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Propane oxydehydrogenation reaction on a VPO/TiO_2 catalyst. Role of the nature of acid sites determined by dynamic in-situ IR studies

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Abstract

A VPO/TiO_2 catalyst tested in the oxydehydrogenation reaction (ODH) of propane between 300 and 400°C shows satisfactory performances (up to 80% of propene selectivity at 2% of propane conversion at 300°C or 56% of propene selectivity at 9% of propane conversion at 400°C). Addition of water or pyridine in the feed gas tends to decrease the propane conversion and enhances the propene selectivity. It is shown that water increases the number of Brönsted surface acid sites by dissociative adsorption which, in turn, enhances propene selectivity at the expense of the CO_x selectivity. These results are in good agreement with spectroscopic IR observations performed under catalytic conditions showing that the Lewis acid sites are linked to CO_x formation, whereas it seems that Brönsted sites would rather be linked to propene formation.

Keywords: Propane oxydehydrogenation; VPO/TiO_2 catalyst; Acid sites; IR studies

1. Introduction

The selective oxidation of light alkanes is an important challenge for heterogeneous catalysis [1–5]. In order to develop new and efficient catalysts, information on catalytic sites and detailed mechanisms of the involved reactions are required. However, up to now, the fundamental investigations on the subject remain quite limited, especially those concerning the oxydehydrogenation reaction (ODHR) of propane to propene [7,8]. For instance, the factors affecting the selectivity in hydrocarbon oxidation are still far from clear [6]. Among these factors, the surface Brönsted (B) and Lewis (L) acidity seems to play an important role and several recent studies emphasized it [6–10].

In earlier investigations, Ai and Suzuki [11] and Ai [12] extensively studied and discussed the role of the acid–base properties of oxide catalysts in the oxidation of different reactants. For example, the Brönsted acidity was shown to be detrimental considering the selective oxidation of xylene to phthalic anhydride on V_2O_5

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catalysts [10]. Busca et al. successively correlated the $(VO)_2P_2O_7$ activity in the selective oxidation of 1-butene and *n*-butane to maleic anhydride first to the concentration and strength of L acid sites [7] and then, rather to strong B acid sites on the basis of poisoning effects induced by K^+ addition [8].

In the present study, we report results obtained by in-situ IR spectroscopy in the ODHR of propane. The catalyst used (VPO/TiO_2) was found to have well dispersed V and P species [13] and interesting selective properties in the ODHR of ethane [14,15] and propane (present study). The influence of the catalyst surface acidity on the reaction performances was examined by adding water in the reactant feed gas. Pyridine was used as a probe molecule for in situ FT-IR measurements.

2. Experimental

The apparatus (IR cell, spectrometer, gas chromatograph, etc.) have already been described [16]. The VPO/TiO_2 catalyst ($V/Ti = 0.027$ and $P/V = 1.15$, 45 m^2/g) was prepared by Rhône-Poulenc according to [14], by impregnation of titania by a solution of $VOPO_4 \cdot 2H_2O$ reduced with oxalic acid and calcined in air at 500°C. For infrared studies, the catalyst was pressed in to the form of a disk ($\approx$ 15 mg) and activated at 350°C under He for 2 h. Then a mixture of propane (60%), O_2 (20%) and He (20%) was flown over the disk (3 cm^3/min) at 350°C (0.14 g l^{-1} of propane/h). A pulse of pyridine (1 μl) was introduced after steady-state had been reached, and the reactivity followed with time on stream.

Conventional testings were, in parallel, carried out with a quartz fixed bed flow reactor using 75 mg catalyst samples under the same conditions. Pyridine stability under oxidizing conditions was studied at 350°C by flowing the VPO/TiO_2 catalyst (75 mg) under a pyridine/O_2/He (5/17/78%) mixture. The results show no reaction of pyridine with O_2 under such conditions.

