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Propane Dehydrogenation on Mixed Ga/Cr Oxide Pillared Zirconium Phosphate Materials

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Porous Ga/Cr mixed oxides were prepared by calcination at 673 K of mixed hydroxooligomers intercalated within the layers of α -zirconium phosphate using a colloidal suspension of the phosphate previously swelled with vapors of *n*-propylamine. The catalytic activity of pillared materials for the dehydrogenation of propane under oxidative and nonoxidative conditions has been investigated in a flow apparatus. Under nonoxidative conditions at 823 K, the initial activity varies between $1.56 \mu\text{mol of propene} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$ for the sample Ga/Cr 70/30 and $2.62 \mu\text{mol of propene} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$ for the sample Ga/Cr 50/50, all catalysts being highly selective to propene. The observed initial deactivation was due to coke originated from side reactions on active sites. Under oxidative conditions, the catalytic activity at 673 K, after 5 h of reaction, varies between 0.45 and $1.22 \mu\text{mol of propene} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$ and the deactivation was inappreciable. In all cases, the observed high activity is attributed to the presence of Cr(III) with coordination vacancies that, in an inert atmosphere, can activate propane molecules, yielding propene and hydrogen; while under oxidative conditions is capable of activating oxygen, by a labile coordination between the metal ion and oxygen, and its subsequent transfer to propane yielding propene and water.

Introduction

The catalytic dehydrogenation of light alkanes has great industrial importance because it represents an alternative route for obtaining alkenes for the polymerization and other organic syntheses from low-cost saturated hydrocarbon feedstocks. Metals deposited on different supports and supported chromium oxide have been used as heterogeneous catalysts for the dehydrogenation of light alkanes. Pt and Pt–Sn supported on γ - Al_2O_3 or SiO_2 show maximum catalytic activity¹ for a dehydrogenation reaction, but a quick deactivation due to coke formation is observed. The activity and selectivity of supported chromia catalysts for the dehydrogenation alkanes have been known for many decades,^{2,3} and a recent investigation of the catalytic activity of $\text{CrO}_x/\text{ZrO}_2$ for the dehydrogenation of propane has been reported.⁴ The system was found to be highly active and selective in the dehydrogenation of propane at 723–823 K. This work concluded that Cr(III) species are the active sites with a possible role of the oxide ions adjacent to Cr(III). The catalytic dehydrogenation of propane using chromium oxide supported on alumina ($\text{CrO}_x/\text{Al}_2\text{O}_3$) has been widely studied.^{5–8} This support is largely employed because of its high refractory surface area, but it presents the undesired feature of catalyzing

side reactions (cracking and coking), leading to catalyst deactivation. The acidic sites responsible for the side reactions can be poisoned with alkali ions (very often potassium) with satisfactory results.

The dehydrogenation of propane in an inert atmosphere has two important inconveniences. The first one is the obliged regeneration process due to coke formation, and the second comes from the high-temperature reaction due to the endothermal nature of the process. An alternative way is to carry out the catalytic process under oxidative conditions (ODH), that is, with oxygen. This alternative has still two unsolved problems: the reaction mechanism not being well-known and the control of the high reactivity of the reaction products derived from the dehydrogenation process.⁹ Vanadium and molybdenum oxides are the main species present in the catalysts used for selective oxidation of alkanes, vanadium oxide being the preferred one. It has been supported on a great variety of oxides such as SiO_2 ,¹⁰ MgO ,^{11–13} Al_2O_3 ,¹⁴ TiO_2 ,^{15–16} AlNbO_4 ,¹⁴ $\text{TiO}_2/\text{SiO}_2$,¹⁷ $\text{TiO}_2/\text{Al}_2\text{O}_3$,¹⁸ $\text{SiO}_2/\text{Al}_2\text{O}_3$,¹⁹ mixed oxides Mg and Al/

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calcined hydrotalcite;²⁰ Mg–Si–O (sepiolite);²¹ microporous aluminophosphates (AlPO₄-5)^{13,22} and aluminophosphates substituted with V have been widely employed (VAPO-5).^{13,23} Very recently, it has been shown that chromium oxide supported on zirconia or incorporated into layered zirconium phosphate displays rather high ethylene selectivities^{24,25} in the ODH of ethane.

There are three fundamental advantages of supported metal oxides: a high degree of mechanical strength, a better thermal stability, avoiding particle sintering, and a large surface area of the support that enable the accessibility of reactants to the active phase. An alternative method for the dispersion of the active species on a metal oxide is to use bidimensional solids with metal oxides intercalated into their interlayer region as active species of the catalysts. In the case of metal oxide pillared zirconium phosphates, pillaring metal oxide nanoparticles permanently separate the layers of the solid, giving rise to a porous structure.

