

Preparation, characterisation and activity of chromia–zirconia catalysts for propane dehydrogenation

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Abstract

Dehydrogenation catalysts based on chromia supported on ZrO₂, containing about 10 wt.% of chromium and increasing amounts of potassium (up to 4 wt.%), were prepared and characterised by chemical analysis, N₂ adsorption–desorption at 77 K, X-ray diffraction (XRD), UV–vis diffuse reflectance spectroscopy (DRS), temperature programmed reduction (TPR) and adsorption microcalorimetry of ammonia. Increasing K amounts deeply modify the ammonia adsorption behaviour, with a progressive decrease in the acidic features, which are completely lost when the K content attains 1 wt.%. Reduction of Cr species seems rather easy for chromia–zirconia and K-containing chromia–zirconia samples with K contents up to 0.5 wt.%. The onset of reduction shifts to higher temperatures as the K concentration increases. Catalytic testing was performed under atmospheric pressure at 813 K. Pure zirconia is very poorly active in propane dehydrogenation; also virtually inactive are the samples with a K content ≥ 1 wt.%. Conversion decreases as the K amount increases up to 0.5 wt.%, propene selectivity being close to 100 mol%. An induction period is observed for all the active samples, which attains a maximum in conversion before being deactivated by coking.

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1. Introduction

The catalytic dehydrogenation of poorly reactive, low-cost propane deserves attention as an interesting route to propene, valuable product for manufacturing functionalised compounds. The high activity and selectivity of supported chromia catalysts for the dehydrogenation of C₃–C₄ alkanes have been known for many decades [1–3]. Widely employed industrial catalysts for this reaction are chromia supported on γ -alumina, a refractory high surface area material, which unfortunately presents the undesired feature of catalysing the side reactions of cracking and cok-

ing, leading to catalyst deactivation. In this respect, the possibility of using supports with different acidic features [4–11] and the addition of alkali or alkaline-earth metals to the catalyst formulation [11–22], have been also investigated.

The present work deals with the preparation, characterisation and testing of potassium-containing (up to 4 wt.%) chromia–zirconia catalysts for the dehydrogenation reaction of propane. All of them were characterised by chemical analysis, X-ray diffraction (XRD), UV–vis diffuse reflectance spectroscopy (DRS), N₂ adsorption–desorption at 77 K, temperature-programmed reduction (TPR) and adsorption microcalorimetry of ammonia. Catalytic testing was carried out in a fixed-bed flow microreactor under atmospheric pressure at 813 K.

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Table 1
Chemical composition and textural properties of the catalysts

Catalyst	Cr _{tot} (wt.%)	Cr ^{VI} (wt.%)	Cr ^{III} (wt.%)	K (wt.%)	S _{BET} (m ² /g)	V _p (cm ³ /g)
ZCr10 ^{*a}	10.90	0.83	10.20	–	37	0.202
ZCr10 ^{**b}	12.90	1.40	11.20	–	72	–
ZCr10K0.2	10.45	0.62	10.12	0.10	37	0.149
ZCr10K0.5	10.55	0.77	10.40	0.27	42	0.239
ZCr10K1	13.40	1.60	11.70	0.81	27	0.136
ZCr10K2	13.10	3.30	10.50	1.59	24	0.054
ZCr10K4	13.50	6.20	7.30	5.52	18	–

^a From which K0.2–0.5 samples were prepared.

^b From which K1–4 samples were prepared.

2. Experimental

2.1. Catalyst preparation

Commercial hydrous zirconia (MEL, S_{BET} = 179 m²/g) samples were impregnated (incipient wetness technique) with aqueous solutions of the appropriate amounts of CrO₃ or CrO₃ + K₂Cr₂O₇. Drying overnight at 383 K and calcination at 973 K for 12 h led to the following catalysts: ZCr10; ZCr10K0.2; ZCr10K0.5; ZCr10K1; ZCr10K2; ZCr10K4 (figures after symbols refer to the nominal wt.% of Cr and K, respectively). Chemical composition and textural properties of the catalysts are summarised in Table 1.

2.2. Catalyst characterisation

Chemical analysis of the total chromium content was carried out by atomic absorption (AA, Varian SpecrAA-30) on samples previously dissolved by fusion with a mixture of KNO₃ and Na₂CO₃ (1:1 by weight). A different portion of the catalyst was repeatedly treated with 1 M NaOH solution heated to incipient boiling in order to extract Cr^{VI} and Cr^V species, and the liquid analysed by AA. The residue was then dissolved by fusion with the mixture of KNO₃ and Na₂CO₃ and analysed by AA for determining Cr^{III}. Potassium content was determined by AA on fresh portions of the samples after extraction with distilled hot water.

