Oxidative conversion of propane over Al_2O_3-supported molybdenum and chromium oxides

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Oxidative dehydrogenation of propane has been studied on Mo/γ-Al_2O_3 catalysts with 13 wt% of MoO_3 and promoted with Cr. The catalysts were characterized by BET, X-ray diffraction, XPS, TPR, TPO and isopropanol decomposition. The ODH results indicated an important increase in propane conversion with Cr loading increase from 0 to 5 wt%. At 773 K the conversion increased 1.5 times whereas the selectivity to propene was not significantly modified. The higher activities obtained on Cr-doped catalysts provide for the technologically important possibility of carrying out the reaction at lower temperatures.

KEY WORDS: propane oxidative dehydrogenation; Cr-Mo/γ-Al_2O_3 catalysts.

1. Introduction

In the past decade there has been great interest in the development of highly selective catalysts for oxidative dehydrogenation (ODH) of light alkanes into alkenes due to their potential application as a source of cheap raw materials. In this process, an oxidizing agent, as O_2 or air, is added to the feed:

$$C_nH_{2n+2} + \tfrac{1}{2}O_2 \longrightarrow C_nH_{2n} + H_2O$$

where the formation of the very stable product, water, makes this reaction thermodynamically favorable and exothermic ($\Delta H^{\circ}_{773} = -28\,\text{kcal mol}^{-1}$ for the ODH of propane). In principle, a complete conversion is obtained even at low temperature. This provides great advantages over the direct dehydrogenation process based on engineering economic considerations [1]. The presence of oxygen and the high reactivity of the product make it difficult to stop the reaction at the desired product and avoid non-selective oxidation under the conditions at which the alkane is activated. The key to this process is the development of stable catalysts capable of activating the alkane molecule at low or intermediate temperatures under an oxygen flow. A wide variety of catalytic systems has been proposed for this reaction. By far the most widely studied systems for propane conversion have been based on vanadium [2–6] and molybdenum [7–12] catalysts. The temperature range for these systems is between 723 and 823 K with a propene yield below 30%.

In previous work the influence of Mo loading on γ-Al_2O_3 was studied in the ODH of propane [12]. It was shown that when γ-Al_2O_3 was covered with a molybdate layer at less than the monolayer values the catalysts were active but the dehydrogenation selectivity was reduced by the formation of carbon oxides. The results indicated that with Mo loading increasing from 3.6 to 12.7 wt% propane conversion increased in parallel with acidity and reducibility. At conversions higher than 20% the selectivity to propene leveled off around 25% irrespective of the Mo content.

The influence of promoters to improve the performance of these catalysts was also studied. The addition of Li on a Mo/γ-Al_2O_3 catalyst with 13 wt% of MoO_3 led to important changes in texture and in the Mo-supported structure. The activity of propane markedly decreased for promoted catalysts at increasing Li content. The selectivity to propene increased at lower conversion whereas at higher values it leveled off around 25%. The apparent activation energy for propane conversion was independent of Li dopant concentration [13]. The addition of Sb to the support also led to a lower conversion of propane with only a small positive effect on selectivity to propene, a lower production of CO_x and a slight increase in the cracking activity [14].

In the present work, the catalytic behavior over a series of Mo supported on Cr-doped γ-Al_2O_3 catalysts of varying dopant concentration has been investigated with the aim of determining their influence on the catalytic activity and selectivity in the ODH of propane.

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2. Experimental

2.1. *Sample preparation*

Alumina support was calcined at 873 K for 3 h before being used. Two different amounts of Cr (3 and 5% w/w) were incorporated onto alumina by dry impregnation with an aqueous solution of CrO_3. After drying at 373 K overnight and calcining in air at 723 K for 3 h, the doped support was impregnated with an aqueous solution containing ammonium heptamolybdate (AHM), 5×10^{-3} M at pH = 5.6 using the wet impregnation method. The volume of AHM was chosen in order to add 13% of MoO_3. After evaporation of the solvent under reduced pressure, the samples were dried at 373 K overnight and further calcined in air at atmospheric pressure according to the following procedure: the temperature was increased linearly for 2.5 h up to 723 K, kept constant at 723 K for 3 h, increased linearly up to 873 K, and then maintained for 5 h at 873 K. Samples were denoted as *x*CrMo where *x* indicates the wt% of Cr.

2.2. *Catalyst characterization*

Samples were characterized using the following physicochemical methods.

