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Intercalation Chemistry in Layered Transition Metal Oxide Structures: Pyridine Vanadium Pentoxide

JEAN-MICHEL SAVARIAULT, DOMINIQUE LAFARGUE,
JEAN-LUC PARIZE, AND JEAN GALY

Centre d'Elaboration de Matériaux et d'Etudes Structurales-C.N.R.S.,
29 rue Jeanne Marvig, BP4347, 31055 Toulouse Cedex, France

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The reaction of pyridine, pyrazine, phenazine and 4-4'dipyridine in *m*-xylene solutions on V_2O_5 yields new intercalation compounds. Only the pyridine compound corresponds to a definite formula: $V_2O_5(C_5H_5N)_{1.1}$. The EXAFS study at the vanadium *K*-edge is consistent with a pyridine molecule bonded to every second vanadium atom of the layer via coordination bond of length V–N = 2.34 Å. From X-ray powder diffraction study, the orthorhombic crystal cell (a = 11.543(8) Å, b = 7.111(4) Å, c = 21.56(1) Å) is built up from two V_2O_5 layers separated by 6.2 Å, leading to a value expected for pyridine intercalation. Temperature dependent susceptibility measurements show that 10% of the total vanadium is in oxidation state IV. An interpretation of the presence of the V^{4+} is established on the basis of the mechanism involved in oxidation reactions catalyzed by V_2O_5.

Introduction

Among its various properties, V_2O_5 has been known to catalyze oxidation reactions since the 1920s, for example, phthalic acid and naphthoquinone (1922) (*1*) or sulfuric acid synthesis (1928) (*2*). It is now well recognized that surface V═O bonds play an important role in catalysis, and mechanisms are proposed which involve vanadium–oxygen bond breaking (*3*).

V_2O_5 exhibits a lamellar structure, the $[V_2O_5]$ layers being built up from VO_5 square pyramids sharing edges and corners (*4–6*). The sheets are held together via weak interactions between the vanadium atoms and the oxygen atoms at the apex of the VO_5 square pyramids of neighboring layers (the V · · · O distance is roughly 2.88 Å) (*6*).

This vanadic oxide is the origin of a wide family of non-stoichiometric insertion compounds called "vanadium oxide bronzes," $M_xV_2O_5$ or $M_x^{n+}V_{2-nx}^{5+}V_{nx}^{4+}O_5$, with M = alkaline metals (*7–14*). Such compounds exhibit electrical properties that are characterized by a remarkable anisotropy: they are all conductors or semiconductors (*15, 16*). It has been possible to dope the V_2O_5 network by intercalation of various cations between the layers without drastic reorganization of the structure (for values of x below 0.02). In one case, a high level of insertion of sodium atoms was attained, $0.7 \leq x \leq 1.0$, without a change of the V_2O_5 layer structure (VO_5 square pyramids being occupied by V^{4+} or V^{5+} cations), and strong electronic localization inducing an ordering between vanadium sites has been demonstrated (*17*). All these compounds in their various phases were prepared by solid state reactions.

New remarkable ways of synthesis were proposed for lithium and sodium vanadium

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oxide bronzes at room temperature by using *t*-butyl lithium or sodium (*18*) or metal iodides (*19, 20*).

Interesting coordination intercalation reactions of pyridine have also been demonstrated in layered compounds such as MoO_3 and $VOMO_4$ (M = P or As) involving little or no reduction of Mo(VI) or V(V) (*21, 22*). Moreover, interlayer adsorption of pyridine and ammonia was demonstrated in V_2O_5 xerogel (*23*).

It is therefore of considerable interest to develop chemistry around the pure V_2O_5 oxide or related layered structure of vanadium oxide bronzes and to synthesize new types of "organic vanadium oxide bronzes," i.e., to introduce neutral molecules into the lattice.

Experimental Section

V_2O_5 microcrystalline powder of controlled purity (99.6% in V(V)), was carefully dried and added to solutions in *m*-xylene of the following organic compounds: pyridine, pyrazine, phenazine, and 4-4'dipyridine. An excess of some 200% was used relative to a 1 : 1 addition reaction. The experiments were carried out at 150°C under nitrogen to avoid the oxidation reaction of *m*-xylene catalyzed by V_2O_5. Some experiments were carried out in pure pyridine corresponding to molecular ratios varying in the 0.3–60.0 range.

