Dehydrogenation of Propane over Chromia-Pillared Zirconium Phosphate Catalysts

F. J. Pérez-Reina, E. Rodríguez-Castellón, and A. Jiménez-López*

Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain

Received April 26, 1999. In Final Form: June 22, 1999

Two series of porous chromia-pillared α-zirconium phosphate materials, prepared using two different methods of colloidization of the initial phase and with variable chromium contents (CrZrP-Xa and CrZrP-Xb) have been tested in the oxidative and nonoxidative dehydrogenation of propane in a flow reactor at atmospheric pressure. All catalysts are highly selective to propene under nonoxidative conditions at 823 K. In both series of catalysts, the initial activity increases with the chromium content, but generally CrZrP-Xb catalysts are more active than those of series CrZrP-Xa, which is in good agreement with their higher chromium contents and greater dispersions. In all cases, deactivation was detected due to coke formed from undesired reactions. When the reactions were carried out under oxidative conditions at 673 K, the activities were enhanced as the observed deactivation was minimum. The activities found vary between 0.47 and 1.31 μmol of propene g⁻¹ s⁻¹ and are maintained after 200 min of reaction. These activity values were also related to the chromium content, being slightly higher for CrZrP-Xb materials. A parallel study to evaluate the influence of acidity in the obtained results has been carried out. The activities found of these catalysts seem to be related to the presence of Cr(III) centers with vacancies in their coordination sphere. These vacancies, in nonoxidative conditions, can activate the reactant molecules originating propene and hydrogen. On the other hand, in an oxidative atmosphere, Cr(III) species can activate oxygen molecules, through an electronic transference process, yielding propene and water.

Introduction

Light alkanes (ethane, propane, butane) are generally environmentally acceptable compounds because of their low chemical reactivity and their low cost. This in turn has provided incentives to use them as feedstock for chemical production. So, the dehydrogenation reactions could be used in industry for the production of propene, butene, butadiene, isobutene, and isoprene to obtain a large variety of products.

The dehydrogenation of alkanes may be performed in inert conditions. Up to the present supported chromia catalysts have been used for this purpose, but this nonoxidative reaction presents some disadvantages. Indeed, at the reaction temperature, usually above 800 K, undesired side reactions take place which are very difficult to control. The most significant side reaction is the cracking of alkane into smaller molecules and deep dehydrogenation leading to a rapid coking of the catalyst. On the other hand, the dehydrogenation reaction is highly endothermic, and heat must be added to sustain the reaction. In practice, the heat released by burning off coke on the catalyst in the regeneration process is used to supply part of that required for the reaction.

An alternative method for dehydrogenation is the reaction of alkane with oxygen, that is, to carry out the catalytic process under oxidative conditions (ODH). This provides great advantages over a nonoxidative process due to engineering and economic considerations. The main limitation is the formation of byproducts, not always of economic interest. The oxidative dehydrogenation of alkanes usually produces a considerable amount of carbon oxides because of the low selectivity of the catalysts employed. Therefore, a key aspect in the development of this technology is in research of catalysts capable of activating only the C–H bonds of the alkane molecule in a flow of O₂. During the past decade, a wide variety of catalytic systems have been proposed. Generally, vanadium oxides are the most commonly used active species in this process, which are supported on several oxides such as SiO₂, MgO, Al₂O₃, TiO₂, AlNbO₄, and Mg–Si O (sepiolite) and other supports as microporous aluminophosphates (AlPO₄) and aluminophosphates substituted with V (VAPO). An important aspect of these catalytic systems is the dispersion of the active phase. For this reason, porous materials with large surface areas are chosen such as pillared layered compounds (PILC), which present properties similar to those of zeolites. These materials have a...
virtually constant distance between layers and therefore interlayer space. They may be one of the most promising kinds of new stable micro- and mesoporous materials available for adsorption, separation, and catalytic applications, together with MCM materials. In pillared solids, the metal oxides maintain the layers apart and enable the accessibility of reactants to the internal surface where they can act on the active sites to produce the catalytic reaction.

Thus, it has recently been found\(^\text{16}\) that chromium oxide intercalated into montmorillonite layers exhibits activity in the oxidative dehydrogenation of ethane, although the selectivity is not high owing to the high reactivity of the olefinic products to produce carbon oxides. More recently Alcántara et al.\(^\text{17}\) have employed a mixed Ga/Cr oxide pillared \(\alpha\)-zirconium phosphate as a catalyst for the dehydrogenation of propane, which is very active and stable, especially under oxidative conditions.