3. Results and discussion

3.1. Catalytic tests

The propane ODH on VPO/TiO_2 was performed in the 300–400°C temperature range (Table 1). It can be shown that the VPO/TiO_2 catalyst is fairly active (up to 10% of propane conversion). The other products are mainly CO and CO_2, almost in the same proportions. Carbon monoxide is observed only at $T \geqslant 350°C$. It is important to note that propane ODH gives rise to water formation in an amount estimated to 1% at 350°C, which will make the study of the water effect rather difficult.

3.1.1. Effect of water

Addition of water to the feed gas leads to lower activities as observed at 350°C (Table 1). Introduction of 2.5% of water in the reactant mixture decreases propane conversion from 6.1 to 4.4%. In the same time, propene selectivity increased (from 64 to 77%) and the CO_x selectivity decreased sensibly, especially that of CO (from 16 to 4%). However, a close examination of the results shows in fact that the yield values of propene were not changed by water addition

Table 1
Catalytic tests. Conditions: propane (60%), O_2 (20%) and He (20%), total flow (15 cm^3/min), 0.14 g l^{-1} of propane/h (conventional reactor)

Added H_2O (%)	*T* (°C)	Conversion C_3H_8	Selectivity (%)			
			C_3H_6	CO_2	CO	By products [a]
0	300	1.9	87	8	0	5
	350	6.1	64	18	16	3
	400	9.8	55	22	19	4
2.5	300	1.7	90	6	0	4
	350	4.4	77	15	4	4
	400	9.6	57	20	18	4
5	300	1.7	90	5	0	5
	350	4.9	75	14	7	4
	400	9.5	58	22	17	4

[a] By products were acetaldehyde, acrolein and acetic acid.

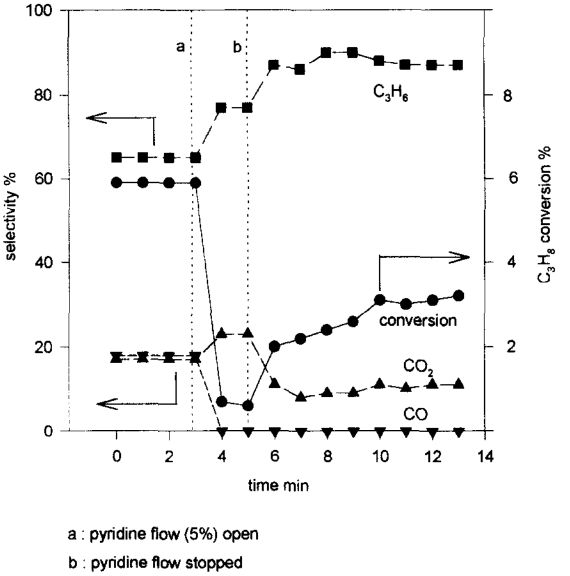


Fig. 1. Effect of a pulse of pyridine on the catalytic reactivity. Conditions: propane (60%), O_2 (20%) and He (20%), total flow (15 cm^3/min) at 350°C.

(3.9 to 3.7%) whereas those of CO_x decrease more (1.1 to 0.7%). Increasing the added amount of water from 2.5 to 5% does not cause further modifications of the catalytic performances.

It is remarkable to note that the water effect is observed at 350°C but neither at lower (300°C) nor at higher (400°C) reaction temperatures (Table 1). The insensivity of the reaction to the presence of added water should be attributed, at low temperature, to the low activity of the catalyst, and at high temperature, to the high water desorption rate.

At 350°C, it is tempting to correlate the observed changes in the catalytic performances to surface acid–base changes induced by water addition. Concerning the drop of propane conversion when water is added, it should be attributed both to an equilibrium displacement and/or to a competitive adsorption between water and propane or even between water and O_2. As to the variations in the propene and CO_x selectivities (Table 1), they should be attributed to the changes in acidity or directly correlate to the weak drop of propane conversion, according to Kung [17]. The in-situ FT-IR studies allowed us to quantify these changes and to correlate the observed performances to the acidity surface variations.

