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Oxidative dehydrogenation of ethane over Cr/TiO_2 modified by phosphorus

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A series of catalysts were prepared by loading titanium dioxide with chromium and different amounts of phosphorus. Investigation in the oxidative dehydrogenation of ethane showed that chromium notably increases the activity of TiO_2 principally toward the total oxidation of the hydrocarbon. Addition of phosphorus to the system simultaneously improved the global conversion and the ethylene selectivity. Moreover, a fairly good correlation between the catalysts acidity, the P/Cr ratios and the activity in the ODH reaction was established. It was also found that an excess of phosphorus, although it increases the acidity, decreases the conversion as if phosphorus effect was optimum for P/Cr ratios equal to 1.6. EPR and UV-visible characterizations of the samples before and after the catalytic tests showed that the improvement of the catalysts performances might be due to the isolated octahedral Cr^{3+} species that appear on the support.

Keywords: oxidative dehydrogenation, ethane, chromium phosphate

1. Introduction

Mild oxidation and oxidative dehydrogenation of light alkanes, as widely reported in the literature, is still an area of research of major importance in heterogeneous catalysis and in economic strategies. Until recently, only butane showed a satisfactory reactivity in producing butene and butadiene on molybdenum-based systems such as $CoMoO_4$ [1,2] or maleic anhydride over $(VO)_2P_2O_7$ [3–6]. The activity of these catalysts is often attributed to the labile oxygen of Mo=O and V=O bonds. In the case of ethane dehydrogenation, despite the numerous studies carried out during the last years, the achieved conversions were still low or totally oriented toward the production of CO and CO_2 [7–9]. Until now, the best results were obtained with oxides of transition metals or rare earth oxides [10]. Lately, the V_2O_5/TiO_2 system enriched with phosphorus showed in the ethane oxidative dehydrogenation reaction (ODH) an ethylene selectivity of 50% and a global conversion around 33% [11]. The introduction of phosphorus in this system clearly improved its activity and selectivity. Tessier et al. showed that the VPO/TiO_2 system is also efficient in the selective oxidation of ethane to acetic acid [12].

Chromium catalysts have been previously investigated, especially under the form of the industrially used Philips catalyst (Cr/SiO_2) [13,14]. Layered zirconium phosphate exchanged with Cr^{3+} ions was also studied and conversions between 20 and 30% with an ethylene selectivity reaching 60% were achieved [15]. The activity was attributed to Cr^{3+} ions in specific environments or/and to small Cr^{3+} clusters [16].

The present work is a contribution to the understanding of the parameters governing the activation of C–H bonds in light alkanes. The catalyst used in the investigations is a chromium- and P_2O_5-loaded TiO_2. The system Cr/TiO_2 without P_2O_5 is known to be quite efficient in the oxidation reactions [17]. Addition of phosphorus modifies the nature of the supported compounds and improves the activity and the selectivity of the catalysts in the oxidative dehydrogenation of ethane. It also changes the surface acidity of the samples [18,19]. These changes were revealed using the butan-2-ol dehydration reaction which is known to depend on the acid properties of the catalyst. Characterization of the solids before and after the catalytic runs was also performed in order to highlight the features of the active sites involved in the ODH reaction.

2. Experimental

The Cr–P/TiO_2 samples were synthesized by adding to the anatase form of titanium dioxide a solution containing the desired quantities of $Cr(NO_3)_3\cdot 9H_2O$ and $(NH_4)_2HPO_4$. The precipitate was then heated at 80 °C, and kept overnight at 120 °C until the complete evaporation of water. The remaining solid was calcined at 550 °C for 4 h under an air stream. Table 1 shows the specific surface areas measured by the BET method, the P/Cr ratios and the corresponding denominations of the catalysts in the text. X-ray diffraction patterns of the samples were recorded with a Siemens diffractometer using Cu Kα radiation. Diffuse re-

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Table 1
Denominations and BET surface areas of the samples.