In the search for a new catalyst for the ODH of alkanes, a montmorillonite expanded with polyoxocations of Cr(III) which were obtained by intercalation of polyhydroxoacetate of Cr(III) into clay and further calcination in an ammonia atmosphere were studied for the ODH of ethane at 773 K and atmospheric pressure, leading to a relatively high activity, but the selectivity was not very high because of the high reactivity of the olefinic products.²⁶

Thus, the aim of the present work was to study the catalytic behavior in the dehydrogenation of propane under inert and oxidative conditions of a family of pillared α -zirconium phosphate (α -ZrP) materials where the pillaring oxide nanoparticles are mixed oxides of Ga and Cr with different compositions.

Experimental Section

Catalyst Preparation. A. Pillared Phosphates. The host material, α -zirconium phosphate (α -ZrP), was synthesized using the fluorocomplex method.²⁷ A colloidal suspension of α -ZrP was prepared by exposing the phosphate to *n*-propylamine vapors overnight. After the excess of *n*-propylamine in a desiccator with concentrated phosphoric acid was removed, the solid was dispersed in 0.03 M acetic acid and the pH was adjusted to 8 with a solution of 0.1 M of *n*-propylamine.²⁸ The preparation of pillared materials was described elsewhere.²⁹ The oligomer solutions were prepared by dissolving Ga(NO₃)₃·9H₂O and Cr(NO₃)₃·9H₂O in water. The pH was maintained at 4.4–4.5 by adding *n*-propylammonium acetate (0.1 M) and *n*-propylamine. The OAc[−]/Cr³⁺ molar ratio was 2.8. Five pillaring solutions, containing a total amount of Ga³⁺ and Cr³⁺ equal to 10 times the cationic

exchange capacity of the α -ZrP (6.64 mequiv·g^{−1}), and with Ga/Cr ratios of 10/90, 30/70, 40/60, 50/50, and 70/30, were mixed with colloidal suspensions of α -ZrP (1 g) and refluxed for 2 days. After a reaction took place, the solids were separated by centrifugation, washed with deionized water until a conductivity <50 μ S of the washing water was obtained, dried in air at room temperature for 1 day, and finally calcined at 673 K flowing N₂ for 12 h.

B. K⁺ Ion-Exchanged Materials. One gram of each pillared solid obtained as indicated above was contacted at 373 K with ammonia for 1 h. The ammonia-treated samples were suspended in 0.1 M KCl solution for 15 h, then separated by centrifugation, washed with deionized water, and dried at 333 K for 1 day. Finally, the solids were calcined at 673 K under a flow of N₂ for 2 h.

Catalyst Characterization. Gallium was analyzed by atomic absorption spectroscopy (AAS), and chromium colorimetrically as chromate ($\lambda = 372$ nm), after the samples were treated with NaOH/H₂O₂. The water content was determined by thermogravimetric analysis. The acetate content was determined by CNH analysis. N₂ adsorption–desorption isotherms were determined in a conventional volumetric apparatus at 77 K and after the samples were degassed at 473 K (1.33×10^{-2} Pa overnight). X-ray diffraction (XRD) of cast films were recorded on a Siemens D501 diffractometer (Cu K α source) provided with a graphite monochromator. Differential thermal analysis and thermogravimetry (DTA-TG) curves were obtained in air with a Rigaku Thermoflex instrument (calcined Al₂O₃ as a reference and 10 K min^{−1} heating rate). X-ray photoelectron spectra (XPS) were recorded with a Physical Electronics 5700 instrument provided with a hemispherical electron analyzer, the band-pass energy being 29.35 eV. The Al K α X-ray excitation source ($h\nu = 1486.6$ eV) was at a power of 300 W. The pressure in the analysis chamber was maintained below 1.33×10^{-7} Pa during data acquisition. The binding energies (BE) were obtained with ± 0.1 eV accuracy and charge compensation was done with the adventitious C(1s) peak at 284.8 eV. Thermal-programmed desorption of ammonia (NH₃-TPD) was used to determine the total acidity of the samples. Before the adsorption of ammonia at 373 K, the samples were heated at 673 K in a He flow (35 mL min^{−1}) for 1 h. The NH₃-TPD was performed between 373 and 673 K, with a heating rate of 10 K min^{−1}, and analyzed by an on-line gas chromatograph (Shimadzu GC-14A) provided with a TC detector.