2.2.1. *BET surface area*

BET surface areas were measured using a Micromeritics Accusorb 2100E instrument by adsorption of nitrogen at 77 K on 200 mg of sample previously degassed at 473 K under high vacuum for 2 h.

2.2.2. *X-ray diffraction (XRD)*

XRD patterns were obtained with a RIGAKU diffractometer operated at 30 kV and 20 mA using Ni-filtered CuKα radiation ($\lambda = 0.15418$ nm). The samples in powder form were analyzed without previous treatment after deposition on a quartz sample holder. The identification of crystalline phases was made by using references from the JCPDS files.

2.2.3. *Acid–base properties*

Decomposition of isopropanol (IPA) was used for determining the acid–base properties of the samples. The reaction was carried out between 433 and 473 K in a fixed-bed continuous flow reactor under atmospheric pressure and in the absence of oxygen. The feed consisted of 4.5% IPA and the balance helium. The amount of catalyst was ~0.5 g and the flow rate was 40 ml STP min^{-1}. The data for rate calculations were taken after the stationary state was reached and the conversion of isopropanol was less than 15%. Product analysis was performed by gas chromatography by using a Carbowax 20 M on Chromosorb W column and a thermal conductivity detector. The isopropanol decomposition proceeds by two parallel routes: dehydration to propene and to di-isopropylether on acidic sites and dehydrogenation to acetone on redox (basic) sites [15].

2.2.4. *X-ray photoelectron spectroscopy (XPS)*

The XP spectra were recorded with a Fisons ESCALAB MK11 200 R spectrometer equipped with a MgKα X-ray excitation source ($h\nu = 1253.6$ eV) operated at 12 kV and 10 mA and a hemispherical electron analyzer. Each spectral region was scanned a number of times in order to obtain good signal-to-noise ratios. The residual pressure inside the analysis chamber was kept at values below 7×10^{-9} torr. MO_{3d}, Al_{2p}, Cr_{2p}, O_{1s} and C_{1s} spectra were recorded for each catalyst. All binding energies (BEs) were referred to the Al_{2p} line at 74.5 eV.

2.2.5. *Temperature-programmed reduction (TPR)*

Studies were performed in conventional TPR equipment. This apparatus consisted of a gas handling system with mass flow controllers (Matheson), a tubular reactor, a linear temperature programmer (Omega, model CN 2010), a PC for data retrieval, a furnace and various cold traps. In each experiment the sample size was ~100 μmol of Mo to ensure a good resolution under the experimental conditions used. Before each run, the samples were oxidized in a 30 ml min^{-1} flow of 20 vol% O_2 in He at 723 K for 30 min. After that, helium was admitted to remove oxygen and then the system was cooled at 323 K. The samples were subsequently contacted with a 30 ml min^{-1} flow of 10 vol% H_2 in Ar and heated, at a rate of 10 K min^{-1}, from 323 K to a final temperature of 985 K and held at 985 K for 2 h. Hydrogen consumption was monitored by a thermal conductivity detector after removing the water formed.

2.2.6. *Temperature-programmed oxidation (TPO)*

Coke deposits produced were quantified and characterized by TPO experiments which were performed with a Shimadzu TGA-DTA-50 analyzer using 30–40 mg of post-reaction samples. The measurements were carried out in an air flow (40 ml min^{-1}) from 293 to 1173 K using a linear temperature program ($\beta = 10$ K min^{-1}).

2.3. *Catalytic test*

The catalysts (0.5–0.85 mm particle diameter) were tested in a fixed-bed quartz tubular reactor operated at atmospheric pressure between 623 and 793 K. The reactor was encased in a furnace, which was controlled by a programmable temperature controller. The reaction temperature was measured with a coaxial thermocouple.

Table 1
Characteristics of CrMo/γ-Al_2O_3 catalysts

Sample	S_{BET} ($m^2\ g^{-1}$)	MO_{3d}/Al_{2p}	Cr_{2p}/MO_{3d}	T_{max}, TPR	$r_{propene}$ (10^7 mol s^{-1} g^{-1})	r_{ether} (10^8 mol s^{-1} g^{-1})	$r_{dehydration}$ (10^7 mol s^{-1} g^{-1})	$r_{dehydrogenation}/r_{dehydration}$
Mo/γ-Al_2O_3	166	0.10	–	725	1.92	3.44	2.26	0.12
3CrMo/γ-Al_2O_3	147	0.09	0.83	721	1.56	4.80	2.04	0.23
5CrMo/γ-Al_2O_3	149	0.10	0.98	714	1.40	5.40	1.94	0.28