Textural analyses were carried out on a Sorptomatic 1990 System (Fisons Instruments), by determining the nitrogen adsorption/desorption isotherms at 77 K. Before analysis, the samples were heated overnight under vacuum up to 473 K (heating rate = 1 K/min).

Phase analysis was performed by XRD using a Philips PW 1729 diffractometer equipped with a PC for data acquisition and analysis (software APD-Philips). Scans were taken with a 2θ step of 0.01°, using Ni-filtered Cu Kα radiation.

Diffuse reflectance spectra were taken in the wavelength range of 200–800 nm (50,000–12,500 cm⁻¹) with a Varian CARY 5E spectrometer equipped with a PC for data acquisition and analysis and using PTFE as a reference.

Tian-Calvet heat flow equipment (Setaram) was used for microcalorimetric measurements. Each sample was pre-treated overnight at 673 K under vacuum (10⁻³ Pa) before the successive introduction of the probe gas (ammonia). The

equilibrium pressure relative to each adsorbed amount was measured by means of a differential pressure gauge (Data-metrics). The run was stopped at a final equilibrium pressure of 133.3 Pa. The adsorption temperature was maintained at 353 K, in order to limit physisorption.

TPR profiles were obtained on a TPD/R/O 1100 apparatus (ThermoQuest), under the following conditions: sample weight 40 mg, heating rate (from 313 to 1173 K) 20 K/min, flow rate 30 cm³/min, H₂ 5% by volume in N₂; the hydrogen consumption was monitored by a thermal conductivity detector (TCD).

2.3. Catalytic runs

Experimental runs lasting 2 h were performed in a fixed-bed quartz-glass microreactor at $P = 1.013 \times 10^5$ Pa and $T = 813$ K, catalyst weight (40–80 mesh) = 0.25 g. Blank runs, performed in the empty reactor, allowed to rule out the contribution of thermal reactions.

Prior to the catalytic test, samples were activated in situ at 773 K for 12 h, under nitrogen flow (15 cm³/min). The reaction mixture contained 12 vol.% C₃H₈ ($p_{C_3H_8} = 0.234 \times 10^5$ Pa) diluted in He (total flow rate = 53 cm³/min). On line GC analysis was carried out with an HP 6890, equipped with a capillary column HP PORAPLOT Q and a TCD. Propane (C₃) conversion and selectivity to products have been calculated as follows:

$$\text{Conversion (mol\%)} = \frac{\text{moles of C}_3 \text{ reacted}}{\text{moles of C}_3 \text{ fed}} \times 100,$$

$$\text{selectivity (mol\%)} = \frac{\text{moles of product } i \text{ formed}}{\text{moles of C}_3 \text{ reacted}} \times \left(\frac{N_i}{N_{C_3}} \right) \times 100$$

where i is propene, ethylene, ethane, methane and CO₂; N_i and N_{C_3} the number of carbon atoms in product and propane, respectively.

3. Results and discussion

3.1. Catalysts characterisation

XRD results are summarised in Table 2. All samples showed the presence of tetragonal ZrO₂ and α-Cr₂O₃. At

Table 2
X-ray diffraction results (see footnotes of Table 1)

Catalyst	Crystal phases	Crystal size (Å)	
		ZrO ₂	Cr ₂ O ₃
ZCr10*	<i>t</i> -ZrO ₂ + α -Cr ₂ O ₃	158	>1000
ZCr10**	<i>t</i> -ZrO ₂ + α -Cr ₂ O ₃	–	–
ZCr10K0.2	<i>t</i> -ZrO ₂ + α -Cr ₂ O ₃	168	>1000
ZCr10K0.5	<i>t</i> -ZrO ₂ + α -Cr ₂ O ₃	162	>1000
ZCr10K1	(<i>t+m</i>)-ZrO ₂ + α -Cr ₂ O ₃	160	>1000
ZCr10K2	(<i>t+m</i>)-ZrO ₂ + α -Cr ₂ O ₃ + K ₂ Cr ₂ O ₇	–	–
ZCr10K4	(<i>t+m</i>)-ZrO ₂ + α -Cr ₂ O ₃ + K ₂ Cr ₂ O ₇	–	–

potassium amounts ≥ 1 wt.%, the typical peaks of monoclinic zirconia started to appear and increased with the K content. In the case of the ZCr10K2 and ZCr10K4 catalysts, signals imputable to the K₂Cr₂O₇ phase were also present. Particle sizes, evaluated by means of the Scherrer equation [23], were found to be about 160 Å for zirconia and >1000 Å for chromia.