Activity Test. Catalysts were tested in the dehydrogenation of propane, under pure (DH) and oxidative (ODH) conditions. A fixed-bed quartz U-tube reactor working at atmospheric pressure and a catalyst charge of 0.120 g without dilution were used in all cases. Samples were pretreated at the reaction temperature under a He flow (30 mL min^{−1}) for 60 min. The DH reaction was performed at 823 K, using a gaseous mixture of 7.06 mol % propane in helium. In ODH, the reaction temperature was 673 K and the gaseous mixture was formed by 7.06 mol % propane in O₂/N₂ (19.51/73.41, mol %). In both reactions, a total flow rate of 28.3 mL min^{−1} and a space velocity of 25.7 g_{cat}·h/mol of propane were used. In our experimental conditions both external and internal diffusional limitations were absent. The analysis of reactants and products was carried out on-line with a gas chromatograph Shimadzu GC-14B with a column (7 m in length, 5 mm internal diameter) filled with sebacitrile, and with a FID detector.

Results and Discussion

Catalyst Characterization. This family of catalysts has been largely described in detail elsewhere.²⁹ The chemical compositions of these pillared materials are compiled in Table 1. The total retention of M³⁺ is higher than the exchange capacity of α -ZrP (6.64 mequiv·g^{−1}) and increases along the series. The surface Ga/Cr atomic ratios of calcined materials determined by XPS preclude any coprecipitation of M³⁺ oxides on the surface of phosphate in all composition ranges studied.

BET surface areas (S_{BET}) of calcined Ga/Cr mixed oxides intercalated in α -ZrP are also listed in Table 1. S_{BET} varies between 247 and 348 m²·g^{−1} and these solids are meso-

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Table 1. Characteristics of Calcined Ga/Cr Mixed Oxides Intercalated in α -ZrP

sample Ga/Cr	Cr (wt %)	Ga (wt %)	K^+ /mequiv g^{-1}	$S_{BET}/m^2 \cdot g^{-1}$		$V_{AC}^a/cm^3 \cdot g^{-1}$		total acidity/ μmol of $NH_3 \cdot g^{-1}$	
				Ga/Cr	K-Ga/Cr	Ga/Cr	K-Ga/Cr	Ga/Cr	K-Ga/Cr
10/90	21.2	3.7	0.63	348	277	0.445	0.355	1709	529
30/70	20.1	9.3	0.58	326	288	0.332	0.311	2020	1049
40/60	15.5	15.4	0.48	283	250	0.279	0.269	1751	994
50/50	14.4	19.3	0.69	247	188	0.311	0.260	1807	1004
70/30	9.0	31.0	0.55	257	212	0.290	0.245	1633	903

^a Accumulated pore volume from the Cranston–Inkley method.

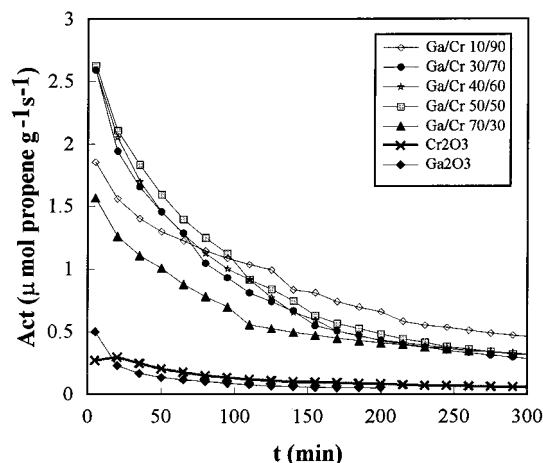


Figure 1. Catalytic dehydrogenation (DH) of propane over calcined Ga/Cr mixed oxides intercalated in α -ZrP, α -Cr₂O₃, and α -Ga₂O₃.

porous with a significant amount of micropores. The microporosity originates from the interlayer region while the mesoporosity is created principally by edge–edge and face–face interactions of the platelets.

These materials are acidic with a total acidity, as determined by TPD of ammonia, ranging between 1.60 and 2.02 mmol of $NH_3 \cdot g^{-1}$. Brönsted and Lewis acid sites are present on the surface of these catalysts and are active in the dehydrogenation of isopropyl alcohol with activities between 18.2 and 12.4 $\mu mol \cdot g^{-1} \cdot s^{-1}$, in the isomerization of 1-butene and in the deep oxidation of methylene chloride.²⁹

K⁺-Exchanged Samples. After K⁺ exchange of the materials an overall decrease of the S_{BET} areas between 12 and 24% is observed (Table 1) as a consequence of the alkaline ion steric hindrance. However, the total acidity decreases to a higher extent, indicating that K⁺ impedes the access to pores where an important fraction of acid sites are located.

