Role of the nature of the acid sites in the oxydehydrogenation of propane on a VPO/TiO$_2$ catalyst. An in situ FT-IR spectroscopy investigation

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Catalytic activity and surface acidity during the oxydehydrogenation of propane over a VPO/TiO$_2$ catalyst were determined by a dynamic in situ FT-IR spectroscopy technique at 350°C. Pyridine was used as a probe molecule for the acidity measurements. The obtained results show that propene formation is linked to Brønsted acid sites and that water increases the number of these sites which, in turn, increases propene selectivity.

Keywords: oxydehydrogenation; propane; propene; in situ FT-IR technique; VPO/TiO$_2$ catalyst

1. Introduction

Following earlier studies by Ai [1,2], recent studies [3–9] emphasize on the importance of surface Brønsted (B) and Lewis (L) acidity in selective oxidation of hydrocarbons on metal oxides. The acid–base properties were determined by adsorption of probe molecules (such as pyridine) [4–7], isopropanol decomposition [1,2,8,9] or surface poisoning by alkali cations [8,9]. However, a close examination of the published results shows that the conclusions about the nature and strength of the acid active sites are still unclear and seem to be related to the investigation method used for the surface acidity. For example, concentration and strength of L acid sites [4] then strong B acid sites [5] were successively believed to be determining factors in the selective oxidation of *n*-butane to maleic anhydride on $(VO)_2P_2O_7$ catalyst. These conclusions were based on pyridine adsorption on the bare [4] and K-poisoned [5,6] surface catalysts respectively.

When specifically considering the B surface acidity studies as determined by alkali metal poisoning, it appears that little is known about the effect of these promoters on the nature and properties of oxygen ions in oxide catalysts [10,11]. Creation of basic sites, or even formation of mixed oxides [10–12], is expected, especially at high alkaline content [5].

It must also be kept in mind that the surface acidity measurements, whatever the method considered, are generally carried out before reaction, using the fresh catalyst and not under working conditions. In addition, hydrocarbon oxidation produces water which, in turn, can transform L surface sites to B surface sites [1]. Thus, it is important to determine the surface acidity in working conditions by less ambiguous methods.

In the present study, we report results obtained by in situ IR spectroscopy in the oxydehydrogenation (ODHR) of propane over a VPO/TiO$_2$ catalyst. This reaction is an important challenge for heterogeneous catalysis [13]. Moreover, supported vanadium oxides are industrially important for the selective oxidation of hydrocarbons [14]. The VPO/TiO$_2$ catalyst used has very well dispersed V and P species [15] and interesting selective oxidation properties [16,17]. Acidity was determined by introduction of pyridine as probe molecule on the catalyst in presence of or without water in the reactant mixture and correlations between reactivity measurements and IR spectroscopy surface observation should lead to the identification of the active sites.

2. Experimental

The devices (IR cell, spectrometer, gas chromatograph, ...) have already been described [17]. The VPO/TiO$_2$ catalyst ($V/Ti = 0.027$ and $P/V = 1.15$, 45 m^2/g) has been prepared by Rhône-Poulenc according to ref. [9] using anatase type TiO$_2$. It has been pressed to the

Table 1
Catalytic results under different percentages of added water

	T (°C)								
	300			350			400		
water added	0	2.5	5	0	2.5	5	0	2.5	5
conv. C_3H_8 (%)	2	1.7	1.7	6	4.5	5	10	9.5	6.5
sel. C_3H_6 (%)	87	90	90	64	77	75	55	57	58
sel. CO_x (%)	8	6	5	32	19	21	41	39	39
by-products (%)	5	4	5	3	4	4	4	4	4

form of a disk (~ 15 mg) and activated at 350°C under He for 2 h. Then a mixture of propane (60%), O_2 (20%) and He (20%) has been flown (total space velocity = 0.017 g ℓ^{-1} h) at 350°C. In general, a pulse of pyridine (1 μl) has been introduced, this amount being found sufficient to saturate all the surface acid sites in the conditions used. Pyridine has been introduced on the activated catalyst, or in the presence of the reactants after the steady state has been reached.

Conventional tests were, in parallel, carried out with a quartz fixed bed flow reactor using 0.1 g catalyst samples and the same reactant mixture and space velocity as above. It was shown that pyridine was quasi not oxidized (< 1%) in the used conditions.