Diffuse reflectance UV–vis spectra of the investigated catalysts are shown in Fig. 1, where the spectrum of α -Cr₂O₃ is also reported for reference. The UV–vis region is diagnostic for the presence of Cr^{VI} in tetrahedral coordination (chromates) and Cr^{III} in octahedral symmetry. Four absorption bands can be evidenced from the figure: two charge transfer bands can be evidenced from the figure: two charge transfer transitions O \rightarrow Cr typical of Cr^{VI} at $\lambda \sim 278$ and 370 nm and two bands due to d–d transitions of Cr^{III} at $\lambda \sim 463$ (A_{2g} \rightarrow T_{1g}) and 600 nm (A_{2g} \rightarrow T_{2g}). An increase in Cr^{VI} concentration with the K-content is manifest from the increasing values of the peaks intensity at 278 nm and, mainly, at 370 nm, thus confirming the results of chemical analyses (Table 1). It should be noted however that previously reported EPR results on chromia–zirconia samples [8] showed that Cr^V in addition to Cr^{VI} species are stabilised on the carrier. The assessment of the Cr^V and Cr^{VI} amounts on a quantitative basis is a difficult task. Cr^V, which is not stable in aqueous solutions likely undergoes disproportionation during extraction according to the following reaction [9]: 3Cr^V \rightarrow 2Cr^{VI} + Cr^{III}. Therefore, the amount of Cr^{VI} reported in Table 1 includes 2/3 of the initially present Cr^V (the rest being most probably retained on the surface as finely dispersed Cr^{III} hydroxide) and is underestimated in comparison with the sum of the original Cr^V + Cr^{VI} concentrations. Nevertheless the Cr^{VI} value in the table can be taken as indicative of the content of the highly oxidised chromium species. In general, these findings are in agreement with the literature, where the existence, in chromia-supported catalysts, of chromium in different oxidation states is reported to depend on the nature of the carrier, metal loading, calcination temperature, hydration degree of the surface and chromium precursor [5,7–9,24–36]. Calcination of CrO₃-impregnated zirconia, with high chromium loadings, mainly leads to Cr^{III}, under the form of clusters and α -Cr₂O₃ [9]. Strong interaction of dispersed Cr^V and Cr^{VI} ions with the support occurs to some extent and prevents complete transformation of the original highly oxidised species into Cr^{III}. The pronounced increase