Catalytic Results

Dehydrogenation (DH) of Propane. Under the described experimental conditions the catalytic activity found for pure α -ZrP for the DH of propane was zero. This result is relevant because it confirms that all observed catalytic activity is derived from mixed oxides inserted between the phosphate sheets. In a similar study with α -Cr₂O₃ and α -Ga₂O₃, (Figure 1) the initial activity of both oxides is low, 0.3 and 0.5 $\mu mol \cdot g^{-1} \cdot s^{-1}$, respectively, showing a decay with time on stream due to coke formation on their surfaces, and this deactivation being faster for α -Ga₂O₃. These results suggest that the catalytic activity is related to the acid centers of both α -Cr₂O₃ and α -Ga₂O₃. Initial conversion, selectivity, and activity values of all studied Ga/Cr mixed oxide pillared solids are listed in Table 2, and Figure 1 shows the evolution of the catalytic activity as a function of time on stream of these materials.

From these data some points are notable: (1) Ga/Cr mixed oxide pillared solids are much more active than those of the pure oxides, α -Cr₂O₃ and α -Ga₂O₃. This is attributed to the porous nature of these materials where Ga/Cr mixed oxides are highly dispersed, forming nanostructures inserted between the layers of the phosphate which imply an increment of the number of accessible active sites. (2) The maximum of the catalytic activity is attained at the beginning of the reaction, showing a fast deactivation with time on the stream due to coke formation on the catalyst surface. This point will be developed in more detail later. The activities of most of the studied catalysts converge to a similar value after 300 min of reaction. Similar behavior has also been reported for other catalysts.^{4–7} (3) The initial activity values found for the Ga/Cr catalysts ranged between 1.52 and 2.62 $\mu mol \cdot g^{-1} \cdot s^{-1}$. There is not a linear correlation between the activity and the Ga/Cr ratio. Samples with intermediate Ga/Cr ratios are the most active initially because these samples are more mesoporous and chromium is more accessible. In the case of the system CrO_x/ZrO₂ reported by De Rossi et al.,⁴ the initial activity found for propene was only 0.68 $\mu mol \cdot g^{-1} \cdot s^{-1}$, working at the same reaction temperature.

The selectivity for the DH product (propene) is much higher (between 78 and 91%) than that for the cracking reaction (methane and ethane). The selectivity to propene increases with time as previously observed in other catalytic systems.^{1,4,5,7} A possible explanation of this behavior could be that, at the beginning of the reaction, the stronger acid centers produce propane cracking, but after the deactivation of these centers with coke, the acid centers of medium strength only give rise to propene, producing a slight increment in the selectivity. That is, strong acid centers produce undesired cracking products and coke.

The deactivation of catalysts of this type for DH reactions is a subject of controversy in the literature. While some authors have proposed a correlation between deactivation and the amount of deposited coke on the catalyst,^{4,30–32} others have attributed this deactivation to the appearance of Cr(II), which would appear simultaneously with the formation and deposition of coke. However, Gorris et al.⁷ have demonstrated that the deactivation rate and the amount of coke formed are a function of the chromium dispersion and content, the deactivation rate being higher at higher amounts of Cr₂O₃ deposited on alumina. In the case of Ga/Cr pillared catalysts, the deactivation is mainly attributed to the coke deposition on the catalyst surface. This deposited coke has been evaluated by CNH analysis. The C percentage in the Ga/Cr pillared solids before the DH catalysis was lower than 0.33; after the catalytic reaction C percentage are between 5.56 and 11.5. The sample with the lowest Cr content exhibits the C percentage minimum value and

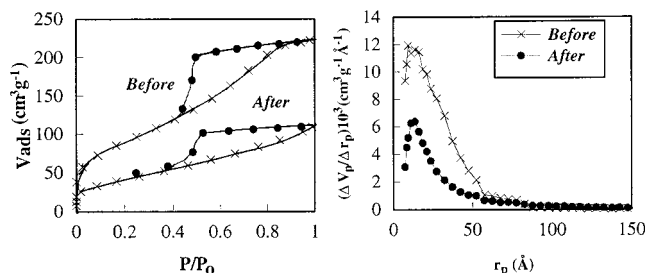
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Table 2. Initial Conversion, Selectivity and Activity for Catalytic Dehydrogenation (DH) of Propane over Calcined Ga/Cr Mixed Oxides Intercalated in α -ZrP

sample Ga/Cr	conversion (%)	selectivity (%)			activity (μmol of propene $\cdot\text{g}^{-1}\cdot\text{s}^{-1}$)
		methane	ethane	propene	
10/90	15.1	6.6	6.5	86	1.85
30/70	27.6	12.5	7.2	80.0	2.58
40/60	27.6	13.0	8.6	78	2.58
50/50	26.2	9.1	6.5	84	2.62
70/30	10.6	5.2	3.7	91.0	1.56