The progress of the reaction was followed by systematic X-ray powder pattern techniques until no variation of the spectrum was observed.

In each case the resulting product of the synthesis consists in an olive-green powder in an orange liquor.

The chemical analysis of the solution, followed by IR and ^1H NMR investigations, yields evidence for the presence of water. The solution coloration is reasonably attributed to dissolved V_2O_5, such an assertion being supported by the growth of V_2O_5 microcrystals after slow evaporation of the solution.

The solid compound, a finely divided powder, keeps its color after it is washed with benzene and vacuum dried. In air it turns slowly dirty yellow, due to a progressive direction oxidation: The amount of vanadium(V) as a percent of the total vanadium increases from 32.5 to 33.7% in 1 week.

The results of the elemental chemical analysis are summarized in Table I. The rather large uncertainty in most of the data is due to the difficulty in ashing these compounds.

Only the compound obtained by intercalation of the pyridine, which corresponds to a ratio C_5H_5N/V_2O_5 close to 1, is a badly crystallized powder showing a new X-ray pattern; the other compounds are amorphous. A more thorough study of the pyridine adduct has been performed in order to elucidate its structure. This compound of formula $V_2O_5(C_5H_5N)_{1.1}$, is named V_2O_5py in the following study.

Physical and Chemical Study of V_2O_5py

Infrared Study

The infrared spectrum was obtained on a PE1725X FTIR in the 4000–400 cm^{-1} with a resolution of 4 cm^{-1} in the whole range. The transmission of the sample, V_2O_5py in KBr pellets, varies from 82 to 17%. A listing of the absorption bands is provided in Table II along with spectra obtained for MoO_3py and WO_3py (*21*), $VOPO_4$py (*22*), and V_2O_5 pyH^+ xerogel (*23*). In the region of the stretching vibrations of the pyridine ring, 1650–1400 cm^{-1}, the bands are characteristic of a pyridine bonded to a metal: the strong band located at 1445 cm^{-1} is characteristic of a Lewis bonded pyridine; the Brønsted bonded pyridine, i.e., the pyridinium ion, exhibits a large band at 1535 cm^{-1} which is missing in V_2O_5py. Moreover, the bands of the spectrum attributed to the pyri-

TABLE I

ELEMENTAL CHEMICAL ANALYSIS (%)

Organic moiety	V_{tot}	V(V)	V(IV)	C	N	H
Pyridine (exp.)	36.5(5)	32.5(5)	4.0(3)	24.97(3)	5.37(3)	2.2(8)
(calc.)	37.9			24.6	5.73	2.06
Pyrazine	46.9(5)	43.2(5)	3.7(3)	1.75(4)	0.13(6)	0.5(9)
Phenazine	40.8(6)	37.7(6)	3.1(5)	3.96(6)	0.29(5)	—
4-4′dipyridine	37.8(4)	31.4(5)	6.4(4)	4.30(5)	0.86(5)	1.1(8)

Note. The results of the elemental analysis of the compound with pyridine correspond to the average of values found for five samples obtained from syntheses done under different experimental conditions. The calculated values correspond to the formula $V_2O_5(C_5H_5N)_{1.1}$.

dine are like the ones observed in $VOPO_4$py (*21*). The first two bands, characteristic of V_2O_5, at 1030 and 835 cm^{-1} are shifted to lower wave numbers, i.e., to 970 and 795 cm^{-1}. The set of three bands at 603, 529, and 495 cm^{-1} are reduced to one huge band at 520 cm^{-1} with a shoulder at 490 cm^{-1}. Such variations indicate a modification of the surrounding to the vanadium atoms, as, for example, a loss of the V–O interactions

TABLE II

INFRARED STUDY OF PYRIDINE INTERCALATED COMPOUNDS (cm^{-1})