The goal of this work is to study the performance of two sets of catalysts based on chromia-pillared \(\alpha\)-zirconium phosphate, prepared by two colloidal methods, in the dehydrogenation of propane in inert and oxidative conditions. Since the resulting catalysts have different chromium contents and dispersions, acidities, and textural properties, we have correlated these properties with their activities in both reactions. On the other hand, we uphold the importance of the relationship between these properties and the catalytic performance of these systems in these kinds of reactions since they will be of great interest in oxidative dehydrogenation of light alkanes.

**Experimental Section**

**Catalyst Preparation.** Two series of chromia-pillared \(\alpha\)-zirconium phosphate (\(\alpha\)-ZrP) have been employed in this study, which were synthesized as described in detail elsewhere.\(^\text{18}\) For this purpose, colloidal suspensions of this phosphate were prepared by two different methods, hereinafter called series a and b. Preparation of series \(a\) consists of adding dropwise a \(0.1\) M aqueous solution of potassium acetate to a colloidal suspension of \(\alpha\)-ZrP under vigorous stirring up to pH \(8\) (70% of the cation exchange capacity (CEC) of \(\alpha\)-ZrP). Preparation of series \(b\) makes use of \(\alpha\)-ZrP fully saturated in nPA as an intermediate prepared from vapor adsorption. A typical preparation of the colloidal phase is as follows: \(\alpha\)-ZrP (2 g) was exposed to nPA vapors overnight, and then the excess of an amine was removed in a desiccator containing concentrated phosphoric acid, the intercalate was dispersed in \(400\) cm\(^3\) of a \(0.1\) M solution of potassium acetate. The mixtures were refluxed for \(4\) days. Chromia-pillared materials at 673 K under nitrogen flow. The \(\alpha\)-ZrP samples were then dispersed for \(15\) h in a \(0.1\) M solution of potassium acetate. Neutralization was performed even of the weakest acid sites. The solids were calcined at 1073 K as reference, which is a nonporous solid with a \(S_{BET}\) of \(34\) m\(^2\) g\(^{-1}\). Total acidity of these samples was determined by thermal programmed desorption of ammonia (NH\(_3\)-TPD).

**Results and Discussion**

1. Characterization of Catalysts. In a previous study we have found that the porous structure and the catalytic behavior of chromium-pillared materials depend on the colloidization method employed during the preparation of the starting phosphates.\(^\text{18}\) In fact, the colloidization method can modify important factors such as basal spacing, degree of polymerization of the intercalated chromium(III) species, surface area and porosity, and acidic properties of the resulting compounds. Taking into account all these considerations we have now studied the catalytic behavior of these two sets of materials, prepared according to methods a and b, in the dehydrogenation of propane in inert and oxidative conditions.

Both groups of samples have been described in detail elsewhere.\(^\text{18}\) The chemical composition, \(d_{001}\) basal spacing at room temperature and 673 K, specific surface area, and textural properties of the resulting compounds. Taking into account all these considerations we have now studied the catalytic behavior of these two sets of materials, prepared according to methods a and b, in the dehydrogenation of propane in inert and oxidative conditions.
and micropore volume, together with the total number of acid sites as determined by NH₃-TPD, are compiled in Table 1. From data listed in Table 1 it is noteworthy that materials prepared by method b appear to have higher chromium contents, basal spacings and better textural properties than those synthesized by method a. It means that a good colloidization leads to a more homogeneous intercalation between all the interlayer spaces in the lamellar host.

II. Catalytic Results. Although the literature generally describes the behavior of chromia-supported catalysts in dehydrogenation processes in nonoxidative conditions, in this paper, the study in oxidative conditions has been considered too. First, the results obtained in nonoxidative conditions shall be dealt with and, second, the results in oxidative conditions.

II.1. Dehydrogenation (DH) of Propane. The evolution of the catalytic activity as a function of time on stream for series a and b of catalysts are plotted in Figure 1. Initial conversion, selectivity, and activity values are compiled in Table 2. The initial activities observed for both sets of catalysts ranged between 0.1 and 2.3 \( \mu \text{mol g}^{-1} \text{s}^{-1} \). The selectivities for propene are very interesting with values of 79–91.8%. Other products such as methane and ethane were found as products of cracking reaction. It is noticeable that while selectivity of cracking products decreases with the time on stream, the selectivity for propene remains constant for a long time. This behavior could mean that strong acid sites are responsible for the cracking reaction, but after deactivation of these centers, only the medium strength acid sites are active, which essentially give rise to propene. The catalytic activity shown by the pristine \( \alpha-ZrP \) was zero. The initial activity of \( \alpha-Cr_{2}O_{3} \) was 0.2 \( \mu \text{mol g}^{-1} \text{s}^{-1} \), showing a decay with time on stream. These results are relevant because they suggest that the catalytic activity in this system is related to the acid centers of chromia inserted between the phosphate layers.