**Figure 2.** Adsorption(\times)–desorption(\bullet) isotherms and pore size distribution of calcined Ga/Cr 30/70 mixed oxides intercalated in α -ZrP before and after DH reaction.

is in good agreement with its total acidity and low selectivity to isobutane in the 1-butene isomerization test.²⁹

This C percentage can also be calculated from the DTA-TG curves of spent catalysts.⁸ The DTA curves show a pronounced exothermal effect centered between 673 and 773 K, which corresponds to the combustion of deposited carbon. Before catalysis, the DTA curves of the materials do not show any exothermal effect in this temperature interval.

The deposited carbon covers active sites of the catalysts and modifies their textural properties, avoiding the access of alkane molecules to other active sites and provoking a progressive loss of the activity, this decay being more pronounced at the beginning of the reaction. Other catalysts described in the literature also undergo pronounced surface and pore volume decrements after alkane dehydrogenation reactions.⁷ In the case of the pillared Ga/Cr 30/70 sample, after catalysis, S_{BET} changes from 266 to 150 $\text{m}^2\cdot\text{g}^{-1}$ and the pore volume decrement is close to 50% (Figure 2). This indicates that deposited carbon on the catalyst closes a great deal of meso- and micropores, avoiding the access of reactive molecules to the active sites located beyond.

XPS spectra of samples before and after the DH reaction at 823 K show a Cr ($2p_{3/2}$) single peak between 577.6 and 578 eV, indicating that the only chromium species on the surface is Cr(III).

Propane DH with K–Ga/Cr Catalysts. Coke formation is commonly attributed to strong Brønsted acid sites, which produce cracking reactions. A well-known method employed to attenuate these side-reactions is to exchange H^+ for K^+ . For this purpose potassium-exchanged Ga/Cr catalysts have been prepared and then tested for the propane DH. The initial activity, conversion to propene, and selectivity of the series of pillared K–Ga/Cr solids for the propane DH are listed in Table 3.

The initial activity values of K–Ga/Cr catalysts are ranged between 0.1 and 0.45 μmol of propene $\cdot\text{g}^{-1}\cdot\text{s}^{-1}$. It is clear that the observed catalytic activities of the potassium-exchanged catalysts are much lower than those observed with the pristine catalysts, but their deactivation is much less pronounced. The dramatic decrease observed of the catalytic activity is not correlated with the decrease in the S_{BET} and porosity after K^+ exchange because only

a moderate reduction of these parameters was observed. Neither is it correlated with the decrease in total acidity because the residual total acidity is still very high (Table 1). That means, according to De Rossi et al.,⁴ that oxygen ions located on pillars and zirconium phosphate layers, neighbors to metallic ions, are involved in the DH of propane. The cationic-exchange process provokes a modification of the basicity of these oxygen ions and simultaneously the presence of K^+ can hinder reactant's access to these ions. So, the surface oxygen, adjacent to active-metal centers, has a significant influence on the catalytic activity of these materials. The same effect has been observed in the 2-propanol decomposition test in the potassium-exchanged pillared Ga/Cr materials.²⁹

Oxidative Dehydrogenation (ODH) of Propane.