3.1.2. *Effect of pyridine*

The intrinsic effect of pyridine on the catalytic performances of the VPO/TiO_2 catalyst on the propane ODHR was studied at 350°C. After the steady-state was reached, gaseous pyridine was introduced in the reaction mixture (the pyridine partial pressure was adjusted to

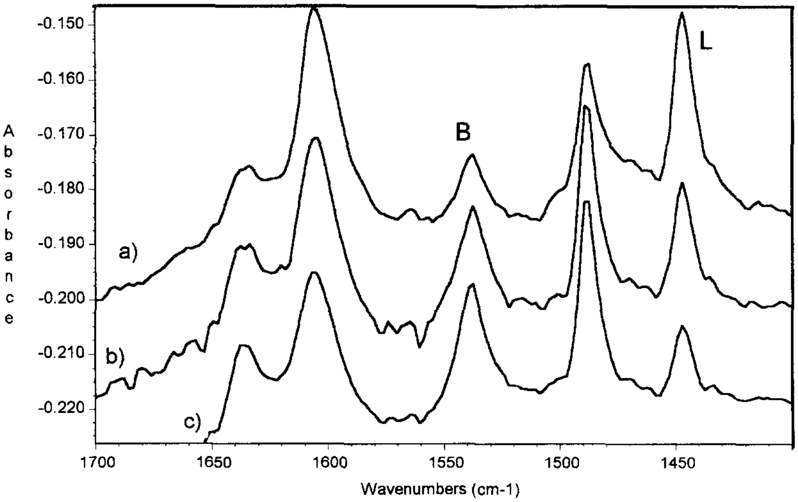


Fig. 2. IR spectra of the catalyst 1 min after pyridine introduction under a flow of: (a) He, (b) $C_3/O_2/He$, (c) $C_3/O_2/He/H_2O$.

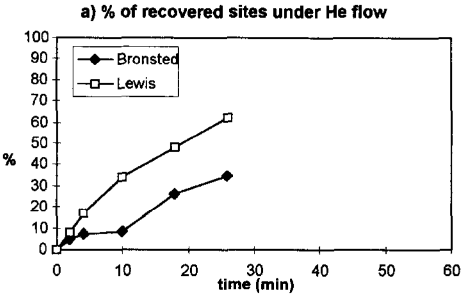
5%) for 2 min. Then, the pyridine flow was stopped whereas the propane/O_2 mixture flow was maintained.

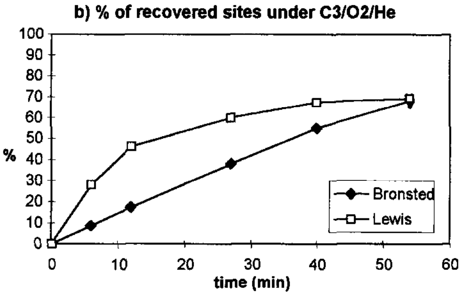
As soon as pyridine was introduced in the reactor (Fig. 1) on the VPO/TiO_2 catalyst, the propane conversion drastically decreased from 6 to 0.6% whereas carbon monoxide disappeared at the benefit of propene and carbon dioxide whose selectivity slightly increased (85% and 15%, respectively). When the pyridine flow was stopped, propane conversion as well as propene selectivity increased whereas CO_2 selectivity decreased. A new state is reached in a few minutes for which the performances are approximately: 2%, 85%, 15% for propane conversion and propene and CO_2 selectivities, respectively.

These trends are similar to those observed with water, with, however, more pronounced activity variations. In order to understand the effects of pyridine and water addition, we performed some in-situ FTIR experiments.