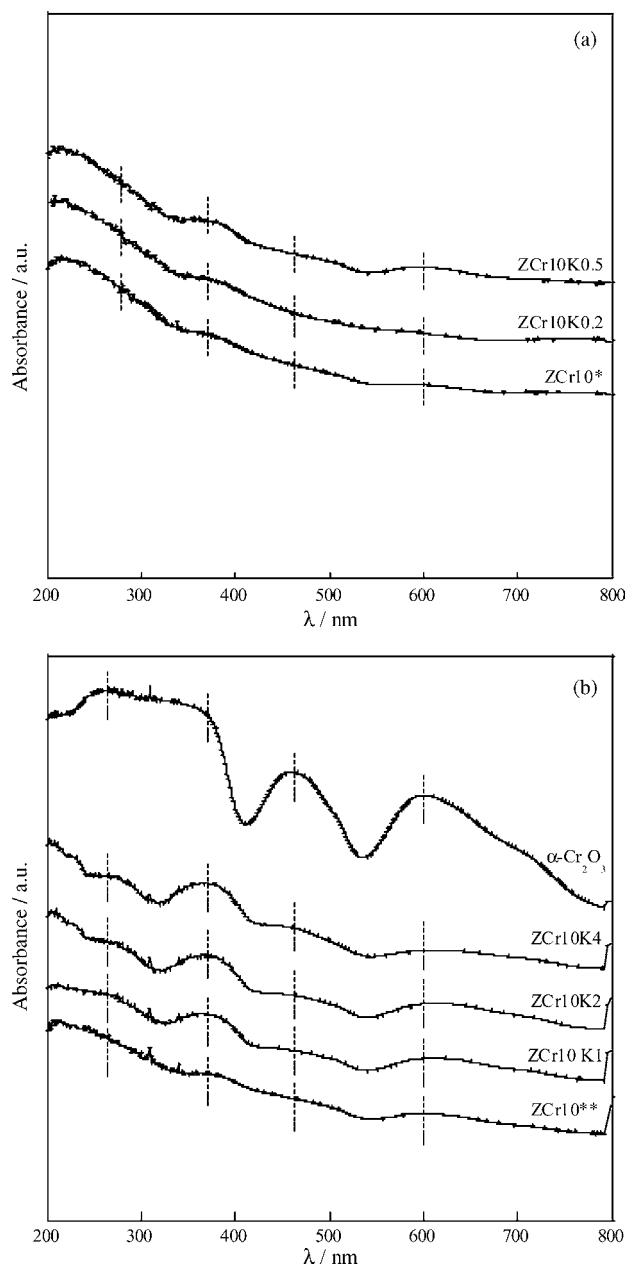


Fig. 1. UV–vis DRS spectra: Cr^{VI} at $\lambda \sim 278$ and 370 nm; Cr^{III} at $\lambda \sim 463$ and 600 nm.

in the concentration of the highly oxidised chromium species observed at potassium loadings ≥ 1 wt.% (Table 1) can be explained by the formation, induced by the presence of the alkali metal, of K-chromates or bichromates, at the expense of Cr^{III} (mainly of the α -Cr₂O₃ phase). This is in agreement with previous reports dealing with chromia–alumina catalysts [22,37].

TPR results are reported in Fig. 2 (on which TPR profiles of the pure ZrO₂ and α -Cr₂O₃ are also showed in the inset) and summarised in Table 3. The two ZCr10 samples show the same profile, with a symmetric peak at about 625 K and a second, badly defined, broad peak above 773 K. Upon reduction of low Cr^{III} content chromia–zirconia catalysts with CO at

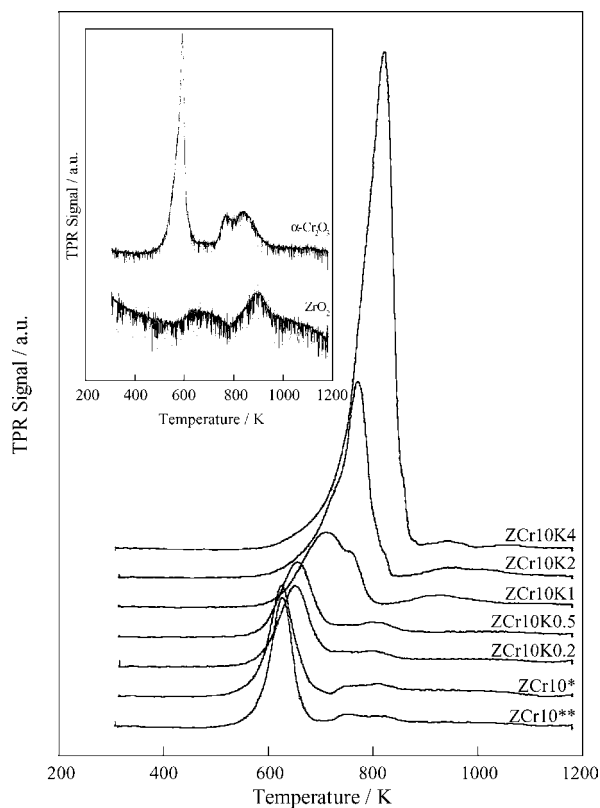


Fig. 2. TPR profiles: heating rate, 20 K/min; reducing agent, 5 vol.% H₂/N₂ at 30 ml/min; $m_{\text{cat}} = 40$ mg.

increasing temperature, it was found [8] that Cr^V is preferentially reduced to Cr^{III} in the early stage of the process and, in succession Cr^{VI} is also reduced to Cr^{II}. The first peak of the ZCr10 samples might hence be reasonably ascribed to the reduction of these highly oxidised chromium species, even though, unfortunately, the contribution of the two different oxidation states is not distinguishable in the TPR profiles. The hydrogen consumption at higher temperatures (above 773 K), also observed for the pure α -Cr₂O₃, might be due to the reduction of bulk chromium species to oxidation states lower than +3 [26] or to an activated hydrogen adsorption on chromia, an event already observed by other authors [38]. However, a contribution of the uncovered ZrO₂ surface cannot be ruled out, since also zirconia has been reported to dissociatively

