Communications to the Editor

Nature of the Active Sites for Alkane-Selective Oxidation on Vanadium–Phosphorus Oxides

Guido Busca,[1] Gabriele Centi, and Ferruccio Trifirò*

Istituto Tecnologie Chimiche Speciali
Università di Bologna, Viale Risorgimento 4
40136 Bologna, Italy

Olefins, generally, provide some of the more versatile feedstocks for heterogeneous oxidation reactions, but alkanes are more plentiful and usually less expensive. However, due to the relatively low reactivity of alkanes, practically the only process with high yields in selective oxidation products is the conversion of *n*-butane to maleic anhydride, carried out on vanadium–phosphorus oxide catalysts.[2] This reaction is thus a useful model for studying the nature of the active sites in alkane-selective activation. In fact, in contrast to the well-studied allylic mechanism of oxidation, no comparable data have been published on the nature of active sites for alkane activation.[3-5]

Recently we reported results showing that the rate-limiting step for *n*-butane oxidation to maleic anhydride is the formation of the corresponding olefins.[4] Furthermore we have indicated[6-10] that it is possible to prepare the $(VO)_2P_2O_7$ pure active phase in two ways differing as regards the solvent used in the preparation of these compounds: (1) an aqueous medium or (2) an organic medium. The second method results in a $(VO)_2P_2O_7$ with (i) a preferential exposition on the surface of the (020) plane, (ii) a much higher activity in *n*-butane oxidation, and (iii) a similar activity in but-1-ene oxidation.[9-10] The $(VO)_2P_2O_7$ phases prepared by the two different methods, therefore, differ as regards the presence of the specific sites of *n*-butane activation.

Reported in this paper are results of a study on the nature of these sites, involving the relationships between surface acidity, surface structure of the $(VO)_2P_2O_7$ phases, and their reactivities in alkane-selective oxidation.

Catalyst (a) was prepared with water as the solvent, by reduction of V_2O_5 with 37% HCl, addition of o-H_3PO_4, concentration of the solution, and subsequent addition of water to obtain a blue precipitate which was removed from the solution by filtration. The precipitate was dried in an oven at 150 °C for 24 h. Catalyst (b) was prepared with an organic medium as the solvent, by reduction of V_2O_5 with isobutyl alcohol, addition of o-H_3PO_4, and subsequent filtration of the slurry. The power was dried in an oven at 150 °C for 24 h. Both catalysts were then activated in a flow of 1% *n*-butane in air at 400 °C for 6 h. X-ray diffraction analysis after the catalytic tests showed the presence of only $(VO)_2P_2O_7$ in both catalysts. Spectroscopic measurements were made on the catalysts after the catalytic tests since the catalysts were activated in a flow of *n*-butane/air; no changes either in the activity in *n*-butane oxidation or in the surface properties were noted during the
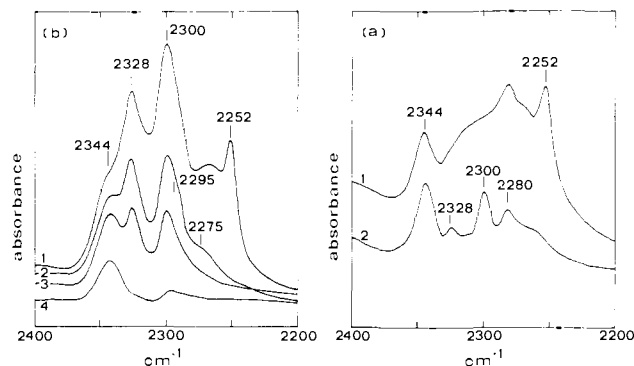
(1) Istituto Chimico, Facoltà di Ingegneria, 40136 Bologna, Italy.
(2) Varma, R. L.; Saraf, D. N. *Ind. Eng. Chem. Prod. Res. Dev.* 1979, *18*, 7.
(3) Centi, G.; Trifirò, F.; Vaccari, A.; Pajonk, G. M.; Teichner, S. *J. Bull. Soc. Chim. Fr.* 1981, *7-8*, 1.
(4) Centi, G.; Fornasari, G.; Trifirò, F. *J. Catal.* 1984, *89*, 44.
(5) Hodnett, B. K.; Delmon, B. *Ind. Eng. Chem. Fundam.* 1984, *23*, 465.
(6) Poli, G.; Resta, I.; Ruggeri, O.; Trifirò, F. *Appl. Catal.* 1981, *1*, 395.
(7) Cavani, F.; Centi, G.; Trifirò, F. *Appl. Catal.* 1984, *9*, 191.
(8) Centi, G.; Manenti, I.; Riva, A.; Trifirò, F. *Appl. Catal.* 1984, *9*, 177.
(9) Busca, G.; Cavani, F.; Centi, G.; Trifirò, F. *J. Catal.*, submitted for publication. Presented at 9th North Amercian Meeting of Catalysis Society, Houston, TX, March 1985.
(10) Cavani, F.; Centi, G.; Trifirò, F. *J. Chem. Soc., Chem. Commun.* 1985, 492.