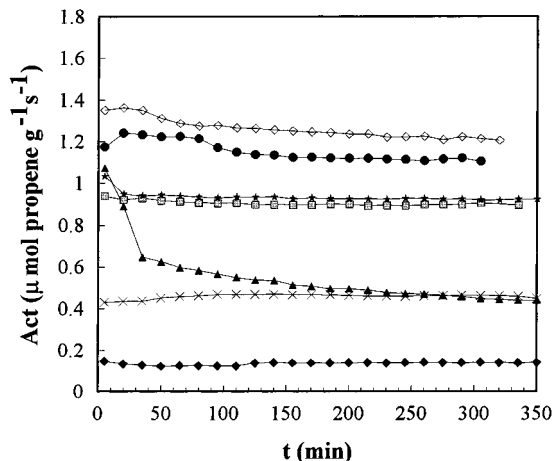
The ODH is defined as the process necessary to remove hydrogen from a compound by reaction with oxygen to produce water. This reaction has been carried out at 673 K, a lower temperature than that used in DH reactions, but the contact time was the same for the pure DH of propane in order to compare catalytic data. In addition to the pillared Ga/Cr samples, α -ZrP, α - Cr_2O_3 , and α - Ga_2O_3 have also been tested. α -ZrP and α - Ga_2O_3 are not active for the ODH of propane, while α - Cr_2O_3 shows a moderate activity value of 0.4 μmol of propene $\cdot\text{g}^{-1}\cdot\text{s}^{-1}$ (Figure 3). The observed catalytic activities of pillared Ga/Cr materials are shown in Figure 3 and Table 4 where the activity to propene increases with the content of Cr(III) in the samples. These results clearly indicate that the Cr(III) oxide in the interlayer region of the phosphate is the cause of the observed catalytic activity.

When comparing DH and ODH data, some interesting points must be noticed: The activity in the conversion of propane to propene is much higher using the oxidative method, the last reaction being at a lower temperature, 673 K. Under these experimental conditions the contribution of the pure DH reaction to the ODH process is negligible.

In contrast to the DH reaction, the activity under oxidative conditions is maintained almost constant for a long period of time. The observed activity values after 300 min of reaction for the pillared Ga/Cr solid series varies between 0.45 μmol of propene $\cdot\text{g}^{-1}\cdot\text{s}^{-1}$ (sample Ga/Cr 70/30) and 1.22 μmol of propene $\cdot\text{g}^{-1}\cdot\text{s}^{-1}$ (sample Ga/Cr 10/90). A comparison study of these results with others reported in the literature is difficult because of different experimental conditions, but for a VAPO-5,¹³ the activity is 0.39 μmol of propene $\cdot\text{g}^{-1}\cdot\text{s}^{-1}$ at 773 K and W/F = 90 $\text{g}_{\text{cat}}\cdot\text{h}\cdot\text{mol}$ of C_3^{-1} . Magnesium molybdate compounds³³ present a maximum activity value of 0.24 μmol of propene $\cdot\text{g}^{-1}\cdot\text{s}^{-1}$ at 788 K, and the activity decays dramatically at 673 K. The VO_x/AlNbO systems¹⁴ show a maximum value of 0.22 μmol of propene $\cdot\text{g}^{-1}\cdot\text{s}^{-1}$ working at 773 K. However, the values found for the V–Mg–O systems¹² vary between 0.44 and 0.74 μmol of propene $\cdot\text{g}^{-1}\cdot\text{s}^{-1}$, close to those found for pillared Ga/Cr catalysts, but at a higher temperature, 773 K. Sometimes, V–Mg–O

Table 3. Initial Conversion, Selectivity, and Activity for Catalytic Dehydrogenation (DH) of Propane over Calcined K-Ga/Cr Mixed Oxides Intercalated in α -ZrP

sample K-Ga/Cr	conversion (%)	selectivity (%)			activity ($\mu\text{mol of propene}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$)	
		methane	ethane	propene	initial	300 min
10/90	2.67	3.2	4.9	91.8	0.45	0.21
30/70	2.22	1.8	9.8	88.3	0.38	0.19
40/60	3.47	3.8	6.6	89.5	0.34	0.29
50/50	2.30	6.1	7.9	85.8	0.23	0.19
70/30	0.99	5.1	15.6	79.2	0.10	0.08