Table 3
TPR results

Catalyst	T_{max} (K)	H ₂ consumption (μmol/g)	Cr ^{VI} (μmol/g)	H/Cr ^{VI}
ZCr10*	625	240	160	3.1
ZCr10**	627	231	269	1.7
ZCr10K0.2	649	187	119	3.1
ZCr10K0.5	655	196	148	2.7
ZCr10K1	711	287	308	1.9
ZCr10K2	772	450	635	1.4
ZCr10K4	822	1051	1192	1.8

The temperature of the maximum hydrogen consumption is referred to the main reduction peak. See footnotes of Table 1.

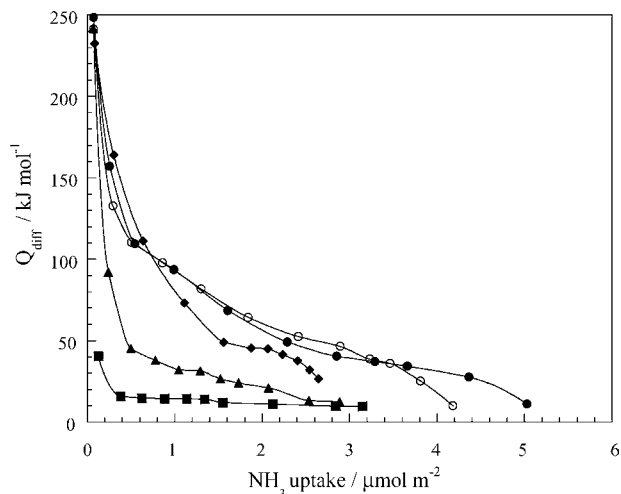


Fig. 3. Differential heat of adsorption, Q_{diff} , vs. NH₃ uptake: (●) ZCr10*; (○) ZCr10**; (◆) ZCr10K0.2; (▲) ZCr10K0.5; (■) ZCr10K1.

adsorb hydrogen [39]. After addition of potassium in low amounts (≤ 0.5 wt.%), the shape of the TPR patterns is not significantly changed with respect to ZCr10* catalyst, but the value of T_{max} for the main peak markedly increases from 625 (ZCr10*) to 649 or 655 K for ZCr10K0.2 and ZCr10K0.5, respectively. Such a behaviour indicates that, in the presence of potassium, the highly oxidised chromium species are less easily reduced. The increase of T_{max} is much more pronounced when the K content is ≥ 1 wt.% (see Table 3). ZCr10K1 catalyst shows a peak at 711 K with a clear shoulder at about 760 K; for the ZCr10K2 sample, the value of T_{max} is equal to 772 K, with an initial sketchy shoulder, suggestive of the presence of two unresolved peaks. Two distinct reduction features, at temperatures between 600 and 800 K, have been already observed on K-containing chromia–alumina samples [37]. The first peak, at lower temperatures, was ascribed to Cr^{VI} species directly interacting with the support; the second one, at higher temperatures, was attributed to the formation of less reducible potassium chromate or bichromate phases. TPR profiles of the ZCr10K1 and ZCr10K2 catalysts, showing the presence of two peaks, even if badly resolved, also suggest the presence of a second kind of highly oxidised chromium species. Most probably the latter are potassium bichromates, as indicated by the presence of the diffraction peaks of K₂Cr₂O₇ in the XRD patterns. It can be supposed that, in the case of the ZCr10K4 sample, which exhibits one peak of reduction at 822 K, only Cr^{VI} in the potassium bichromate phase is accessible to hydrogen during the TPR experiment.

