] Hence the complete substitution of sodium in α'-NaV_2O_5 is equivalent to the replacement of two sodium ions by one copper ion and one water molecule. The new compound obtained, $Cu_{0.5}V_2O_5(H_2O)_{0.5}$, does not exhibit intense XRD lines and possesses a high surface area (21 m^2 g^{-1}). The amorphization was enhanced by dehydration at 543 K. A further thermal treatment at 973 K led irreversibly to the XRD pattern of the already known β'-$Cu_{0.5}V_2O_5$ phase.[24,25]

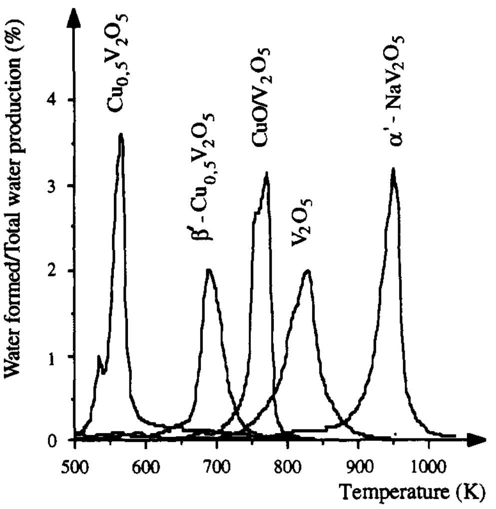

Figure 4. TPR profiles under atmospheric pressure of hydrogen at 7 K min^{-1} heating rate for the studied compounds.

Table I. T_m Values and H_2O Stoichiometries for Reduction under H_2

compound	T_m main peak, K	total H_2O produced, mol/$M_xV_2O_5$ unit
V_2O_5	823	2.00
α'-NaV_2O_5	951	1.47
β'-$Cu_{0.5}V_2O_5$	691	1.97
$Cu_{0.5}V_2O_5$	565	1.92
CuO/V_2O_5	774	2.00

Temperature-Programmed Reduction under Hydrogen. The formation of water by reduction under pure hydrogen has been studied after dehydration of $Cu_{0.5}V_2O_5(H_2O)_{0.5}$ under helium at 523 K. For comparison the related compounds V_2O_5, α'-NaV_2O_5, β'-$Cu_{0.5}V_2O_5$, and supported CuO on V_2O_5 (2.9 CuO wt %) were also studied. The TPR profiles of water production as the temperature increases are reported in Figure 4. One main peak is present for each sample. Its maximum corresponds to a temperature, T_m, which characterizes the reducibility of the system. Clearly the copper-containing samples have the lowest values, indicating a lower activation energy of the reduction process. Among them the new compound, $Cu_{0.5}V_2O_5$ is reduced at the lowest temperature. The order of reducibility observed is as follows:

$$Cu_{0.5}V_2O_5 < \beta'\text{-}Cu_{0.5}V_2O_5 < CuO/V_2O_5 < V_2O_5 < \alpha'\text{-}NaV_2O_5$$

with the major peaks appearing at 560, 683, 774, 830 and 950 K, respectively. It is noteworthy that the profiles of the copper-containing samples, including CuO/V_2O_5, are not the superposition of the reduction of CuO and V_2O_5. A mechanical mixture composed of 15 wt % CuO and 90 wt % V_2O_5 exhibits two peaks at 523 and 820 K due to the reduction of CuO and V_2O_5, respectively.

The quantitative analysis of the water evolved during the reduction is reported in Table I. Under these experimental conditions V_2O_5 is reduced to V_2O_3 with the evolution of 2 mol of water/V_2O_5. The reduction of α'-NaV_2O_5, which contains V^{4+} and V^{5+} ions in a 1:1 ratio, produces 1.47 mol of water, close to the theoretical value of 1.5 mol for the final oxidation state V^{3+}. For the copper-containing compounds, the XRD spectra of the reduced

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Table II. T_m Values and CO_2 Stoichiometries for Reduction under CO

compound	T_m, K peak	T_m, K reverse peak	CO_2 produced, mol/$M_xV_2O_5$ unit
V_2O_5	828		2.00
α'-NaV_2O_5	804		1.61
β'-$Cu_{0.5}V_2O_5$	671	719	$\gg 2$
$Cu_{0.5}V_2O_5$	554	628	$\gg 2$

samples show only the diffraction of metallic copper. No vanadium oxide phase could be detected. Water formation close to 2 mol indicates that the final oxidation state of vanadium is also +3.