In both series it is clearly observed that activities increase with the chromium content. This effect is more acute in the initial activity. CrZrP-Xb catalysts are comparatively more active than the homologous series of CrZrP-Xa. Although initial deactivation is faster for 3a, the extent of deactivation is higher for 3b catalyst in agreement with its high activity. Samples with low activity exhibit less deactivation. On the other hand, because the activities are related with the chromium content and being higher in the CrZrP-Xb catalysts, factors such as the high...
dispersion of chromia and the creation of a porous structure (which implies an increment in the number of accessible active sites) play an important role in the activity of these catalysts.

The deactivation is a characteristic fact of catalysts for dehydrogenation reactions, but the deactivation mechanism is not made clear in the literature. Some studies have established a relationship between catalytic deactivation and coke deposition. Thus, Noda et al.\(^\text{21}\) showed that during butane dehydrogenation the reaction rate decreases as a function of reaction time and there is a simultaneous increase in coke. A similar behavior has been reported by Toei et al.\(^\text{22}\) for isopentane dehydrogenation and by Dumez and Froment\(^\text{23}\) for 1-butene dehydrogenation. However, other authors suggest that this relation is not so clear. Heineman\(^\text{24}\) has reported that during methylcyclopentane dehydrogenation, the decrease in the amount of the coke does not considerably modify global conversion. However, more recently Gorriz et al.\(^\text{25}\) have demonstrated in supported chromia on alumina catalysts that the amount of coke formed and the deactivation rate are a function of the chromium content and its dispersion, this being higher at higher amounts of supported chromia.

In chromia-pillared catalysts, we have attributed the observed deactivation to the coke deposition on the catalyst surface. In fact the amounts of deposited coke after DH reaction have been determined by CNH analysis (Table 2), and for each series of catalysts the C% increases with the chromium content and is therefore related to the observed initial activities. This behavior seems to be related to the acidity of these materials. As commented before, in both series the total number of acid sites increases with the chromium content (Table 1) as a result of increasing the number of nanoparticles located between layers and the accessibility to the interlayer region to propane molecules, but this high concentration of acid sites is also responsible for the undesired side reactions such as coking.

Evidently, this deposited coke has negative consequences in the textural properties of catalysts, because these carbonaceous particles inhibit the access of alkane molecules to the active sites. To verify the hypothesis that coke formation influences both the specific surface area and pore size distribution,\(^\text{25}\) the CrZrP-3b catalyst has been chosen to study this effect. Figure 2a shows the comparative results obtained in the textural analysis of this sample. After DH reaction, \(S_{\text{BET}}\) decreases from 426 to 245 \(\text{m}^2\ \text{g}^{-1}\). It is clear from Figure 2b that although pore radii have not essentially been modified in size, the abundance of pores with this value is clearly lower. These results suggest that the observed decrease in the catalytic activity due to coke deposition is related to the loss of accessibility to the active sites located behind the coke.

Other authors\(^\text{2}\) have attributed the deactivation of the catalysts to the formation of Cr(II). The XPS technique was used to investigate the changes of the immediate environment surrounding chromium and the oxidation state before reaction as well as after catalytic reaction. In all cases, the binding energies of Cr 2p\(_{3/2}\) in the spent catalysts (577.2–577.3 eV) are close to those reported for chromia (576.7–576.9 eV),\(^\text{26}\) and therefore only Cr(III) is present on the surface of these materials.

Influence of Acidity in the Catalytic Behavior. Industrial dehydrogenation chromia/alumina catalysts are known to contain small quantities (up to a few percent) of alkali ions: very often potassium. Indeed, it is generally accepted that potassium has a beneficial effect, related to the poisoning of acidic sites responsible for undesired side reactions (cracking and coking), which reduces the selectivity and shortens the lifetime of the catalyst. To verify whether potassium exerts a similarly positive influence, two K\(^+\)-exchanged chromia-pillared materials have been chosen, K\(^+\)-CrZrP-3a and K\(^+\)-ZrP-3b.