Sample	Molar ratio P/Cr	S_{BET} ($\mathrm{m^2\,g^{-1}}$)
TiO_2	0	98
Cr/TiO_2	0	69.7
$CrP1/TiO_2$	1	86.5
$CrP2/TiO_2$	1.6	83.7
$CrP3/TiO_2$	3.3	70.9

flectance spectra were obtained between 190 and 1000 nm on a Varian Cary 5E spectrometer equipped with an integrating sphere coated with tetrafluoroethylene, using $BaSO_4$ as a reference. A Bruker EPR 300 spectrometer was used to take X-band EPR spectra of the samples at $-196\,^{\circ}\mathrm{C}$.

Catalytic behavior and acid properties of the samples were compared using the dehydration of butan-2-ol as the probe reaction. The runs were performed at $158\,^{\circ}\mathrm{C}$ in a differential flow reactor containing 100 mg of the catalyst. The alcohol was diluted with pure nitrogen and introduced in the reactor at a partial pressure of 8.3×10^2 Pa and a total flow rate equal to 60 $\mathrm{cm^3\,min^{-1}}$.

The ethane ODH tests were carried out in a quartz microreactor operated at atmospheric pressure. The sample sieved at a particle size of 125–180 μm was placed in the reactor between two quartz wool plugs and submitted to the reaction mixture which was constituted of 6% of ethane, 3% oxygen and 91% nitrogen at a total flow rate of 60 $\mathrm{cm^3\,min^{-1}}$. The reaction mixture was introduced in the reactor at $30\,^{\circ}\mathrm{C}$, then the temperature was linearly increased until $550\,^{\circ}\mathrm{C}$. Analysis of the products was performed using a FID chromatograph for the hydrocarbons separation and another one equipped with catharometers for the analysis of the CO_x.

3. Results

Typical X-ray diffraction patterns of the samples are displayed in figure 1. They show that the titanium dioxide did not suffer any structural modification after the impregnation. The newly loaded compounds were not detected either because they were probably amorphous or very well dispersed on the support.

UV-visible spectra of the samples are shown in figure 2. Beside the bands belonging to TiO_2, the spectrum of Cr/TiO_2 (curve (a)) exhibits a shoulder located at 370 nm and attributed to the transfers of charge from O^{2-} to Cr^{6+} [20]. The bands appearing at 700 and 750 nm were, respectively, assigned to the d–d transitions in the Cr^{3+} and Cr^{5+} species [21,22]. Addition of phosphorus to Cr/TiO_2 causes the disappearance of the shoulder at 370 nm and an increase of the intensity of the band centered at 700 nm. This shows clearly that the introduction of phosphorus increases the stabilization of the Cr^{3+} ions in square pyramidal coordination like in $CrPO_4$. Simultaneously, it reduces most of the Cr^{6+} ions which are known to be quite effective in the total oxidation of hydrocarbons.

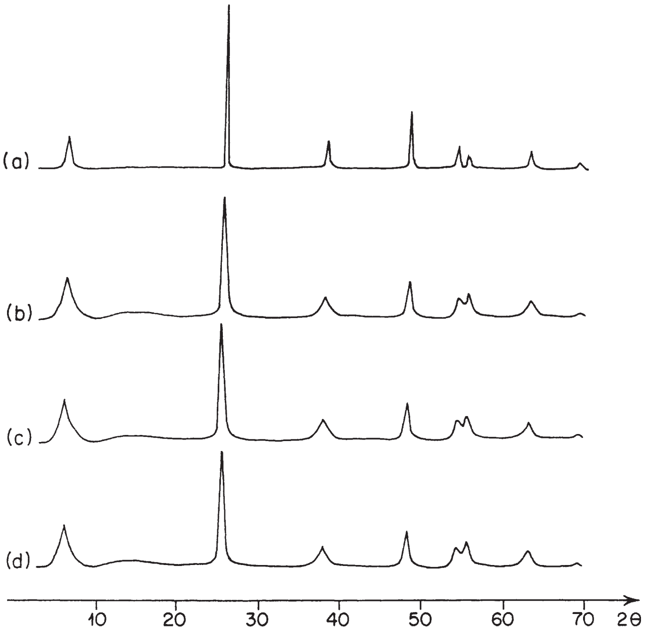

Figure 1. X-ray diffraction patterns of (a) Cr/TiO_2, (b) $CrP1/TiO_2$, (c) $CrP2/TiO_2$, (d) $CrP3/TiO_2$.