3. Results and discussion

(1) Preliminary tests carried out under the same conditions as in the in situ FT-IR spectroscopy experiments showed that the VPO/TiO_2 used is fairly active (up to 10% of propane conversion) and its selectivity to propene is quite high (up to 80%) (table 1). The other products are mainly CO and CO_2, almost in the same proportions. Minor products are acrolein (< 2%), acetone (< 1%) and acetic acid (< 2%). The testing data also showed that, at 350°C, adding water in the feed gas decreased propane conversion (from 6 to 5%) and the carbon oxides selectivity (from 32 to 21%) but increased propene selectivity (from 64 to 75%) at 350°C. This

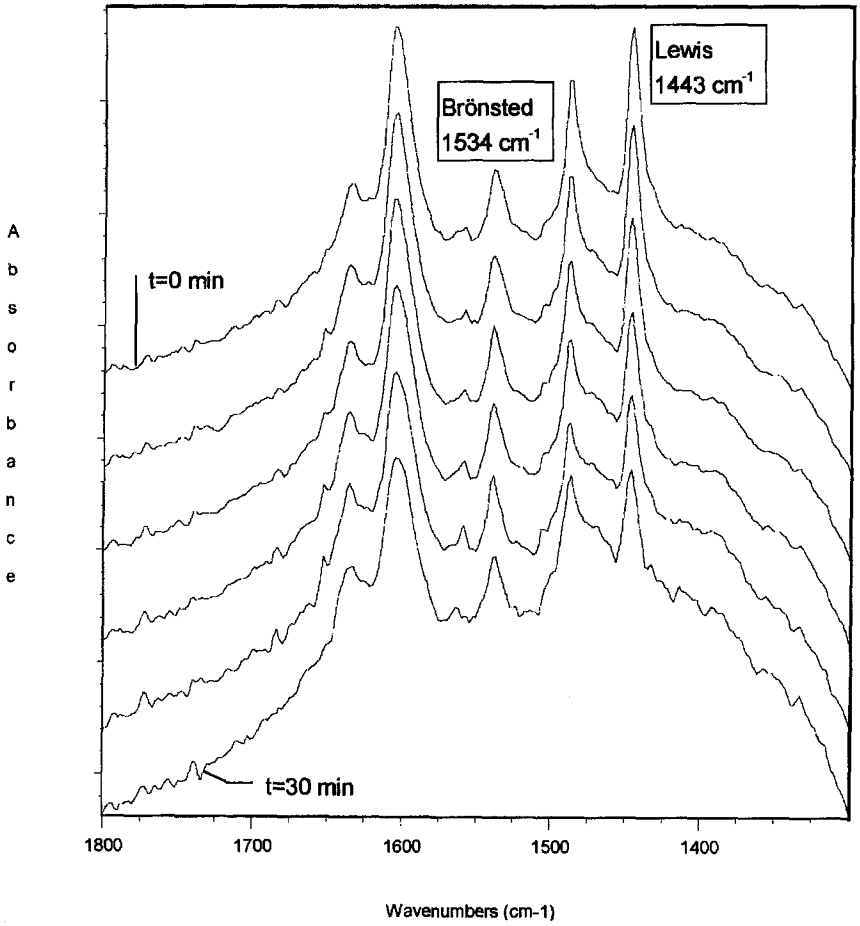

Fig. 1. Evolution with time on stream under He flow (total space velocity = 0.017 g ℓ^{-1} h at 350°C) of adsorbed pyridine species formed on VPO/TiO_2 activated under He at 350°C.

effect was observed neither at higher (400°C) nor at lower (300°C) reaction temperatures. At 300°C, the reaction is not sensitive enough to the water effect, probably due to the very low conversion obtained (2%) and the high propene selectivity (87%). At 400°C, the absence of any water effect may be attributed to the low amount of adsorbed water formed.

(2) The in situ FT-IR experiments showed the presence of coordinated pyridine species (1443 cm^{-1}) and pyridinium species (1534 cm^{-1}) (fig. 1) adsorbed on L and B acid sites respectively. Using the molar extinction coefficient ε of 1.8 and 1.5 cm μmol^{-1} for pyridinium and coordinated species, respectively [19] allows us to estimate the total amount of B and L acid sites to 0.5 ± 0.1 site/nm^2. Interestingly, it is observed that coordinated pyridine species are less stable than pyridinium species because of their higher rate of desorption.