Figure 1. Fourier-transform infrared spectra (FT-IR) of acetonitrile adsorbed at room temperature [(a, 1), catalyst (a); (b, 1), catalyst (b)] and after different evacuation treatments: evacuation at room temperature for $^1/_2$ h [(a, 2), catalyst (a); (b, 2), catalyst (b)], evacuation at 390 K for 10 min [(b, 3), catalyst (b)], evacuation at 430 K for 10 min [(b, 4), catalyst (b)].

working time (about 100 h) of the catalysts.

In order to study the surface acidity of these oxides, the adsorption of a number of basic molecules (including ammonia, pyridine, CO, and acetonitrile) on our catalysts was followed by FT–IR spectroscopy. The best discrimination between sites having different strengths was obtained by using the very weak base acetonitrile (Figure 1). Several peaks can be distinguished in the ν_{CN} region, beyond the peak at 2345 cm^{-1} which is related to a perturbation of the band of trapped CO_2 formed during the catalytic runs. Evacuation at room temperature caused the disappearance of the maximum at 2252 cm^{-1} which may be assigned to hydrogen-bonded acetonitrile. A similar frequency is observed on H-bonded acetonitrile on Al_2O_3.[11] A simultaneous restoration of the ν_{OH} band due to free OH, perturbed by acetonitrile adsorption, was observed.

The assignment of the remaining bands is more difficult. Acetonitrile is expected to give coordination adducts with exposed coordinatively unsaturated cations and this interaction, according to data from the literature,[11] gives rise in the 2200–2400-cm^{-1} region to two bands due to Fermi resonance between (i) the C≡N stretching (ν_{CN}) and (ii) the combination of symmetric CH$_3$ deformation and C—C stretching ($\delta_{CH_3} + \nu_{CC}$). On liquid acetonitrile these two bands are found at 2254 and 2293 cm^{-1}, respectively, with an intensity ratio of 4.0. On medium-strong Lewis sites, such as ZnO[12] and α-Fe$_2$O$_3$,[13] these two bands are shifted to 2282 and 2300 cm^{-1} with an intensity ratio of 3.0, whereas on very strong Lewis sites, such as on Al_2O_3,[11] the two bands are shifted to higher frequencies, namely, 2328 and 2300 cm^{-1}, with an intensity ratio of 1.0.

On catalyst: (b) the two bands of equal intensity at 2328 and 2300 cm^{-1} that persist even after evacuation at 390 K may be thus assigned to coordinatively bonded acetonitrile on very strong Lewis sites [ν_{CN} and ($\delta_{CH_3} + \nu_{CC}$), respectively]. The weak band at 2275 cm^{-1}, probably related to a weaker adsorption near 2295 cm^{-1}, can be assigned to the ν_{CN} band of acetonitrile adsorbed on medium-strong Lewis sites. On catalyst (a) beyond the band at 2252 cm^{-1}, attributed to H-bonded acetonitrile, the two peaks at 2280 and 2300 cm^{-1} may be attributed to coordinatively bonded acetonitrile on medium-strong Lewis sites; the very weak peak at 2328 cm^{-1}, probably related to a weak adsorption at 2300 cm^{-1}, may

(11) Knözinger, H.; Krietenbrink, H. *J. Chem. Soc., Faraday Trans. 1* 1976, 2421.
(12) Lavalley, J. C.; Gain, C. *C. R. Acad. Sci., Ser. 3* 1979, *288*, 177.
(13) Lorenzelli, V.; Busca, G.; Sheppard, N. *J. Catal.* 1980, *66*, 28.