The initial activity, conversion, and selectivity to propene of these two exchanged materials are compiled in Table 2. In both cases, the initial catalytic activities of the potassium-exchanged catalysts are much lower than those observed with the pristine catalysts (about 40%), although their deactivation is less acute. This behavior cannot be related to the modifications of the textural parameters, because they undergo only a moderate reduction compared with a high decrease in the catalytic activities. A similar conclusion is arrived at by comparing the initial activities and the acidities, because the remanent acidities are still enough (1526 \(\mu\)mol of \(\text{NH}_3\) g\(^{-1}\) in K\(^+\)-CrZrP-3a and 1194 \(\mu\)mol of \(\text{NH}_3\) g\(^{-1}\) in K\(^+\)-ZrP-3b). These results are analogous to those obtained by

Alcántara-Rodríguez et al.\textsuperscript{17} in the DH reaction of propane on gallium–chromium mixed oxides pillared α-zirconium phosphate, where the activities were dramatically reduced after doping the catalysts with K\textsuperscript{+}. Similar results were found by De Rossi et al.\textsuperscript{2} in propane dehydrogenation on chromia/zirconia catalysts. They concluded that potassium is very likely bonded to O\textsuperscript{2−} ions, whose properties (for instance, Lewis acidity and coordinative unsaturation) are therefore changed. Taking these facts into account, the oxygen ions, located on pillars and zirconium phosphate layers, near chromium in the active site, could be involved in the dissociative adsorption of propane as well as in the hydrogen desorption. After the cationic exchange, the basicity of these oxygen ions is modified and, as a consequence, the activity is negatively influenced. The same behavior has been observed in the 2-propanol decomposition test in the K\textsuperscript{+}-exchanged chromia-pillared materials, where the 2-propanol conversions undergo a dramatic decrease after the cationic exchange.

11.2. Oxidative Dehydrogenation (ODH) of Propane. An alternative method for dehydrogenation of alkanes is by reaction with oxygen: C\textsubscript{n}H\textsubscript{2n+2} + 1/2O\textsubscript{2} + H\textsubscript{2}O → C\textsubscript{n}H\textsubscript{2n} + H\textsubscript{2}O. The formation of water, a very stable product, makes this reaction thermodynamically very favorable. Thus, in principle, a high level of conversion percentage can be obtained even at low temperatures. This alternative could provide great advantages over nonoxidative processes due to engineering and economic considerations.

**Influence of Reaction Temperature in ODH Reaction.** First, a study has been carried out to establish the optimum temperature in this reaction. For this purpose, the CrZrP-3b catalyst has been chosen. In all tests, the reaction conditions were maintained constant, only varying the temperature from 473 K up to 773 K. The activity increases as a function of the reaction temperature up to 673 K, where the activity was maximum, and then it falls off (Table 3). Figure 3 compares the selectivity to propene with the total conversion. It is clear from this graph that conversion increases with temperature at the same time as the selectivity decreases. This means that the higher the temperature is, the higher the rate of secondary reactions are such as the formation of CO\textsubscript{x} and cracking. Because the yield of propene is maximum at 673 K, we have chosen this temperature to study all the other catalysts. This temperature is considerably lower than that used in nonoxidative conditions, although the contact time was unchanged in both reactions in order to compare the catalytic results.

**Catalytic Activity.** In the same way as in the DH reaction, α-ZrP was inactive in the ODH reaction, while α-Cr\textsubscript{2}O\textsubscript{3} showed a moderate activity (0.4 µmol g\textsuperscript{−1} s\textsuperscript{−1}). Figure 4 shows the evolution of the catalytic activity as a function of time on stream of both series of chromia-pillared materials. Conversion and activity values are listed in Table 4. In general, the activity for propene increases with the chromium content, although in a different way in both series. In the CrZrP-Xa series, the CrZrP-2a and CrZrP-3a catalysts present a similar activity, although chromium contents are higher in the latter. CrZrP-1a clearly showed a low activity, due to the reduced accessibility of the reactive to the chromia in the interlayer region of this material. On the CrZrP-Xb series, there is a slight increment in activity with the chromium

<table>
<thead>
<tr>
<th>temp (K)</th>
<th>conversion (%)</th>
<th>selectivity (%)</th>
<th>activity (µmol of propene g\textsuperscript{−1} s\textsuperscript{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>19.1</td>
<td>2.8</td>
<td>5.7</td>
</tr>
<tr>
<td>573</td>
<td>40.2</td>
<td>1.8</td>
<td>2.3</td>
</tr>
<tr>
<td>673</td>
<td>51.1</td>
<td>2.3</td>
<td>8.3</td>
</tr>
<tr>
<td>773</td>
<td>51.1</td>
<td>2.3</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Figure 3. Dependence of the conversion (O) and selectivity (●) with the reaction temperature in ODH process for CrZrP-3b catalyst.