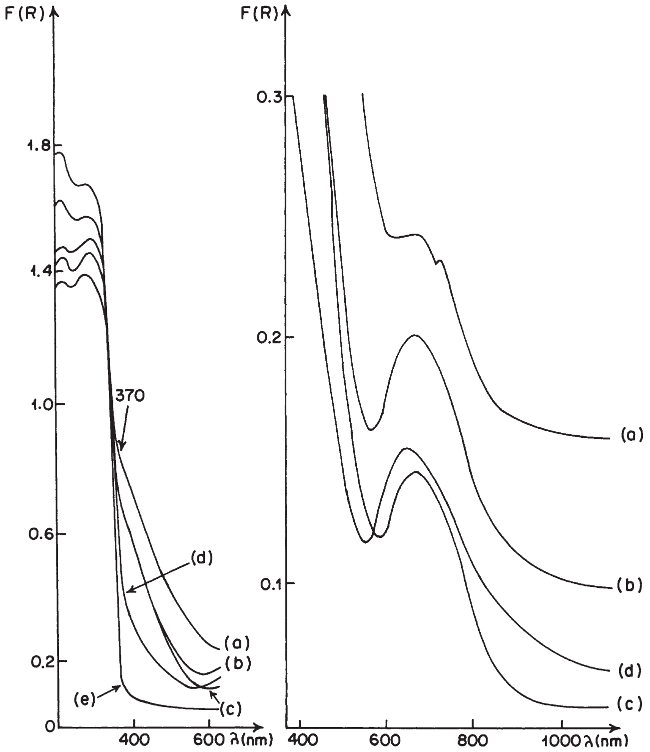

Figure 2. UV-visible spectra of (a) Cr/TiO_2, (b) $CrP1/TiO_2$, (c) $CrP2/TiO_2$, (d) $CrP3/TiO_2$, (e) TiO_2.

The literature reported several EPR studies of chromium ions dispersed on different supports [22–25]. Generally, the samples exhibit three kinds of signals:

- A signal (denoted γ) with EPR parameters $g = 1.97$ and $\Delta H \leqslant 60$ G. This signal is assigned to Cr^{5+} species in an octahedral coordination.

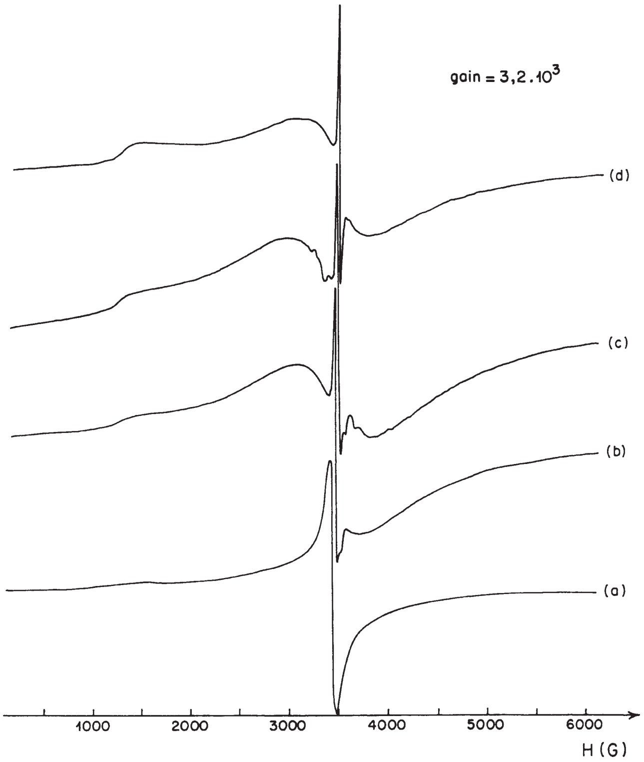

Figure 3. EPR spectra of the catalysts: (a) Cr/TiO_2, (b) CrP1/TiO_2, (c) CrP2/TiO_2, (d) CrP3/TiO_2 recorded before the catalytic tests.