Table I. Specific Rate per Meter Squared of Surface Area of Maleic Anhydride Formation from *n*-Butane, Specific Rate of *n*-Butane Depletion, and Specific Rate of But-1-ene Depletion on the Catalysts (a) and (b)[a]

| catalyst | temp, K | *n*-butane oxidn | | but-1-ene oxidn |
		$r_{maleic\ anhydride}$, mol s^{-1} m^{-2}	$-r_{n-butane}$, mol s^{-1} m^{-2}	$-r_{but-1-ene}$, mol s^{-1} m^{-2}
(a)	560			0.88×10^{-9}
(a)	620			0.81×10^{-8}
(a)	660	0.29×10^{-9}	0.58×10^{-9}	
(a)	690	1.02×10^{-9}	2.68×10^{-9}	
(b)	560			1.03×10^{-9}
(b)	620			0.92×10^{-8}
(b)	570	1.58×10^{-9}	1.95×10^{-9}	
(b)	600	2.58×10^{-9}	3.79×10^{-9}	

[a] Experimental conditions: reagent composition, 0.5% hydrocarbon, 12.6% oxygen, 86.9% nitrogen, conversion lower than 10%; 1 g of catalyst.

be attributed to ν_{CN} of coordinatively bonded acetonitrie on very strong Lewis sites.

In conclusion, the acetonitrile adsorption on the two catalysts suggests the following surface properties: (i) both medium-strong and very strong Lewis sites are present on the $(VO)_2P_2O_7$ surface and (ii) a much higher concentration of very strong Lewis sites is present in the catalyst prepared in an organic medium [(b)] as compared to the catalyst prepared in an aqueous medium [(a)].

The catalytic properties of these two catalysts in *n*-butane and but-1-ene selective oxidation to maleic anhydride are reported in Table I. Catalyst (b) is much more active in *n*-butane-selective oxidation than catalyst (a), whereas no significant differences are found in but-1-ene oxidation.

It has been shown that the first step in the conversion of *n*-butane on solid super acid[14] is the extraction of an H$^-$ from the butane by very strong Lewis sites. Similarly it is possible to hypothesize that the very strong Lewis sites evidenced on catalyst (b) and to a lesser extent on catalyst (a) are the sites responsible for the first step in alkane activation. The presence on the vanadium–phosphorus oxides of an oxidizing function (V=O double bond) together with the strong Lewis sites modifies the successive steps of the reaction and leads to selective products (maleic anhydride) instead of the isomerization or cracking products which occur on solid super acid.[14]

The presence of medium-strong Lewis sites is related to the structure itself of the $(VO)_2P_2O_7$[9] and it is not usual on vanadium oxides. Our FT-IR studies of the adsorption of bases indicate that such sites are not present on V_2O_5 even after reducing treatments. On the predominantly exposed (020) plane of $(VO_2)_2P_2O_7$,[9,10,15–17] coupled vanadyl ions in trans positions leave coordinatively unsaturated V(IV) ions that, due to the higher electronegativity of the neighboring phosphorus atoms, give rise to a medium-strong Lewis site. Accordingly, the quantitative determination by temperature-programmed desorption[18] of the presence of medium-strong Lewis sites indicates that their concentration is fairly independent of the preparation method and depends only on the surface area, just as in the case for the oxidation of but-1-ene. The presence of very strong Lewis sites, on the contrary, would be due to defective crystal states, their concentration depending on the preparation method, as shown in Figure 1.

During the $VOHPO_4\cdot^{1/2}H_2O$ precursor preparation in an organic medium, alcohol remains trapped between the layers.[9] During successive calcination to form $(VO)_2P_2O_7$ the presence of the alcohol provokes local deformation[9] of the crystalline structure as shown by X-ray diffraction analysis, thus inducing

local straining of the V–(O–P) bonds. As a result, the coordination requirements of the vanadium are not completely satisfied, with the consequent enhancement of the Lewis acid strength and creation of new very active sites able to activate the paraffins.