	V_2O_5py	Mo_3py (*21*)	WO_3py (*21*)	$VOPO_4$py (*22*)	V_2O_5pyH$^+$ (*23*)	V_2O_5
ν_{CH}	3112			3090		
	3076			3075		
	3047					
ν_{ring}	1631	1644	1647	1628	1637	
	1605	1603	1605	1605	1607	
	1572	1573	1572	1573		
			1538		1534	
	1485	1486	1488	1489	1488	
	1445	1443	1446	1447		
δ_{CH}	1238	1239	1239			
	1225	1220	1220	1222		
	1152	1156	1159			
	1069	1062	1063			
	1043	1041	1042			
	1017	1012				
	755			760		
	689			695		
δ_{ring}	638			626		
	427			431		
ν_{VO}	968					1036
	794					837
						603
	520					529
	490					495

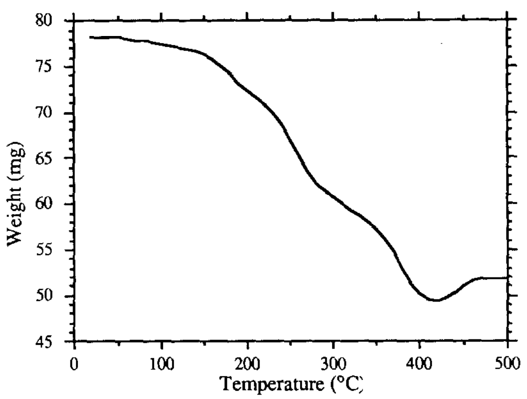

FIG. 1. TGA study of V_2O_5py.

between the layers, an increase of the V–O bond Pengths, due to the formation of V^{4+} (*17*), or a change of the symmetry of the coordination polyhedra around the vanadium atom by coordination of the pyridine.

EPR and Magnetic Study

EPR investigations were carried out on a Brucker ER200D at room temperature. The broad peak, 200 gauss in width, with g = 1.97, corresponds to a V^{4+} cation. The magnetic study was done on a computer-controlled Faraday-type magnetometer in the temperature range 300–90 K. The material is paramagnetic and follows the Curie–Weiss law: $\chi = 0.388(8)/(T\text{-}0.3(2))$. The effective moment, μ_{eff} = 1.737 BM confirms the existence of some vanadium atoms in the oxidation state IV. This permits a calculation of the number of V^{4+} in the compound: the amount found, roughly 10% of the total vanadium number, agrees with the corresponding one obtained through elemental analysis, about 11%.

Thermal Study

A TGA experiment, using a SETARAM TGC85 apparatus, was carried out up to 500°C under oxygen with a 2.5°C/mn heating speed. The loss of weight, presented in Fig. 1, exhibits three smooth features in the range from 50 to 420°C. The total loss, 43.5% of weight, corresponds to 1.1 molecules of pyridine per V_2O_5 unit which confirms the formula obtained by chemical analysis. Since the final compound should be V_2O_5, the observed increase of weight occurring from 420 to 470°C must correspond to an oxidation. In order to determine what was oxidized, the compound was heated at 250°C under vacuum for 6 h. A liquid mixture of essentially water and pyridine (according to IR and ^{1}H NMR investigations) in the proportion of two moles of pyridine per one mole of water (elemental analysis, experimental (calculated): %C = 68.9 (68.2), %H = 7.0(6.8), %N = 15.9(15.9)) was obtained. The composition of the black solid residue, as determined by elemental analysis (%V = 66.0(66.2), %C = 2.1(2.0), %H = 0.3(0.2), %N = 0.5(0.5)), corresponds to the chemical formula $V_2O_3(C_5H_5N)_{0.05}$.

A mass spectroscopy study, performed on a NERMAG R10,10 from 50 to 300°C with a 35 to 500 amu scanning range, indicates (i) up to 220°C, only pyridine is observed; (ii) above 220°C, a peak corresponding to CO_2 occurs.

From such a thermal study and subsequent chemical analysis, it appears that the pyridine molecule remains intact in the oxide network up to a temperature close to 220°C. Above 220°C, the pyridine is oxidized and the vanadium reduced down to the III oxidation state.