The microcalorimetric results are summarised in Fig. 3, where the differential adsorption heat of ammonia, Q_{diff} , is plotted as a function of the uptake, expressed as $\mu\text{mol}/\text{m}^2$ to take into account the different values in surface areas. The decreasing trend of Q_{diff} with coverage is consistent with the chemical as well as structural heterogeneity of the samples. As expected, the calorimetric curves for the two ZCr10 cata-

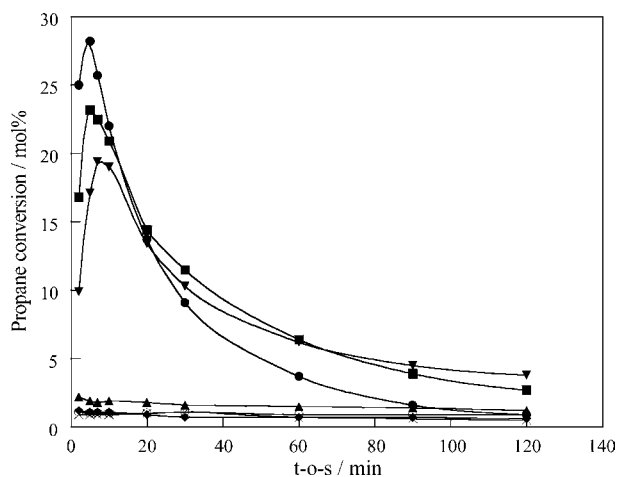


Fig. 4. Propane conversion vs. time on stream: (●) ZCr10*; (■) ZCr10K0.2; (▼) ZCr10K0.5; (▲) ZCr10K1; (◆) ZCr10K2; (×) ZCr10K4; (○) ZrO₂.

lysts are very similar at any ammonia coverage. Increasing K amounts deeply modify the ammonia adsorption behaviour, with a progressive decrease in the acidic features. After the addition of the lowest amount of potassium (see ZCr10K0.2 sample) a considerable decrease in both the concentration and strength of the acid sites is manifested. Such a diminution is much more pronounced in the case of ZCr10K0.5 catalyst. Acidity is completely lost when the K content attains 1 wt.%, ammonia adsorption on ZCr10K1 being non-specific, as revealed by the very low Q_{diff} values. ZCr10K2 and ZCr10K4 samples do not adsorb NH₃ at all.

3.2. Catalytic results

Propane conversion and propene selectivity are plotted as a function of time-on-stream (t-o-s) in Figs. 4 and 5, respectively. Pure zirconia is virtually inactive in propane dehydrogenation. Also inactive are the samples with a K content ≥ 1 wt.%. The active catalysts can be ranked according to conversion as follows: ZCr10* > ZCr10K0.2 > ZCr10K0.5. All

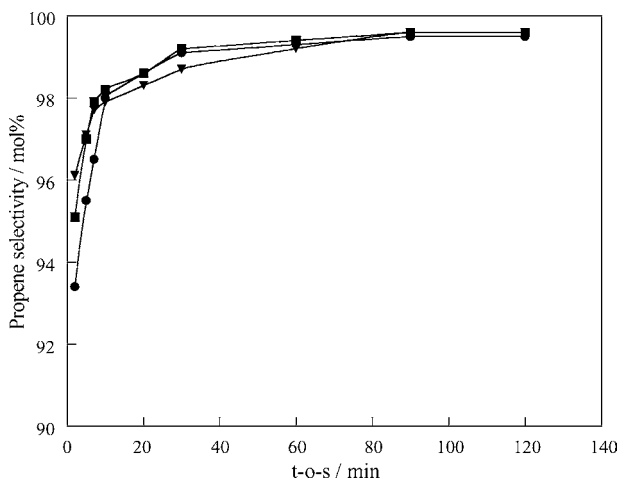


Fig. 5. Propene selectivity vs. time-on-stream. Symbols as in Fig. 4.

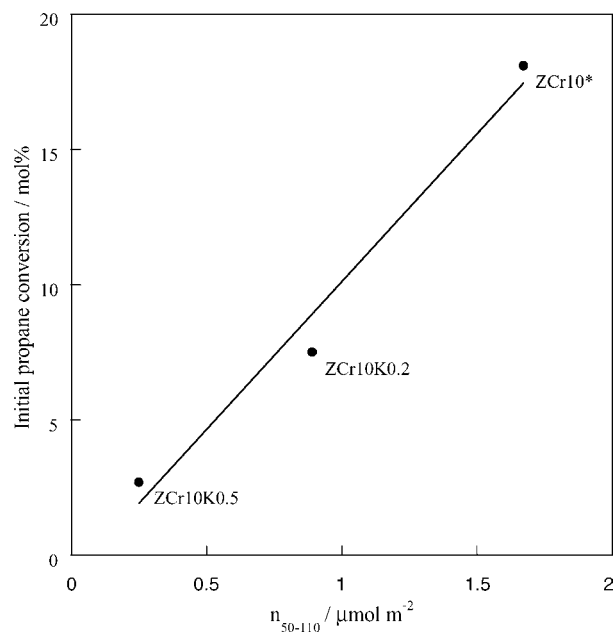


Fig. 6. Initial propane conversion vs. acidity.

of them show an induction period, during which conversion increases up to a maximum and then decreases. Besides the desired product (propene), methane, ethene, ethane and CO₂, the latter during the very early moments on-stream, were also detected as by-products. Though very high since the beginning (ca. 94–96 mol%), propene selectivity rapidly increases attaining a plateau at about 99 mol%.