The activation energies have been determined from T_m variations of the main peak with the heating rate for $Cu_{0.5}V_2O_5$, β'-$Cu_{0.5}V_2O_5$, and V_2O_5 samples.[26] In our experimental conditions, the degree of reduction corresponding to the maxima of the main peaks nether exceeded 3.7% of the total value obtained (Figure 4). Therefore the determination of the activation energies does not appear to be perturbed by any heat release from the samples. The values were found to be 52, 90 and 83 ± 5 kJ mol^{-1} for $Cu_{0.5}V_2O_5$, β'-$Cu_{0.5}V_2O_5$, and V_2O_5, respectively. Hence $Cu_{0.5}V_2O_5$ is different from the other compounds since it exhibits the lowest value which reflects the enhancement of the lability of the lattice oxygen atoms of the V_2O_5 host.

Temperature-Programmed Reduction under Carbon Monoxide. The reduction of the copper-containing compounds under atmospheric pressure of carbon monoxide occurs at lower temperatures, similar to that under hydrogen (Table II). The reverse order of reducibility observed between α'-NaV_2O_5 and V_2O_5 for which V_2O_5 is reduced at higher temperature is assigned to the difference in the activation modes of hydrogen and carbon monoxide. The adsorption of carbon monoxide is associative whereas that of hydrogen involves a dissociative process.

The stoichiometry of the reduction is the same as that found under hydrogen for α'-NaV_2O_5 and V_2O_5. The final oxidation state of vanadium is +3 (Table II). For the copper-containing samples, the stoichiometry was always found to be above 2 and could not be quantified very precisely. It is noteworthy that the TPR profiles include a negative peak after the reduction peak (Figure 5a). This phenomenon is attributed to carbon monoxide consumption without the compensation of gaseous product formation. Such a behavior has been previously described by Severino *et al.*[29] for cupric oxide supported on alumina. These authors suggested the possibility of CO consumption through Boudouard's reaction ($2CO \rightarrow C + CO_2$). The comparison of the TPR profile (Figure 5a) with the production of CO_2 analyzed by GC (Figure 5b) shows that to the negative peak corresponds an important formation of CO_2. To prove the occurrence of Boudouard's reaction, the TPR of $Cu_{0.5}V_2O_5$ was performed after a prereduction under hydrogen at 623 K (Figure 5c). During the temperature increase the baseline is shifted toward the negative values which means that the CO consumption is higher than the CO_2 production as the result of carbon deposition on the sample.

Catalytic Carbon Monoxide Oxidation. Table III reports the activities, normalized to surface areas, at 523 K to avoid Boudouard's reaction on the copper-containing samples. The highest activity is found for the new compound $Cu_{0.5}V_2O_5$. The V_2O_5 and α'-NaV_2O_5 samples are inactive at 523 K. Therefore the comparison between all the compounds studied is better achieved by determining the reaction temperature giving the same conversion with carbon monoxide. The temperatures for 0.5% isoconversion are reported in Table III. From these values it can be deduced that the activity in carbon monoxide oxidation increases in the order

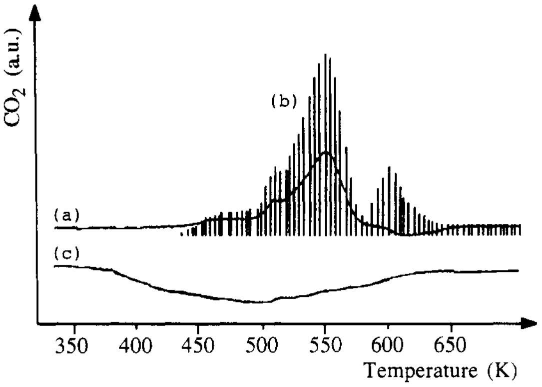

Figure 5. Carbon dioxide formation with the temperature at 2 K min^{-1} heating rate for $Cu_{0.5}V_2O_5$: (a) TPR profile, (b) simultaneous GC analysis, and (c) TPR profile after hydrogen reduction at 623 K.