X-ray Diffraction Study

X-ray powder diffraction measurements were performed at room temperature for the Cu*Kα* wavelength using a XRD3000TT Seifert diffractometer equipped with a diffracted beam monochromator. The cell determination and the indexation of the powder pattern, displayed in Table III, were obtained using the TREOR program (*24*).

TABLE III

X-RAY PATTERN OF $V_2O_5(C_5H_5N)_{1.1}$

d_{obs}(Å)	d_{calc} (Å)	h	k	l	I_{obs}	d_{obs}(Å)	d_{calc} (Å)	h	k	l	I_{obs}
10.7(1)	10.8	0	0	2	585	2.815(9)	2.828	0	1	7	75
10.2(1)	10.2	1	0	1	1000		2.804	2	1	6	
6.09(4)	6.10	1	0	3	201	2.404(6)	2.405	3	0	7	33
	6.05	1	1	0			2.399	4	0	5	
5.13(3)	5.09	2	0	2	40	2.324(6)	2.328	0	2	7	108
4.02(2)	4.02	1	1	4	76		2.322	1	3	0	
3.98(2)	3.94	2	0	4	76	2.152(5)	2.157	0	0	10	18
3.82(2)	3.81	2	1	3	125		2.152	5	1	2	
3.51(1)	3.51	1	1	5	47		2.149	2	3	2	
	3.51	0	2	1			2.148	0	2	8	
3.38(1)	3.39	1	2	0	114	1.985(4)	1.988	4	2	5	20
	3.39	3	0	3			1.987	0	2	9	
	3.38	3	1	0			1.984	3	3	2	
	3.37	0	2	2		1.925(4)	1.928	5	2	1	27
3.24(1)	3.24	1	2	2	92		1.924	6	0	0	
	3.23	3	1	2		1.775(3)	1.777	0	4	0	43
3.20(1)	3.21	0	1	6	99		1.776	1	0	12	
	3.19	0	2	3			1.775	4	3	3	
3.07(1)	3.07	1	2	3	88		1.772	0	4	1	
	3.06	3	1	3		1.467(2)	1.468	6	1	9	13
2.97(1)	2.97	1	0	7	67		1.467	7	1	6	
	2.97	0	2	4			1.465	7	2	3	
2.927(9)	2.915	2	2	2	88	1.423(2)	1.424	7	1	7	13
2.874(9)	2.886	4	0	0	48		1.422	0	5	0	
	2.875	1	2	4			1.421	1	3	12	
	2.872	3	0	5		1.221(1)	1.222	1	3	15	16
	2.866	3	1	4			1.221	2	1	17	
							1.220	5	0	15	

Note. $a = 11.543(8)$ Å, $b = 7.111(4)$ Å, $c = 21.56(1)$ Å, $V = 1770$ Å^3, $M = 268.9$ g, $d_m = 2.02(8)$, $d_x = 2.02$, $\lambda CuK\alpha = 1.5418$ Å.

A comparison of the crystal cell parameters with those of V_2O_5 (*6*) leads to the following remarks.

— The a parameters are similar in both compounds: 11.54 Å (V_2O_5py) and 11.52 Å (V_2O_5).

— The b parameter is doubled: 7.11 Å (V_2O_5py) against 3.56 Å (V_2O_5).

— The c parameter is larger than the corresponding one: 21.56 Å (V_2O_5py) and 4.37 Å (V_2O_5).

— The unit cell is orthorhombic as in V_2O_5.

The density associated with the volume of the cell and the mass of the formula unit imposes the multiplicity $z = 8$. This multiplicity, compared to the $z = 2$ value in V_2O_5, and the doubling of the b parameter infer that the c parameter corresponds to a doubling of the number of (V_2O_5) layers. The increase of the interlayer space, d, due to pyridine intercalation is equal to 21.56/2-4.37 = 6.3 Å. This distance is comparable to those observed with pyridine intercalated in $VOPO_4$, $d = 5.5$ Å (*25*), and in chalcogenides, $d = 5.9$ Å (*26*). Moreover, the volume occupied by the intercalated pyridine molecules must be equal to the increase between the volume of the cell and the volume of the equivalent number of V_2O_5 cells: $1770 - 4 \times 179 = 1054$ Å^3. Thus, the volume occupied by a molecule of pyridine in V_2O_5py is equal to $1054/8 = 131$ Å^3, a value which is in good agreement with the volume determined earlier by Schöllhorn *et al.* (134 Å^3) (*27, 28*) and by Bak *et al.* (124 Å^3) (*29*).