In Cr-containing catalysts, it is Cr^{III} that, in a concerted way with O²⁻, dissociatively adsorbs and activates the hydrocarbon [4,5]. Such coordinatively unsaturated surface Cr^{III} species (Cr^{III}_{cus}) should act as Lewis centres for ammonia adsorption during the microcalorimetric runs. Simultaneous ammonia adsorption on different surface chromium species as well as on Brønsted sites occurs, which makes rather difficult to find a clear-cut correlation with activity. Close inspection of Fig. 3 shows however that the calorimetric curves for ZCr10, ZCr10K0.2 and ZCr10K0.5 significantly differ in the Q_{diff} region between 110 and 50 kJ/mol, which suggests that the sites of this strength should be relevant for the catalytic activity. To confirm this, propane conversion was extrapolated from Fig. 4 at t-o-s = 0 and plotted in Fig. 6 as a function of the number of acid sites with adsorption heats in the range of 50–110 kJ/mol (n_{50-110}). (The choice of such conversion values stems from the need to assure that surface modification effects arising during the reaction do not superimpose.) A fairly linear correlation is manifested.

The induction period observed on these catalysts could be reasonably ascribed to the reduction, by the hydrocarbon, of the highly oxidised chromium species to new active Cr^{III} sites during the early moments of the reaction, a phenomenon already reported for chromia-containing catalysts [11,35,40,41]. Fast deactivation then follows, due to coke for-

mation. Selectivity results confirm the occurrence of reduction by propane, as revealed by the presence of oxygenated products (mainly CO₂ and H₂O) in the early moments on-stream. The strong acid sites initially favour cracking reactions of propene leading to methane and ethene. The transformation of both propane into oxygenated compounds and propene into cracking products affects the initial selectivity values, as also suggested in [11,35].

In this light, the lack of chromium species of any kind explains the inactivity of pure zirconia. As for ZCr10K1, ZCr10K2, ZCr10K4, it is worth to note that neither Cr^{III} nor Cr^V and Cr^{VI} are able to interact with ammonia, probably because: (i) Cr^{VI} is mostly present as bichromate phase, and hence stabilised by a basic environment; (ii) Cr^{III}, mostly present as α-Cr₂O₃, is largely covered by the bichromate phase. Under such situation no significant amount of Cr^{III} is exposed at the surface before reaction. Neither, Cr^{III} can be formed from bichromate by action of propane during the reaction, the reduction of bichromate species being rather difficult, as evidenced by TPR experiments. As a result, no catalytic activity is observed on these samples.

4. Conclusions

On chromia–zirconia catalysts, containing about 10 wt.% of Cr and increasing amounts of potassium (up to 4 wt.%), chromium is present on the surface under the form of α-Cr₂O₃, Cr^{III} clusters and as highly oxidised chromium species (Cr^V + Cr^{VI}). The concentration of the highly oxidised chromium species increases with the K content, most probably because of formation of a surface K₂Cr₂O₇ phase at the expense of Cr^{III}. TPR profiles of the investigated catalysts show a shift of *T*_{max} towards higher and higher values when passing from ZCr10 to ZCr10K4 catalyst, the reduction of bichromate species being rather difficult. Besides affecting reducibility, increasing K contents also determine deep modifications in the ammonia adsorption behaviour, with a progressive decrease in acidity, which is definitively absent for the ZCr10K1–4 samples. The reactivity studies show that the addition of any amount of potassium to ZCr10 samples leads to a decrease in catalytic activity, which is completely lost when K content attains 1 wt.%. All these findings show that some acidity is necessary for the dehydrogenation reaction. Potassium hinders the reduction of Cr^V and Cr^{VI} to Cr^{III} and decreases the Lewis acidity of Cr^{III} in the Cr^{III}_{cus}–O²⁻ acid–base couples which are suggested to be the sites for propane activation.

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