The feed was a mixture of 4 vol% propane, 4 vol% oxygen and the balance helium. The flow rates of gas streams were controlled by mass flow meters. The flow rate was 100 ml min^{-1} at room temperature. The reactants and reaction products were alternately analyzed on-line by a Shimadzu GC9A gas chromatograph equipped with a thermal conductivity detector. A Porapaq Q (80–100 mesh) column for separating hydrocarbons and CO_2 and a 1.8 m Carbosphere (80–100 mesh) column for carbon monoxide, methane and oxygen were used. Four analyses were performed at each temperature. For catalysts with 5 wt% of Cr and without dopant, different contact times (W/F in g_{cat} h(mol C_3H_8)$^{-1}$) were used in order to obtain different propane conversion levels. In these cases the weight of catalyst varied between 0.2 and 0.9 g. For the other catalyst the weight was 0.7 g. The homogeneous contribution was tested with the empty reactor. These runs showed no activity below 853 K. The results were very similar with and without the use of quartz particles. The conversion and selectivity to products were evaluated for the exit stream.

3. Results and discussion

The characterization results of CrMo/γ-Al_2O_3 catalysts are shown in table 1. The addition of Cr to the base catalyst containing 13% MoO_3 leads to a decrease in the specific surface area but no variation was observed with increasing Cr loading. XRD of the samples reveal the typical pattern of γ-Al_2O_3 (JCPDS 10-425) and the MO_{3d}/Al_{2p} ratio measured by XPS is not altered suggesting that a quite homogeneous dispersion of the active phase was obtained.

Catalyst reducibility was examined by TPR. The reduction profiles of fresh samples present two well-resolved reduction peaks with some differences in the temperature at the maximum. As seen in table 1, the maximum in the first reduction peak slightly shifts to lower temperatures with increasing Cr content. This behavior suggests that the reducibility of the catalysts increases on addition of Cr. For 5CrMo/γ-Al_2O_3 an incipient shoulder appears at 648 K which is attributed to a Cr reduction species.

The acid–base properties of the catalysts are modified by Cr addition. When the catalysts were tested in the decomposition of IPA important changes in product distribution were observed with Cr loading. The main dehydration products were propene and di-isopropylether in the temperature range studied, indicating the acid nature of the catalytic surface. An important increase in di-isopropylether and acetone formation rates was observed with increasing Cr whereas the propene formation rate decreased. In table 1 the dehydration (an indirect measure of acidity) and dehydrogenation (an indirect measure of basicity) rates at 433 K are shown. Greater amounts of acetone can be observed for both chromium catalysts compared with the base catalyst which is indicative of a higher redox (basic) site contribution. The increase in the amount of di-isopropylether could be interpreted as an increase in strong acid sites leading to a mechanism of E2 type [16].

3.1. Catalytic activity

The catalytic results obtained in the oxidative dehydrogenation of propane in the temperature range between 623 and 773 K are shown in table 2. Propene and carbon oxides were the main products. Small amounts of ethane and ethene, C2, were also detected. Oxygenated products other than carbon oxides were not observed under the experimental conditions used. Two important effects can be observed on Cr addition. At a given temperature propane conversion (X) increases with Cr loading and the catalyst becomes active at 623 K, a temperature for which the base catalyst does not show activity. Thus, conversions of 1.1 and 2.3% are obtained on 3CrMo/γ-Al_2O_3 and 5CrMo/γ-Al_2O_3, respectively, with propene selectivity around 60%. This result is interesting for developing catalytic systems able to activate the alkane molecule at a low temperature (propene yield higher than 1% at 623 K with 5% Cr). At 773 K the conversion is 1.5 times higher (from 14 to 20.7%) when the Cr content increases from 0 to 5%. Several studies have proposed that alkane ODH rates increase as active metal oxides become more reducible [17,18]. The reducibility of catalysts increases on addition of Cr, although the changes observed by TPR are not so significant. The reducibility is not the only factor that can explain the improvement in propane conversion. Recently, Chen *et al.* [19] have found that the C–H bond dissociation of alkanes depends more sensitively on the ability of the active oxide domains to transfer electrons from lattice oxygen atoms to metal

Table 2
Catalytic results for propane oxidative dehydrogenation on CrMo/γ-Al_2O_3