EXAFS Study

X-ray absorption spectra were recorded in the transmission mode on the DCI-EXAFS spectrometer at LURE (Orsay, France) (*30*). All experiments were done at room temperature near the vanadium K-edge using a step-by-step technique over 1000 eV, with 2 eV steps, and with a one second accumulation time per point. The experiments were calibrated by using the 5463.9 eV peak at the top of the edge of a metallic foil of vanadium. Samples were in the form of well-ground powders of homogenous thickness compressed between two transparent windows. Their masses were calculated to obtain at the edge an absorbance jump of 1. The data analysis was performed according to the classical EXAFS formula developed by Teo (*31*), using the Michalowitz process (*32*) associated with the MINUIT function minimization program (*33*) and the tabulated amplitudes and phase shifts of Teo and Lee (*34*).

In order to avoid systematics errors, and to test the validity of the parameters necessary in EXAFS analysis, a measurement was carried out on V_2O_5, whose structure is known (*6*). In the R space spectrum (Fourier transforms of $k^3[\chi(k)]$) (Fig. 2a), two shells, extending from 1.0 to 2.0 Å and 2.0 to 3.5 Å, were isolated by means of a Fourier filtering technique and were handled separately. The optimization of the structural parameters within a shell is carried out in the wave vector range 4–12 $Å^{-1}$.

The shortest distances shell includes the first coordination sphere of the vanadium atoms. But the huge dispersion of V–O bonds (*6*) does not permit a good fit by use of a single V–O shell. Thus, subshells were included until the calculated distances agreed with the corresponding X-ray structure distances. Such an operational method increases the number of parameters to be fitted; only four V–O subshells were used with the multiplicity adjusted to the one obtained from the X-ray structure. The same process was applied to the second shell, which corresponds to the vanadium–oxygen and vanadium–vanadium intralayer distances. Four subshells were created, with type, distance, and multiplicity taken from the X-ray study. The results of the fits are presented in Table IV; comparison with the corresponding values of the X-ray structure shows that the parameters and the method used are suitable for such study.

The same parameters were introduced in the treatment of the EXAFS signal of V_2O_5py. Figure 3 sums up the EXAFS study, and the results of the refinement are presented in Table V. In the first shell, the best fit was obtained when a V–N subshell, with a multiplicity of 0.5, is added; the agreement factor is thus diminished from 4.5% to 2.3%. The V–N distance derived from the fit shows that the pyridine molecule is bonded via a nitrogen atom to a vanadium atom of the layer. The V–O bonds are larger than the corresponding one observed in V_2O_5.

The second shell is mainly dominated by intralayer distances. The good agreement obtained between calculated and experimental EXAFS spectra, Table V and Fig.