Figure 4. Catalytic oxidative dehydrogenation (ODH) of propane at 673 K over CrZrP-Xa (a) and CrZrP-Xb (b) catalysts.
Comparatively, CrZrP-Xb materials are more active than CrZrP-Xa materials, probably as a consequence of their higher specific area, accessibility to the reactants, and their chromium contents. It is important to emphasize that pristine α-Cr2O3 has an activity for propene much lower than that for chromia-pillared phosphates (except CrZrP-1a). Thus, these results suggest that the chemical ambient created by chromia pillars is appropriate to carry out this reaction. Indeed, the dispersion of chromium and the accessibility of reactants (propene and oxygen) to the active sites in the porous structure make these materials very active in this catalytic process.

Some interesting aspects can be seen when DH and ODH results are compared. In all catalysts, the activity remained constant during the oxidative reactions. This behavior is considerably different compared to that in nonoxidative conditions, where the deactivation process is more acute. So, in oxidative conditions, deactivation is not observed because the formation of coke is absent, as was confirmed by CNH analysis, where the carbon content in spent catalysts was insignificant. On the other hand, when the DH reaction was carried out at 673 K (ODH reaction temperature), the activity values suffered a dramatic decrease, so it can be concluded that under oxidative conditions the contribution of the pure dehydrogenation reaction is negligible. These results clearly suggest that the mechanism for the ODH is completely different to that of the DH reaction. This aspect will be discussed later.

Table 4 also included the selectivity of reaction products. Selectivity to propene is moderate, from 16% to 38.2%, being higher at low conversions. Selectivities to cracking products are low, but selectivity to oxidation products (COx) is very high, with values ranging between 58.2% and 77.5%.

Chromia-pillared zirconium phosphate materials show activity values for the ODH of propane similar to or higher than other catalysts reported in the literature, but working at lower temperatures. A typical catalyst based on vanadium oxide (VAPO-5) has been chosen to achieve a comparative study in the same experimental conditions. This catalyst has been synthesized as described by Concepcion et al.26 The crystallinity of the VAPO-5 sample was determined by measuring the intensity of the characteristic peaks of the ALPO-5 structure, appearing at 19.8°, 21.1°, and 22.4°. The activity value was 0.14 μmol of propene g−1 s−1, a much lower value than those obtained for pillared catalysts (Figure 5), even that of CrZrP-1a. It is necessary to increase the temperature up to 773 K to achieve a similar activity value to those observed for chromia-pillared materials (1.24 μmol of propene g−1 s−1). So, the low-temperature reaction used in the oxidative reaction is an additional reason for the use of chromia-pillared materials as catalysts.

### Table 4. Conversion, Selectivity, and Activity for Catalytic Oxidative Dehydrogenation (ODH) of Propane at 673 K over CrZrP-Xa and CrZrP-Xb and K+-Exchanged Catalysts (200 min reaction)

<table>
<thead>
<tr>
<th>sample (K)</th>
<th>conversion (%)</th>
<th>selectivity (%)</th>
<th>activity (μmol of propene g−1 s−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>methane</td>
<td>ethane</td>
</tr>
<tr>
<td>CrZrP-1a</td>
<td>8.0</td>
<td>0.28</td>
<td>3.31</td>
</tr>
<tr>
<td>CrZrP-2a</td>
<td>43.4</td>
<td>2.3</td>
<td>7.1</td>
</tr>
<tr>
<td>CrZrP-3a</td>
<td>47.5</td>
<td>2.1</td>
<td>5.3</td>
</tr>
<tr>
<td>K+-CrZrP-3a</td>
<td>38.9</td>
<td>2.4</td>
<td>3.7</td>
</tr>
<tr>
<td>CrZrP-3b</td>
<td>49.0</td>
<td>1.9</td>
<td>2.8</td>
</tr>
<tr>
<td>K+-CrZrP-3b</td>
<td>40.4</td>
<td>1.5</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Figure 5. Comparative catalytic behavior in ODH of propane at 673 K over CrZrP-1a (O), CrZrP-3b (●), and VAPO-5 (x) catalysts.