Under the reactant mixture, a significant amount of L acid sites was transformed into B acid sites (fig. 2): the respective amounts are 0.15 B site/nm^2, 0.37 L site/nm^2 before reaction and 0.30 B site/nm^2, 0.22 L site/nm^2 under the reactant mixture. This trend is even more pronounced if water (5%) is added to the reaction mixture (0.33 B site/nm^2, 0.15 L site/nm^2) (fig. 2). The water effect on the surface acidity was also observed for the catalyst before reaction: flowing the catalyst with 5% H_2O/He increased the amount of B sites at the expense of the L sites.

(3) After introduction of the pyridine pulse, the variation of the number of B and L sites has been followed with time on stream. Fig. 3 shows the calculated numbers of the sites which are occupied by the pyridine (coordinated pyridine for the Lewis sites and pyridinium species for the Brønsted sites). A decrease of these calculated numbers shown on fig. 3 means that the liberated sites increase and are thus able to act in the catalytic reaction: the activity is then recovered. Fig. 3 shows the liberation of acid sites depends on the reactive atmosphere. Without reactant, a large part of the L acid sites is rapidly liberated whereas the number of pyridinium species decreased very slowly.

Under reactants (fig. 3b), the number of pyridinium species continuously decreases whereas the number of pyridine coordinated species first decreases more rapidly up to 10 min of time on stream and then reaches a plateau. This effect is even more pronounced under reactant + water feed gas (fig. 3c).

Transient experiments show that, as soon as pyridine is introduced, the yields in CO_2 and propene decrease drastically, mainly that in propene when water is added in the flow. Table 2 compares the catalytic results with and without water but CO and the other products are not reported because of their low value due to the decrease in propane conversion. At $t = 0$, all the acid sites are poisoned by pyridine. After about 10 min of time on stream, and notably in presence of water, pro-

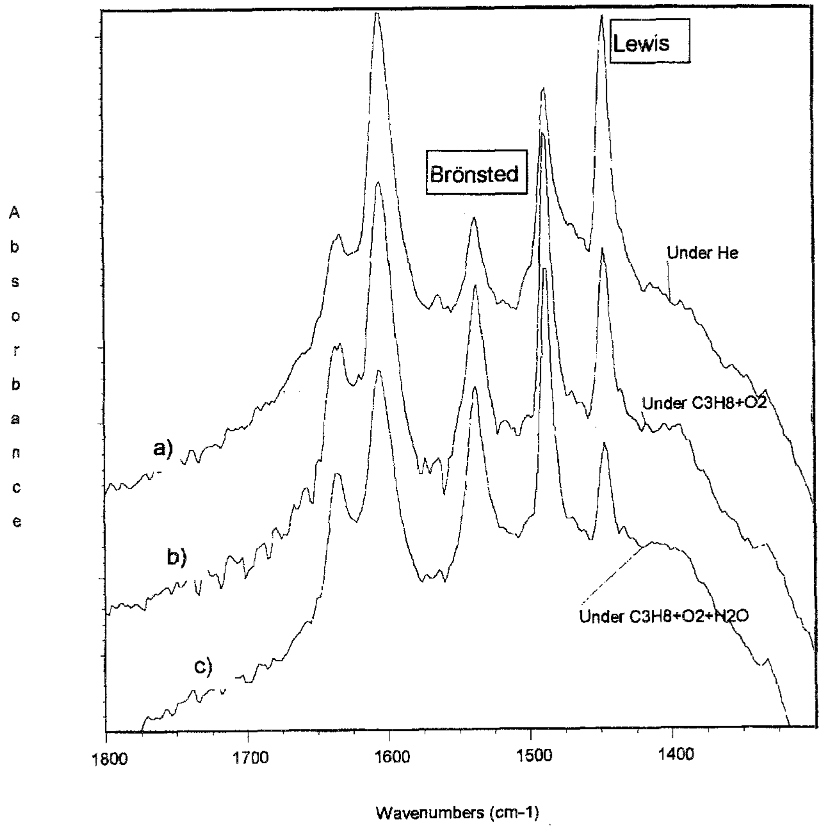

Fig. 2. Pyridine adsorption on VPO/TiO_2 at 350°C, 1 min after Py introduction under: (a) He flow; (b) 60% C_3H_8, 20% O_2, 20% He flow; (c) 57% C_3H_8, 19% O_2, 19% He, 5% H_2O flow.