Table III. Surface Areas, Intrinsic Activities, and Temperatures for Isoconversion (0.5%) in Carbon Monoxide Oxidation

compound	surface area, m^2 g^{-1}	activity, 10^{-8} mol m^{-2} s^{-1}	T (0.5%), K
V_2O_5	4.8	0	895
α'-NaV_2O_5	0.6	0	833
β'-$Cu_{0.5}V_2O_5$	1.0	5.2	588
CuO/V_2O_5	7.2	5.7	518
$Cu_{0.5}V_2O_5$	21	8.1	475

$$V_2O_5 < \alpha'\text{-}NaV_2O_5 < \beta'\text{-}Cu_{0.5}V_2O_5 < CuO/V_2O_5 < Cu_{0.5}V_2O_5$$

To reach 0.5% conversion, it is necessary to perform the reaction at 895 and 833 K for V_2O_5 and α'-NaV_2O_5, respectively. The order of activities observed is in agreement with that obtained by TPR under carbon monoxide (Table II). The onset temperatures for carbon dioxide formation in TPR experiments and in catalytic studies are very close.

Catalytic Decomposition of 2-Propanol. The compounds $Cu_{0.5}V_2O_5$, β'-$Cu_{0.5}V_2O_5$, CuO/V_2O_5, and V_2O_5 were pretreated at 523 K under helium and examined for 2-propanol decomposition under oxidative conditions between 373 and 523 K. The alcohol undergoes decomposition into acetone *via* oxidative dehydrogenation and into propene and diisopropylether *via* the dehydration process (diisopropyl ether was equivalent to propene). Both reactions coproduce water. The selectivity (dehydration *vs* dehydrogenation) has been used as a probe for the acid-base properties of oxides.[30] For vanadium-based oxides, Lewis acid centers are responsible for dehydration, whereas basic sites are involved in dehydrogenation.[31,32]

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Table IV. Intrinsic Activities in 2-Propanol Decomposition and Temperatures for Isoconversion (10%)

	dehydration		oxidative dehydrogenation	
compound	activity, 10^{-8} mol m^{-2} s^{-1}	*T* (10%), K	activity, 10^{-8} mol m^{-2} s^{-1}	*T* (10%), K
V_2O_5	51.6	405	5.2	480
β'-$Cu_{0.5}V_2O_5$	38.0	475	21.0	490
CuO/V_2O_5	3.7	490	4.2	460
$Cu_{0.5}V_2O_5$	0.4	495	25.9	415

Table IV reports the intrinsic activities for both reactions at 523 K and the temperature for isoconversion (10%) on four catalysts.

V_2O_5 and β'-$Cu_{0.5}V_2O_5$ are the most active systems, and CuO/V_2O_5 is by far the least active one. The catalysts exhibit also different selectivities. Dehydration is predominant over V_2O_5 in agreement with published data,[32,33] whereas the bronze β'-$Cu_{0.5}V_2O_5$, together with CuO/V_2O_5, has comparable dehydration and dehydrogenation activity. Interestingly the new compound $Cu_{0.5}V_2O_5$ is selective in the dehydrogenation reaction. These results have to be compared with those obtained for different phases of vanadium alkali bronzes.[32] It was found that the α-phases $Li_{0.02}V_2O_5$, $Na_{0.02}V_2O_5$, and $Na_{0.06}V_2O_5$ were selective toward dehydration, whereas the β-phases $Li_{0.33}V_2O_5$ and $Na_{0.33}V_2O_5$ gave comparable amounts of dehydration and dehydrogenation. The enhancement of dehydrogenation activity was attributed to the increase in V^{4+}:V^{5+} ratio. Like β'-$Cu_{0.5}V_2O_5$, the new compound $Cu_{0.5}V_2O_5$ has a V^{4+}:V^{5+} ratio of 1. Therefore, the selectivity changes which are observed are due to additional factors which have not been identified through this preliminary study but which could be related to structural differences. Further characterization by EXAFS is in progress to get more data on the coordination shells of copper and vanadium. It is noteworthy that the promoting effect of a metallic ion on the lability of the oxygens of the V_2O_5 matrix was also proposed for a supported palladium catalyst to explain the selective oxidation of ethylene into acetic acid at 473 K.[34]

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