Formation of a Novel η^3:η^4-1,2,3-Trimethyl-4,5-dimethylenecyclopentenyl Ligand by Hydrogen Abstraction from a Permethylcyclopentadienyl Group in Permethyltitanocene Carbyl and Related Systems

Johannes W. Pattiasina, Catharina E. Hissink,
Jan L. de Boer, Auke Meetsma, and Jan H. Teuben*

*Department of Chemistry, University of Groningen
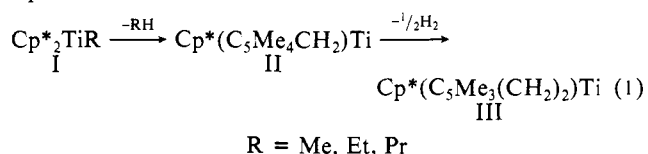Nijenborgh 16, 9747 AG Groningen, The Netherlands*

Anthony L. Spek

*Department of Structural Chemistry
University of Utrecht
Padualaan 8, 3508 TB Utrecht, The Netherlands*

Received July 1, 1985

We wish to report a new type of transformation of a pentamethylcyclopentadienyl group (Cp*) by stepwise hydrogen abstraction into an η^3:η^4-1,2,3-trimethyl-4,5-dimethylenecyclopentenyl ligand.

The reaction was observed during a study of the thermolysis of paramagnetic titanium(III) compounds Cp*$_2$TiR (I).[1] A stepwise reaction was observed, with the stoichiometry[2] given in eq 1.

$$Cp^*_2TiR \xrightarrow{-RH} Cp^*(C_5Me_4CH_2)Ti \xrightarrow{-^{1/2}H_2}$$
$$\underset{I}{} \qquad \underset{II}{}$$
$$Cp^*(C_5Me_3(CH_2)_2)Ti \quad (1)$$
$$\underset{III}{}$$

$$R = Me, Et, Pr$$

Hydrogen abstraction from a transition-metal-bonded Cp* ligand with formation of a 1,2,3,4-tetramethylfulvene metal complex has been observed before[3,4] and in fact II was reported as a product of the thermal decomposition of Cp*$_2$Ti.[5] Similar reactivity of the Cp* functionality is suggested for group 3 and 4f element compounds Cp*$_2$MR (M = Sc,[6] Lu[7]), where intermediates like II are of crucial importance to explain the rapid C–H activation of these systems.

When we studied the thermal decomposition of I, quantitative formation of RH and II[8] was observed. Prolonged heating of paramagnetic II at 150 °C resulted in the formation of H$_2$ and

(14) Hattori, H.; Takahashi, O.; Takagi, M.; Tanabe, K. *J. Catal.* **1981**, *68*, 132.

(15) Johnson, J. W.; Johnson, D. C.; Jacobson, A. J.; Brody, J. F. *J. Am. Chem. Soc.* **1984**, *106*, 8123.

(16) Bordes, E.; Courtine, P.; Johnson, J. W. *J. Solid State Chem.* **1984**, *55*, 270.

(17) Bordes, E.; Courtine, P. *J. Catal.* **1979**, *57*, 236.

(18) Busca, G.; Centi, G.; Trifirò, F.; Lorenzelli, V. *J. Phys. Chem.*, submitted for publication.

(1) Hissink, C. E.; Luinstra, G. A.; Pattiasina, J. W.; Teuben, J. H., unpublished results.

(2) (a) The stochiometry was confirmed by isolation of the titanium compounds and Toepler pump determination of the gaseous products. (b) Thermolysis of I was carried out with 10.0 g (30 mmol) of Cp*$_2$TiMe in 25 mL of toluene at 110 °C. In 12 h the color of the solution had changed from green to purple. The solvent was stripped and the product crystallized from ether. Yield 7.5 g (9.3 mmol, 75%) of II.

(3) (a) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219–1238. (b) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629–1634.

(4) Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H. J.; Krueger, C. *Organometallics* **1983**, *2*, 1369–1377.

(5) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087–5095.

(6) Thompson, M. E.; Bercaw, J. E. *Pure App. Chem.* **1984**, *56*, 1–11.

(7) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491–6493.

(8) Identical with the compound in ref 5, on basis of elemental analyses (C, H, Ti), mass spectrum, molecular weight (cryoscopically determined in benzene), IR, and ^{1}H NMR.