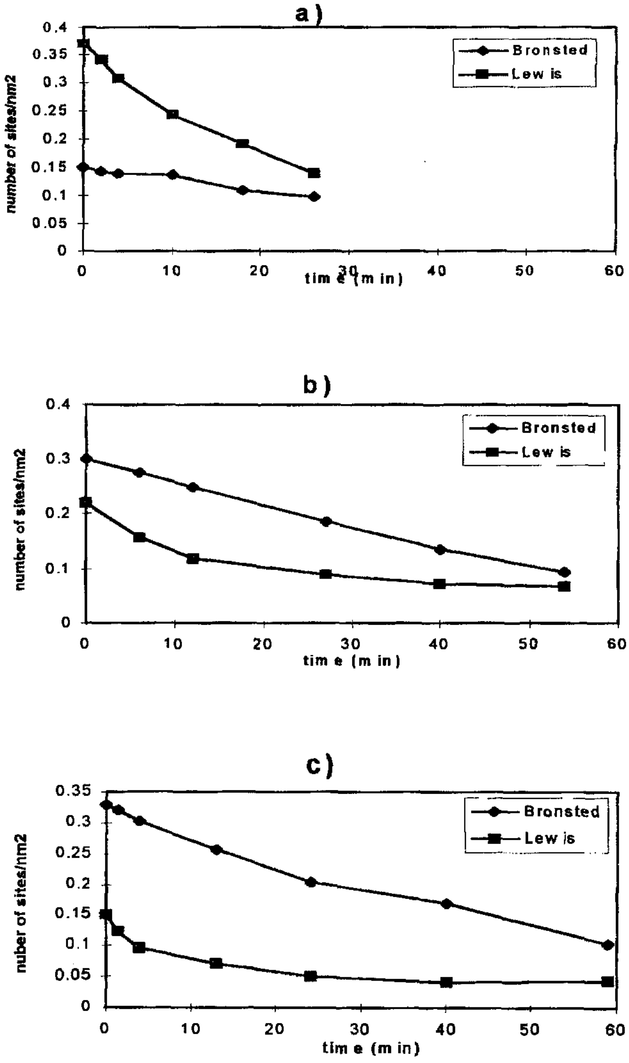

Fig. 3. Variation with time on stream of the number of Py adsorption sites at 350°C under flow of: (a) He; (b) propane + O_2 + He; (c) propane + O_2 + He + H_2O.

pene yield increases continuously whereas that of CO_2 seems to reach a plateau (the recovered activity is due to the liberation of the sites by pyridine desorption). In the same time, the pyridine desorption occurs differently with the sites nature as seen previously. As shown by Busca et al. [5], comparison of activity measurements (table 2) and pyridine infrared measurements (fig. 3) evidences that propene formation seems to be linked to liberation of B acid sites whereas CO_2 formation is certainly correlated to the Lewis sites. This latter result is in good agreement with the water effect which increases the number of B acid sites which, in turn, increases propene selectivity.

4. Conclusion

The present spectroscopic IR observations performed under catalytic conditions provide information, without addition of alkalines of which the effect is complex (crea-

Table 2
Effect of water and pyridine on the activity and selectivity of the VPO/TiO_2 catalyst in the oxydehydrogenation of propane

Water (%)	Reaction time[a] (min)	Propane conv. (%)	Yield C_3H_6 (%)	Recovered activity (%)	Yield CO_2 (%)	Recovered activity (%)
0	0	6	3.7	–	1.30	–
5	0	5	3.9	–	1.00	–
5	8	1.5	0.8	22	0.6	64
5	68	2.5	1.9	49	0.7	70

[a] Time 0 values correspond to the reactivity measurements before pyridine introduction.

tion of basic sites), and show the role of Brønsted acid sites in the ODHR of propane. These results are in good agreement with the activity measurements, showing the promoting effect of water for this reaction.

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