3.2. FTIR experiments

Introduction of pyridine on the catalyst under He flow at 350°C shows the presence of coordinated pyridine species (1447 cm^{-1} band) and pyridinium species (1538 cm^{-1} band) (Fig. 2) adsorbed on Lewis (L) and Brönsted (B) acid sites, respectively. The initial total amount of B and L acid sites is estimated at 0.5 ± 0.1 site/nm^2 (0.15 B site/nm^2, 0.37 L site/nm^2), using a molar extinction coefficient ϵ value of 1.8 and 1.5 cm μmol^{-1} for pyridinium and coordinated species, respectively [18]. Under the reactant mixture, a significant amount of L acid sites is transformed into B acid sites: their initial amounts is then 0.3 B site/nm^2, 0.22 L site/nm^2. This trend is even more pronounced by adding water (5%) to the reaction mixture: 0.33 B site/nm^2, 0.15 L site/nm^2, as shown in Fig. 2c, which allows one to compare the initial spectra obtained under different atmospheres. The water effect on the surface acidity was also confirmed for the fresh catalyst under He atmosphere: flowing the catalyst with 5% H_2O/He increases the B sites amount at the expense of the L sites.


a) % of recovered sites under He flow


b) % of recovered sites under C3/O2/He

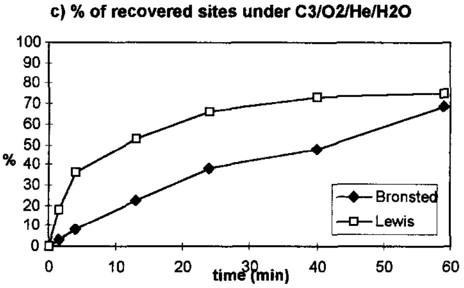

c) % of recovered sites under C3/O2/He/H2O

Fig. 3. Percentages of recovered sites followed with time on stream, under different flows of: (a) He, (b) $C_3H_8/O_2/He$, (c) $C_3H_8/O_2/He/5\%\ H_2O$.

After introduction of the pyridine pulse, the recovery of the number of B and L sites has been followed with time on stream. Fig. 3 shows that whatever the flow, Lewis acid sites are preferentially recovered. This is particularly clear in the few minutes after the pyridine has been switched off under reactants (Fig. 3b) or even clearer when water has been added to the reactants (Fig. 3c). It is worthwhile to note that the catalytic results obtained at 350°C using the IR-cell as reactor are in nice agreement with those obtained with the conventional reactor. After pyridine introduction, Fig. 4 shows that

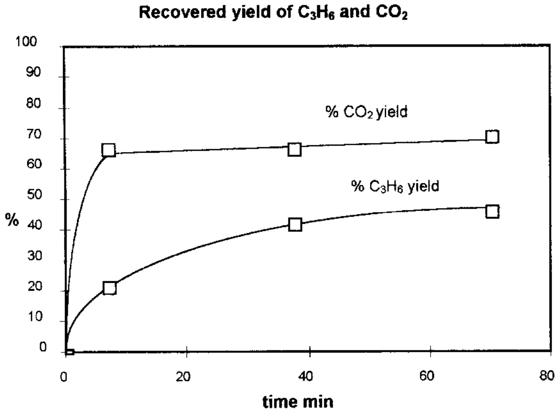


Fig. 4. Percentage of recovered yield of C_3H_6 and CO_2 followed with time on stream, after injection of a pulse of pyridine under a flow of 5% of H_2O in $C_3/O_2/He$.

propene yield increases with time on stream less rapidly than that of CO_2. As in parallel, IR spectra analysis shows (Fig. 3) that L acid sites are preferentially recovered, we conclude that CO_x formation is linked to L acid sites, whereas propene formation is rather linked to B acid sites.

4. Conclusions

Our studies on the performances of a VPO/TiO_2 catalyst in the ODH of propane show that water tends to inhibit propane conversion and CO_x yield whereas it does not influence propene yield, and, as a result, enhances propene selectivity at the expense of CO_x selectivity. These features, observed at 350°C, are attributed on one hand, to competitive adsorptions between water and the reactants and, on the other hand, to water dissociative adsorption which enriches the catalyst surface in B acid sites. The spectroscopic IR observations, performed under catalytic conditions with pyridine as probe molecule, allows one to specify this effect of water in the ODH of propane. They clearly showed that CO_x formation is linked to Lewis sites whereas it seems that Brönsted sites are rather linked to propene formation. A further study on the nature and strength of the Brönsted sites created by addition of water is in progress.

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