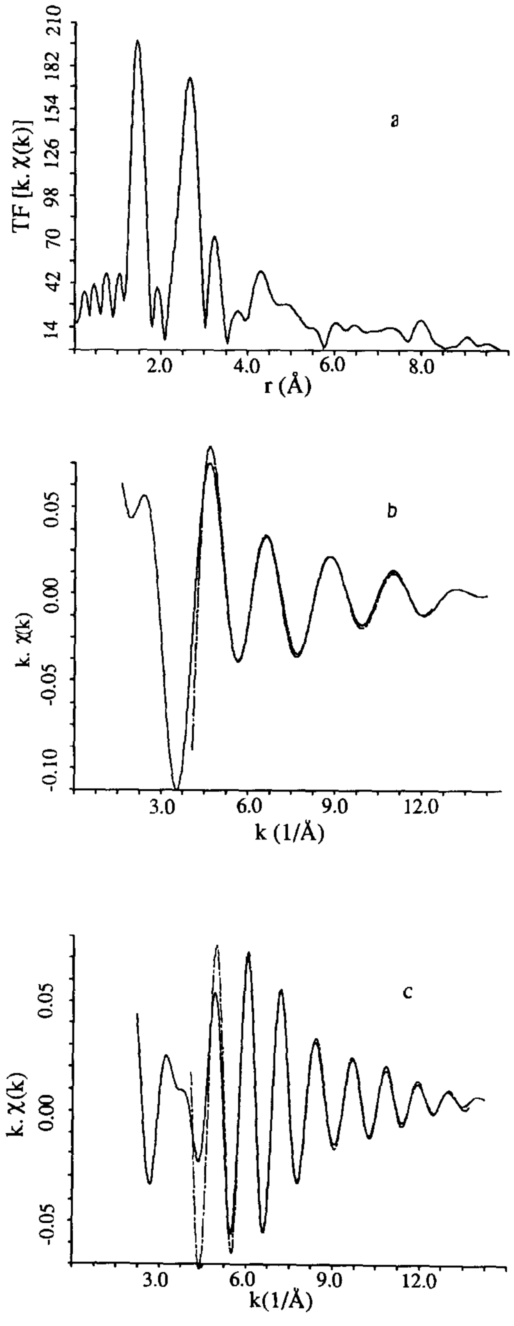

FIG. 2. EXAFS study of V_2O_5 at the vanadium *K*-edge: (a) *R*-space Fourier Transform spectra; (b) EXAFS spectra of region 1.0 to 2.0 Å; (c) EXAFS spectra of region 2.0 to 3.5 Å. Experimental, full line; calculated, dash line.

TABLE IV

EXAFS STUDY OF V_2O_5 AT THE VANADIUM K-EDGE

Subshell	Distance(Å)		Multiplicity	Debye–Waller factor (Å^2)
	X ray (6)	this study		
First shell: threshold energy shift				$\Delta E_0 = 5.0$ eV.
fit index				$\rho = 0.2\%$
V–O	1.577(3)	1.58(2)	1	0.07
V–O	1.779(2)	1.75(2)	1	0.07
V–O	1.878(1)	1.90(3)	2	0.03
V–O	2.017(3)	2.06(3)	1	0.04
Second shell: threshold energy shift				$\Delta E_0 = -3.0$ eV.
fit index				$\rho = 0.1\%$
V–O	2.791(3)	2.86(2)	1	0.03
V–V	3.081(2)	3.10(2)	2	0.06
V–V	3.50(6)	3.60(3)	3	0.06
V–O	3.8(2)	3.70(3)	6	0.09

Note. $\rho = \sum k^3[\chi_{\text{exp}}(k) - \chi_{\text{calc}}(k)]^2 / \sum k^3[\chi_{\text{exp}}(k)]^2$; k, wave vector of the ejected photoelectron; $\chi(k)$, EXAFS modulation; summation of k between 4 and 12 Å^{-1}.

3, supports our hypothesis concerning the presence of a V_2O_5-type layer in the V_2O_5py compound.

Discussion

The physical characteristics of V_2O_5py, a finely divided powder poorly crystallized due to damage caused to the crystallites by intercalation, do not permit a structural investigation using single crystal diffraction techniques. However, a knowledge of the structure is of great importance to confirm the intercalation process and to interpret the physical properties of the material.

Several studies have already shown that pyridine intercalation occurs according to two geometrical types (*25, 26, 35–37*). The first, proposed in metal chalcogenide intercalation studies (*26, 27*), assumes that the plane of the molecular ring of the pyridine is parallel to the layers. The second locates this plane perpendicular to the layers and considers possible interactions between the pyridine and the metal included in the layer (*25, 37*).