Figure 6. Dependence of activity at steady state in the oxidative dehydrogenation (ODH) of propane reaction on the I_Cr/I_Zr intensity ratio (from XPS) for both series of catalysts.

The oxidation state of chromium after reaction was (III) in all cases. XPS spectra of spent chromia-pillared catalysts show a Cr 3p3/2 peak centered at 577.1 eV, close to the values reported for chromia (576.6-576.9 eV). Figure 6 shows the linear relationship between the surface chromium content (I_Cr/I_Zr, obtained by XPS) and the ODH activity. This fact suggests that the number of chromium-(III) active sites, as well as the accessibility that the catalysts present, is an important key factor in this catalytic process.

**Influence of Prereduction and Acidity in ODH Reaction.** To determine the influence of some pretreatments such as partial reduction, the CrZrP-3b catalyst
has been chosen. The curve of thermal-programmed reduction with hydrogen (TPR–H₂) of this sample shows a peak of hydrogen consumption at about 773 K, which can be assigned to a partial reduction of Cr(III) species to Cr(II). This fact has been used to establish the active oxidation state of chromium. After treatment of CrZrP-3b with a H₂/Ar (10%H₂) flow at 773 K for 15 min, the catalytic behavior of this sample is slightly different compared to that of the pristine catalyst, because the initial activity in the prereduced sample is lower (Figure 7). However, the activity increases with time on stream up to achieving a similar catalytic activity value after 250 min. A tentative explanation of this behavior can be offered by assuming that the active phase for this catalytic process is Cr(III). In fact, owing to Cr(II) species appearing after prereduction treatment and the low initial activity, it can be deduced that they do not participate in this process. But the presence of oxygen favors the oxidation of Cr(II) to Cr(III), and it supposes an increment in the number of Cr(III) active species with the consequent increment in propene.

On the other hand, the acidity of chromia-pillared materials could be a key factor in the ODH of propene. Potassium-ion exchanged CrZrP-3a and CrZrP-3b samples have been prepared to evaluate this effect. The catalytic behavior is shown in Figure 8 and included in Table 4. The activities found are similar, that is, the cationic exchange (H⁺ by K⁺) does not modify the activity in ODH processes, so it can be deduced that Brønsted acid sites do not participate significantly in this reaction. These results are opposite to those obtained in DH reactions. It means that the mechanism for the ODH is quite different to that of the DH one. In this case, the first stage seems to be the activation of O₂ molecules by means of Cr(III) species. Cr(III) ion, with a t₂² configuration, is able to supply electronic density to an empty π* of O₂, provoking its dissociation. This stage must control the reaction rate, because the activity of pristine catalysts and potassium-exchanged samples is quite similar. During this process, the oxidation state of Cr(III) must be changed, probably to Cr(V), which oxidizes propane to obtain propene and water, regenerating Cr(III) again. But there is no evidence from XPS measurements, probably due to the high speed of this process.

Regarding selectivity, the presence of potassium gives rise to an increment of selectivity to propene (Table 4). This is a consequence of the substitution of the strongest acid sites by K⁺. Several authors have reported this behavior. The basic catalyst surface has also been claimed to increase the alkene selectivity during the ODH of alkanes. Thus, on supported vanadium or molybdenum oxides, it was shown that incorporating alkaline metals decreased both the conversion of propene and the yields of products but increases the selectivity to propene at the expense of CO₂ selectivity. The reason should be that basic surfaces facilitate the desorption of alkanes (more basic compounds than the corresponding alkenes), thus preventing them from further oxidation to carbon oxides. However, the effect of acid–base properties on selective oxidation of hydrocarbons is more complex since it should depend on the nature of the catalyst (and therefore on its oxidizing properties) and even, on the nature of the hydrocarbon molecules.
Conclusions

Two series of chromia-pillared phosphates have been tested in the DH and ODH reaction of propane. The presence of chromia in the interlayer region gives rise to the formation of porous materials with high surface areas in which the active phase is well dispersed as nanoparticles between the layers of α-zirconium phosphate. That confers to this catalyst a very high activity in both dehydrogenation and oxidative dehydrogenation reactions of propane.

In both series, the initial activity in the DH of propane increases with the chromium content, but it decays due to the deposited carbon which covers the active sites of the catalysts which modify their textural parameters. In oxidative conditions, the deactivation process is absent and the activities are comparable to that obtained in other catalytic systems but the performance temperature is very low, only 673 K.

Acknowledgment. This research was supported by the CICYT (Spain) Project MAT 97-906.