Table 2
Catalytic activity and selectivity of the samples.

Sample	α_{g}[a] (%)	$S_{C_2H_4}$[b] (%)	S_{CO_x}[c] (%)
TiO_2	3.9	38	62
Cr/TiO_2	23.8	29.7	70.3
CrP1/TiO_2	31	41.6	58.4
CrP2/TiO_2	29.5	63.2	36.8
CrP3/TiO_2	19.8	66	34

[a] α_{g} = ethane global conversion.
[b] $S_{C_2H_4}$ = ethylene selectivity.
[c] S_{CO_x} = CO_x selectivity.

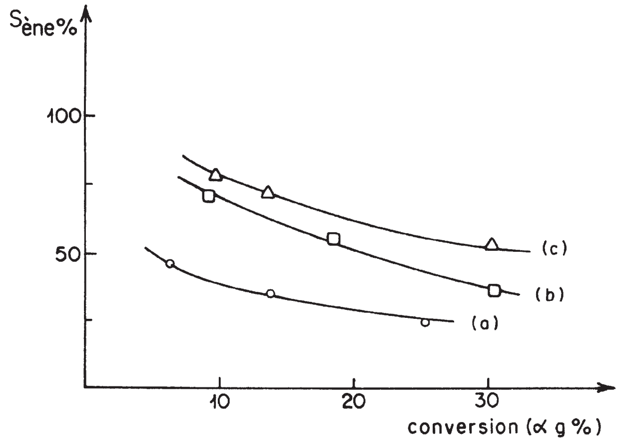

Figure 4. Variation of ethylene selectivity versus ethane conversion on (a) Cr/TiO_2, (b) CrP1/TiO_2, CrP2/TiO_2.

- A positive lobe (denoted δ) with a parameter g around 4 attributed to Cr^{3+} ions in an octahedral environment.
- The third signal at $g = 2$–2.5 (denoted β) with $\Delta H \leqslant 900$ G was generally assigned to clustered Cr^{3+} ions.

EPR spectra of the samples evacuated at room temperature were recorded in X-band at liquid-nitrogen temperature (figure 3). One should note that the catalyst free of phosphorus exhibits the typical sharp signal with the parameters $g = 1.98$ and $\Delta H = 46$ G corresponding, as reported above, to isolated Cr^{5+} ions in an octahedral symmetry [23]. The sample contains also Cr^{6+} species that are not detected by EPR. After the adjunction of phosphorus to Cr in the ratio P/Cr = 1, a broad β signal with $g = 1.98$ and $\Delta H = 820$ G appears in addition to the γ signal. An analogous signal was observed by Loukah et al. in characterizing the catalytic behavior of $CrPO_4$ phosphate [15]. It might be attributed to the presence of clustered Cr^{3+}–O–Cr^{3+} species in amorphous $CrPO_4$. When the ratio P/Cr is equal to 1.6, one observes an increase of the β signal intensity and the apparition of a positive lobe at $g = 4.1$ assigned to dispersed Cr^{3+} ions in an octahedral environment. In the case of CrP3/TiO_2 the broad isotropic β signal is better solved and the intensity of the δ signal increased.

These spectroscopic characterizations tend to confirm that the introduction of phosphorus in the Cr/TiO_2 system promotes the reduction of Cr^{6+} and Cr^{5+} species and the stabilization of the Cr^{3+} ions in a nearly octahedral coordination. The Cr^{3+} are probably involved in the formation of monophosphates such as $CrPO_4$ or even pyro- and metaphosphates for ratios P/Cr superior to 1.5.