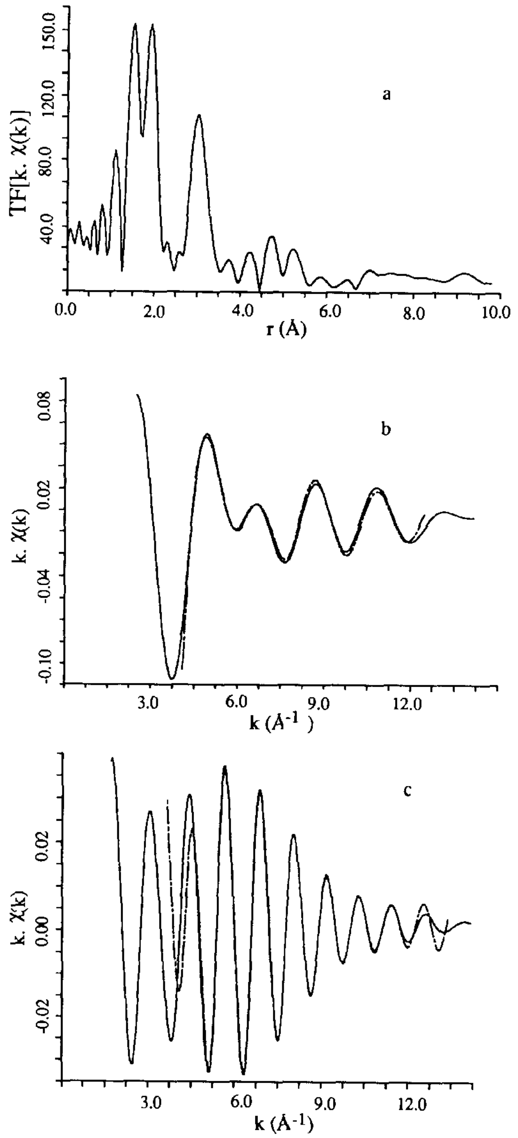

FIG. 3. EXAFS study of V_2O_5py at the vanadium K-edge: (a) R-space Fourier Transform spectra; (b) EXAFS spectra of region 1.1 to 2.5 Å; (c) EXAFS spectra of region 2.7 to 3.5 Å. Experimental, full line; calculated, dash line.

The main results deduced from our experiments are that pyridine effectively is intercalated between the V_2O_5 layers and, moreover, is bonded to the vanadium atoms of the layers. This favors the second geometrical scheme of intercalation. The distance

TABLE V

EXAFS RESULTS OF $V_2O_5(C_5H_5N)_{1.1}$

Subshell	Distances (Å)	Multiplicity	Debye–Waller factors (Å^2)
First shell:	threshold energy shift fit index		$\Delta E_o = 5.0$ eV $\rho = 0.2\%$
V–O	1.62(2)	1	0.06
V–O	1.86(2)	1	0.09
V–O	1.92(3)	2	0.03
V–O	2.05(3)	1	0.06
V–N	2.34(3)	0.5	0.03
Second shell:	threshold energy shift fit index		$\Delta E_o = -3.0$ eV. $\rho = 0.1\%$
V–O	2.75(2)	1	0.06
V–V	3.20(2)	2	0.08
V–V	3.45(2)	3	0.07
V–O	3.60(2)	4	0.03

Note. $\rho = \Sigma\, k^3[\chi_{exp}(k) - \chi_{calc}(k)]^2/\Sigma\, k^3[\chi_{exp}(k)]^2$; k, wave vector of the ejected photoelectron; $\chi(k)$, EXAFS modulation; summation of k between 4 and 12 Å^{-1}.

V–N (2.34 Å) determined from EXAFS measurements is larger than the V–N distance (2.10 Å) observed in molecular complexes (*38*). This long V–N distance is to be correlated with the corresponding expansion of the V–O distances from V_2O_5 to V_2O_5py, as shown in Table VI. Such an increase was already observed in compounds which involved either V^{4+} ions (*17*) or octahedral surrounding of the vanadium atom (*39–41*). Moreover, in the octahedral environment, an axial deformation is observed, with a short V–O bond, 1.7 Å, and a long one, 2.3 Å, corresponding to an offset of the vanadium atom of 0.3 Å outside the basal plane. The V_2O_5py compound, which includes both V^{4+} and octahedral surrounding of the vanadium atom, must involve an expansion of the bonds and a deformation of the octahedral coordination sphere: the V–N bond situated *trans* to the shortest V–O bond, 1.62 Å, is effectively the longest bond, 2.34 Å. A long bond distance associated with weak binding energy can be easily cut. The extraction of pyridine at a temperature lower than 220°C is an indirect way of confirming that pyridine is bonded to vanadium by a weak bond, and consequently the V–N bond distance must be large.