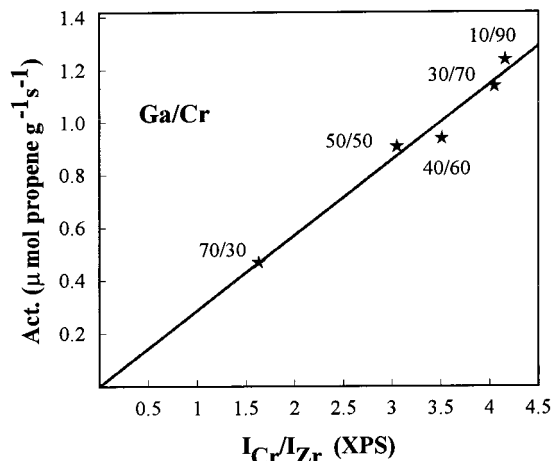
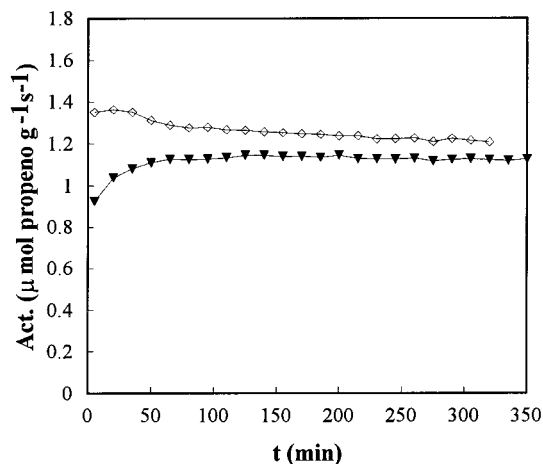
**Figure 3.** Catalytic oxidative dehydrogenation (ODH) of propane over calcined Ga/Cr mixed oxides intercalated in α -ZrP: (\diamond) Ga/Cr 10/90, (\bullet) Ga/Cr 30/70, (\star) Ga/Cr 40/60, (\blacksquare) Ga/Cr 50/50, (\blacktriangle) Ga/Cr 70/30, (\times) α -Cr₂O₃, and (\blacklozenge) VAPO-5.**Table 4. Conversion, Selectivity, and Activity at Steady State for Catalytic Oxidative Dehydrogenation (ODH) of Propane over Calcined Ga/Cr Mixed Oxides Intercalated in α -ZrP**

sample Ga/Cr	conversion (%)	activity ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$)			selectivity (%)	
		C ₁	C ₂	C ₃ H ₆	C ₃ H ₆	CO _x
10/90	42.4	0.18	0.47	1.22	19.1	70.5
30/70	36.6	0.08	0.37	1.12	20.2	71.2
40/60	35.5	0.07	0.44	0.92	17.2	72.9
50/50	32.1	0.04	0.35	0.89	18.5	73.2
70/30	7.54	0.03	0.05	0.45	40	55.1

compounds¹¹ reach activity values of up to 1.8 $\mu\text{mol of propene}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$ but always working at 773 K. In summary, pillared Ga/Cr mixed oxides zirconium phosphate materials show activity values for the ODH of propane similar to, or higher than, those observed with other catalysts, but interestingly, working at lower temperatures.

A VAPO-5 has been prepared as described by Concepcion et al.¹³ for a comparative study and tested under the same conditions as the pillared Ga/Cr solids. On one hand, this aluminophosphate presents an activity value of 0.14 $\mu\text{mol of propene}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$, a much lower value than those observed for pillared catalysts (Figure 3). On the other hand, comparing the observed activity value with pure α -Cr₂O₃ (Figure 3), it is clear that the formation of particles of Ga/Cr mixed oxides between the phosphate layers, which exhibit an open structure, provokes a significant increment of the catalytic activity for the ODH of propane. In this structure, Cr(III) active sites are more accessible for propane oxidation than those in the case of Cr₂O₃ with a corindon-type structure where vacancies are only restricted to the particle surface. The accessibility of propane and oxygen to the active sites is a key factor that determines the efficiency of a catalyst. In this way, the porous structure of the pillared material improves the accessibility of both molecules to the catalytic active sites.

XPS spectra of the pillared Ga/Cr catalyst series, before

**Figure 4.** Dependence of activity at steady state in the oxidative dehydrogenation (ODH) of the propane reaction on the $I_{\text{Cr}}/I_{\text{Zr}}$ intensity ratio (from XPS).**Figure 5.** Catalytic oxidative dehydrogenation (ODH) of propane over calcined Ga/Cr 10/90 mixed oxides intercalated in α -ZrP (\diamond) and over this prereduced material (\blacktriangledown).

and after reaction tests, show a symmetric Cr(3p_{3/2}) peak between 577 and 578 eV and reveal the existence of surface chromium as Cr(III). In Figure 4 the ODH activity is represented as a function of the $I_{\text{Cr}}/I_{\text{Zr}}$ ratio determined by XPS, clearly showing that the catalytic activity at the steady state increases linearly with the surface chromium content. We have noted above that the S_{BET} and the porosity also increase with the chromium content, and with this additional information it is possible to deduce that the higher the chromium content on the catalysts, the higher the number of active sites and the accessibility for the ODH of propane and oxygen, Cr(III) possibly being the active phase.