Catalytic activity and selectivities of the catalysts were studied at 550 °C. The results at stationary state are displayed in table 2. Ethylene and carbon oxides were the only reaction products detected. Moreover, the results showed that loading TiO_2 with chromium substantially increased the global activity which is mainly oriented toward CO_x production. The first addition of phosphorus to Cr/TiO_2 lowered the oxidation state of chromium giving rise to the formation of an amorphous phosphate on the support. It also remarkably improved the global conversion and the ethylene selectivity. When the proportion of phosphorus reached P/Cr = 3.3, the catalytic behavior of the system changed once again. The global conversion decreased and ethylene selectivity increased. However, since the selectivity considerably depends on the extent of the reagents transformation, it is extremely important to perform the comparison of the samples at the same conversion. The results are displayed in figure 4. They confirm that the best performances were achieved with CrP2/TiO_2.

Phosphorus, on the other hand, is known to increase the dispersion of the active phases and to modify the acid–base properties of the catalysts surfaces [18,26]. In the case of our samples, this was investigated using the butan-2-ol dehydration as a probe reaction, because it involves acidic sites in its mechanism [27]. Figure 5 reports the conversion rate of butan-2-ol and the ethylene selectivity versus the ra-

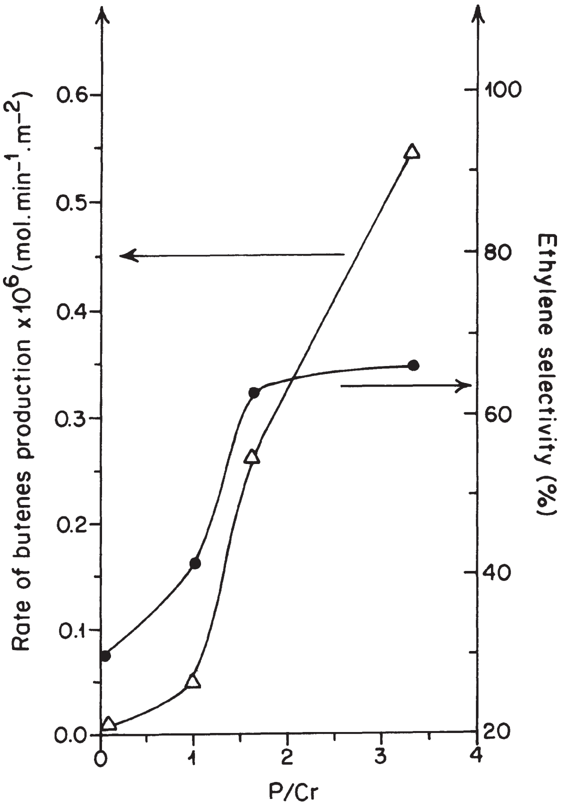

Figure 5. Influence of the surface acidity on ethane ODH: variations of the rate of butan-2-ol dehydration and ethane selectivity versus P/Cr ratio.