TABLE VI

DISTANCES AROUND VANADIUM ATOM (Å)

			VO$_6$ (octahedral site)		
V_2O_5py	V_2O_5 (*6*)	V^{4+} ions $\alpha'NaV_2O_5$ (*17*)	VOMoO$_4$ (*39*)	V_3O_5 (*40*)	εCuV_2O_5 (*41*)
1.62	1.58	1.69	1.68	1.72	1.61
1.86	1.78	1.80	1.97	1.92	1.78
1.92	1.88	1.93	1.97	1.93	1.93
1.92	1.88	1.93	1.97	2.03	2.10
2.05	2.02	2.01	1.97	2.03	2.10
2.34 (V–N)	2.87		2.59	2.18	2.31

The presence of vanadium in oxidation state (IV) is more difficult to understand. Two principal mechanisms can be invoked to obtain V(IV) in compounds generated from V_2O_5: insertion of a cation, by example $\alpha'NaV_2O_5$ (*17*), εCuV_2O_5 (*41*), or crystallographic shear (*42*). Insertion of cation supposes the presence of a pyridinium cation in the compound. Two observations serve as a basis to reject this hypothesis: No IR band characteristic of pyridinium is observed and pyridinium cannot make a Lewis bond with metals. Crystallographic shears impose both a loss of oxygen atoms and a large change of the structure which is not observed with V_2O_5py; the (V_2O_5) layers are kept and only an increase of the interlayer distance is observed. The mechanism of the oxidation reactions catalyzed by V_2O_5 can give a solution of this problem. In the catalytic process authors agree that the V═O bonds play a preferential role. Moreover, an exchange of the oxygen atom involved in this bond with the oxygen atom of the oxidizing agent is demonstrated (*43–45*). The reaction is of the first order with respect to the surface of the particles, i.e., the number of V═O bonds in the surface, zero order regarding the oxygen pressure, and has an activity energy of only 45 kcal/mole. Assuming that pyridine plays the role of the oxidizing oxygen, the same mechanism, applied in this case, allows one to understand why the same compound is obtained whatever the experimental process is. Since the reaction is carried out at a temperature lower than 150°C, while the catalytic reactions occur above 400°C, only few oxygen atoms can be substituted. This phenomenon, which occurs at the surface of the particles, may explain the excess of 0.1 pyridine found relative to the number of pyridine molecules which can be intercalated, one for every other vanadium atom. From the electroneutrality point of view, the substitution of one pyridine molecule to one oxygen atom occurs during a two electron process, which corresponds to the reduction of two vanadium atoms, from V^{5+} to V^{4+}. The excess of 0.1 pyridine found in the compound must lead to the formation of 0.2 V^{4+}, i.e., 10% of the total amount of vanadium, which is the value found by elemental analysis and a magnetic study.

The compound V_2O_5py is fully characterized and consists of one pyridine molecule coordinated to every other vanadium atom, and a tenth of one pyridine molecule which substitutes for oxygen atoms of the surface of the crystallite, giving rise to the following formula: $V_2[O_{4.9}(C_5H_5N)_{0.1}](C_5H_5N)$. The rather poor precision of the elemental analysis does not permit a confirmation of the oxygen atoms nonstoichiometry.

Conclusion

The chemistry developed around reaction of V_2O_5 with pyrazine, phenazine, and 4-4′dipyridine shows some remarkable possibilities for intercalation but, in such cases, the resulting powders are completely amorphous and are difficult to characterize structurally. However, the tentative model developed for the compound obtained by intercalation of pyridine in vanadium pentoxide is a basis for further investigations:

— to use and to create new layer oxide structures;

— to vary the nature of inserted molecules or ions;

— to explore the potential applications of such compounds with regard to their chemical properties, particularly in the field of catalysis, and their physical properties, particularly, the electric and/or magnetic properties.

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