The TPR-H₂ curve of sample Ga/Cr 10/90 shows a peak of H₂ consumption at 723 K assigned to a partial reduction of Cr(III) to Cr(II). This sample has then been treated with a H₂/Ar (10% H₂) flow at 773 K for 15 min and tested in ODH of propane. The prereduced sample presents a

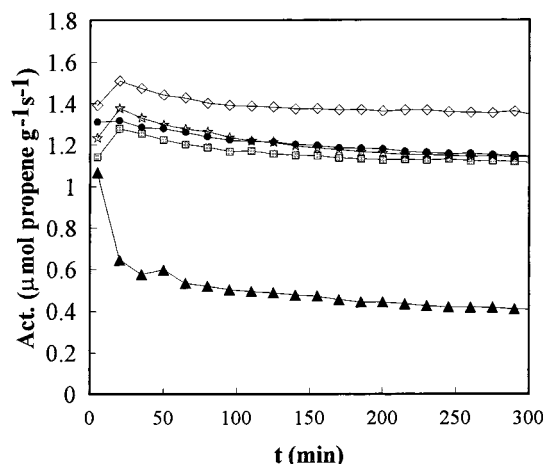
Table 5. Conversion, Selectivity, and Activity at Steady State for Catalytic Oxidative Dehydrogenation (ODH) of Propane over K⁺-Exchanged Calcined Ga/Cr Mixed Oxides Intercalated in α -ZrP

sample K-Ga/Cr	conversion (%)	activity ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$)			selectivity (%)	
		C ₁	C ₂	C ₃ H ₆	C ₃ H ₆	CO _x
10/90	42.3	0.18	0.40	1.36	21.3	69.5
30/70	41.4	0.15	0.60	1.15	18.4	69.4
40/60	38.2	0.10	0.33	1.14	19.7	72.6
50/50	34.4	0.12	0.33	1.11	21.5	69.6
70/30	18	0.09	0.09	0.40	14.5	78.5

lower initial catalytic activity than that observed with the sample without reduction. But the activity increases with time, attaining a constant value nearly equal to the pristine sample (Figure 5). This fact again indicates that the active phase for this reaction is Cr(III) because the oxidation of Cr(II) to Cr(III) with oxygen supposes an increment in the number of Cr(III) active species and the consequent increment in activity. Table 4 also included the selectivities of reaction products. Selectivities to propene are high: between 17.2 and 40%, increasing for materials with low conversion. However, selectivities to cracking products are very low. In contrast, the selectivity to oxidation products is very high, ranging between 55 and 73%.

Potassium Ion-Exchanged Samples. Table 5 and Figure 6 show the catalytic behavior of pillared K-Ga/Cr samples for the ODH of propane. In this case, the activity is practically constant for a long time and the observed activity is also related to the surface chromium content.

When the catalytic activity for the ODH of propane of potassium-exchanged samples is compared to their unexchanged homologues, it is evident that the activities found are similar or higher. This behavior is the opposite of that observed before in the case of pure DH. Hence, the mechanism for the ODH is totally different to that of the DH reaction. In this case there is also a direct relationship between activity and the amount of surface Cr(III). Possibly chromium species are responsible for the activation of the oxygen molecules in the initial step. Because Cr(III), with a t_{2g}^3 configuration, can supply electric charge to the empty π^* orbitals of O₂, dissociation can be provoked with the formation of Cr(V) which oxidizes hydrocarbon-forming propene and water, regenerating again Cr(III) centers. This step probably controls the reaction rate because all observed activities of potassium-exchanged

**Figure 6.** Catalytic oxidative dehydrogenation (ODH) of propane over K⁺-exchanged calcined K-Ga/Cr mixed oxides intercalated in α -ZrP: (\diamond) Ga/Cr 10/90, (\bullet) Ga/Cr 30/70, (\star) Ga/Cr 40/60, (\blacksquare) Ga/Cr 50/50, and (\blacktriangle) Ga/Cr 70/30.

pillared solids and of unexchanged homologues are very similar. This mechanism precludes Ga(III) ions as active sites because they do not have any d electrons available, as deduced from the curves of activity and the chemical composition of the catalysts. However, XPS data also indicate the single existence of Cr(III) on the surface of pillared K-Ga/Cr after the catalytic reaction.

Conclusions

Intercalation of Ga/Cr mixed oxides with chromium contents between 90 and 30% in α -ZrP originates porous material with high surface areas and acidity. These systems represent a new way to obtain mixed oxides largely dispersed as nanoparticles between the layers of zirconium phosphate which are active in the pure dehydrogenation of propane at 823 K and specially active in the oxidative dehydrogenation of propane with activities comparable to that obtained with vanadium-containing catalysts but working at temperatures as low as 673 K.

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