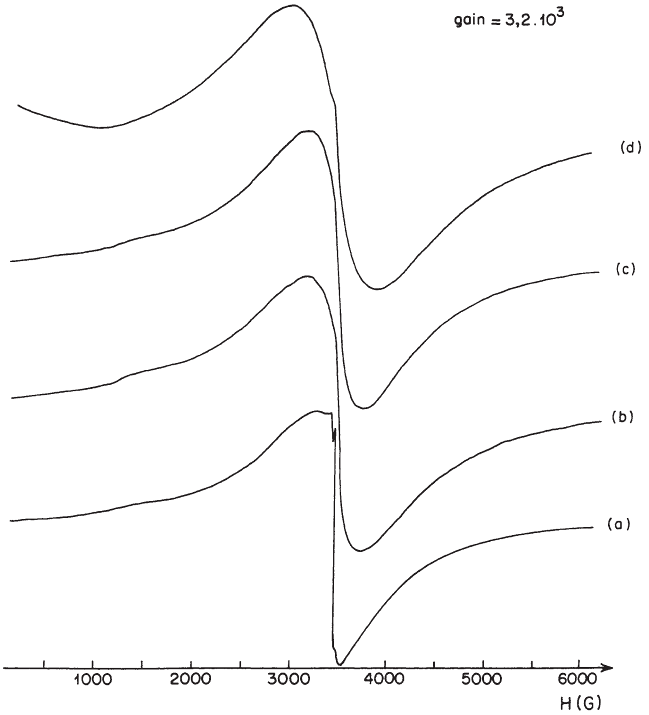

Figure 6. EPR spectra of the catalysts recorded after the catalytic tests: (a) Cr/TiO$_2$, (b) CrP1/TiO$_2$, (c) CrP2/TiO$_2$, (d) CrP3/TiO$_2$.

tio P/Cr. It shows that the increase of phosphorus content in the catalysts increases the dehydration activity and improves at the same time the ethylene selectivity in the ODH reaction. However, for ratios P/Cr superior to 1.6 the acidity increase decreases the ethane conversion and enhances the ethylene selectivity. It seems that the enrichment of the system with phosphorus beyond P/Cr equal to 3.3 results in a poisoning of the active sites in ODH reaction. The phosphorus has a definite influence on the selectivity, but it is certainly not the only factor that controls the behavior of the catalysts.

Figure 6 displays the EPR spectra of the samples after the catalytic tests. The spectrum of the catalyst free of phosphorus, Cr/TiO$_2$, shows a sharp γ signal due to Cr^{5+} ions overlapped by a broad line at $g = 1.97$ with $\Delta H = 370$ G assigned to the appearance of Cr^{3+} ions in the sample. The catalysts loaded with more phosphorus showed signals containing larger contributions of Cr^{3+} species (located at $g = 1.97$ with $\Delta H = 840$ G) than before the catalytic tests. These results are in positive agreement with a pronounced reduction of the catalysts during the dehydrogenation process despite the presence of oxygen in the reaction mixture. Phosphorus also considerably changes the catalytic performances the Cr/TiO$_2$ system. It improves the selectivity but, unfortunately, decreases the global conversion. This behavior was imputed to the catalysts features evidenced by the characterizations. New supported phases such as CrPO$_4$ and Cr^{3+} clusters appear on the catalyst and participate, as suggested by several authors, in the ethane ODH via the mechanism of Mars and van Krevelen [28]. In addition, the presence of Cr^{5+} species also seems to be necessary for the activation of the ethane molecule. The phosphate acts as an agent of isolation of the active sites. It permits a decrease of the liability of the oxygen atoms surrounding the active centers, thus yielding more selective reactions, but with a negative effect on the reactivity of the ethane molecule. Analogous results were achieved with V$_2$O$_5$/TiO$_2$ modified by phosphorus [11,12]. In this system TiO$_2$ intervenes not only as a conventional support but also in the construction of the bidimensional monolayer of V$_2$O$_5$ responsible for the catalytic performances. Titanium dioxide probably plays a similar role in the case of the CrP/TiO$_2$ system.

4. Conclusion

From all the results presented the following conclusions can be drawn:

- Loading TiO$_2$ with chromium improved its activity, but the selectivity is essentially oriented toward CO$_x$ production. EPR and UV-visible spectroscopies showed that the sample essentially contained Cr^{6+} and Cr^{5+} ions, which are not very efficient in mild oxidation.
- Addition of phosphorus to Cr/TiO$_2$ resulted in a remarkable increase of the activity and ethylene selectivity. These improvements were attributed to the appearance in the samples of phosphates and clustered Cr^{3+} ions. The phosphorus probably also contributed to the stabi-

lizing octahedral Cr^{3+} species in a well defined environment and adjusted in an advantageous way the acid properties of the active surface.

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