Sample	T (K)	X (%)	R_{O2} (%)	S_{C3} (%)	S_{CO2} (%)	S_{CO} (%)	S_{C2} (%)	Y_{C3} (%)
Mo/γ-Al_2O_3	623	n.d.						
	673	4.1	9.1	48.1	24.3	27.6	–	2.0
	723	13.9	35.9	34.2	26.1	39.1	0.6	4.8
	773	29.3	80.7	27.4	27.3	44.0	1.3	8.1
3CrMo/γ-Al_2O_3	623	1.1	2.2	56.5	21.5	22.0	–	0.6
	673	5.2	12.8	41.9	29.0	29.0	–	2.2
	723	15.1	40.0	35.4	33.3	29.8	1.4	5.4
	773	31.9	96.3	23.4	37.0	38.2	1.4	7.5
5CrMo/γ-Al_2O_3	623	2.3	4.4	58.4	22.4	19.2	–	1.4
	673	8.7	22.2	38.4	29.3	32.2	–	3.3
	723	20.7	60.9	27.8	39.0	31.7	1.4	5.8
	773	33.5	99.8	22.4	38.1	37.7	1.7	7.5

Note: $W/F_{C3} = 4720\ g_{cat}\ min\ (mol\ C_3H_8)^{-1}$; X, propane conversion; R_{O2}, oxygen consumption; Y_{C3}, propene yield; S, selectivity.

centers than on the tendency of oxides to reduce in H_2. Chromium is an element that can modify quite easily the oxidation state as was verified by XPS and TPR; it becomes in an efficient agent of electron transfer, a fundamental aspect of the dynamics of the catalytic cycle and the activation of propane at low temperature. Stern and Grasselli have also reported an increase in propane conversion by the addition of chromia over molybdate-based catalysts having the formula $AMoO_4$ (where A = Ni, Co) supported on SiO_2 [20]. The addition of elements capable of one-electron redox shuttle increases the catalytic activity of the base molybdate by keeping the latter in a high and active oxidation state (Mo^{6+}). However, Valenzuela *et al.* [21] found that Cr addition to V–Mg–O catalysts decreases the activity and selectivity to propene, the loss in selectivity being attributed to the lower reducibility of V species.

In figure 1 the conversions as a function of W/F_{C3} ($g_{cat}\ min\ (mol\ C_3H_8)^{-1}$) at different temperatures are shown for the base and 5CrMo/γ-Al_2O_3 catalysts. As expected the conversion increases with W/F_{C3} and temperature. At low temperature the conversion varies linearly with the space velocity but deviations from linearity are observed due to some inhibition by a product or due to higher oxygen conversion at higher temperatures and W/F_{C3}. In fact, at 823 K oxygen is almost exhausted on the base catalyst and totally converted on the doped catalyst.

In figure 2 the values of propene selectivity on 5CrMo/γ-Al_2O_3 as a function of conversion are compared with those of the base catalyst. This behavior is a common feature of many ODH catalysts. Chromium changes the acid–base character to a more basic system (table 1). This shift should account for the better selectivity in propane ODH. It is known that an increase in basicity allows the easier desorption of propene and the selectivity should be higher over the Cr-doped catalyst. However, this is not the case. No changes in selectivity are observed.

It is clear that Cr is an interesting component because it retains the selectivity values with improved conversions at lower temperatures. Another interesting possibility is to combine the paraffin-activating Cr–Mo catalysts with one of the well-known multicomponent mixed metal molybdates [20] in a single reactor, converting the propene intermediate formed *in situ* to other oxygenate products such as acrylonitrile.

In figure 3 selectivities to CO_x on 5CrMo/γ-Al_2O_3 are shown. The CO/CO_2 ratio is less than or equal to unity, in contrast to other catalytic systems where the selectivity to CO is markedly higher than selectivity to CO_2 in particular at higher temperatures or conversions. It seems that the presence of Cr allows more efficient oxidation of CO to CO_2 than other Mo-based catalysts studied [12].

Concerning C2 selectivity, the values are low but an increase on Cr-doped catalysts in agreement with IPA results is observed. The increase in the di-isopropylether formation rate is indicative of a higher concentration of strong acid sites. These sites promote cracking reactions.

3.2. *Catalyst stability*

The stability of the catalysts is another important point to be considered. The loss of Mo by sublimation is one of the most important mechanisms leading to deactivation. Other deactivation phenomena such as carbon deposition and sintering can also be present depending on the operation conditions during ODH reaction.

A stability test was carried out on Mo/γ-Al_2O_3. The experimental run was performed during 25 h between 673 and 793 K. Propane conversion as a function of time on stream is shown in figure 4. After this experiment, the run was started again without withdrawing the catalyst. The results are shown in table 3. It can be seen that conversion levels in the second run are slightly lower at temperatures below 773 K and from

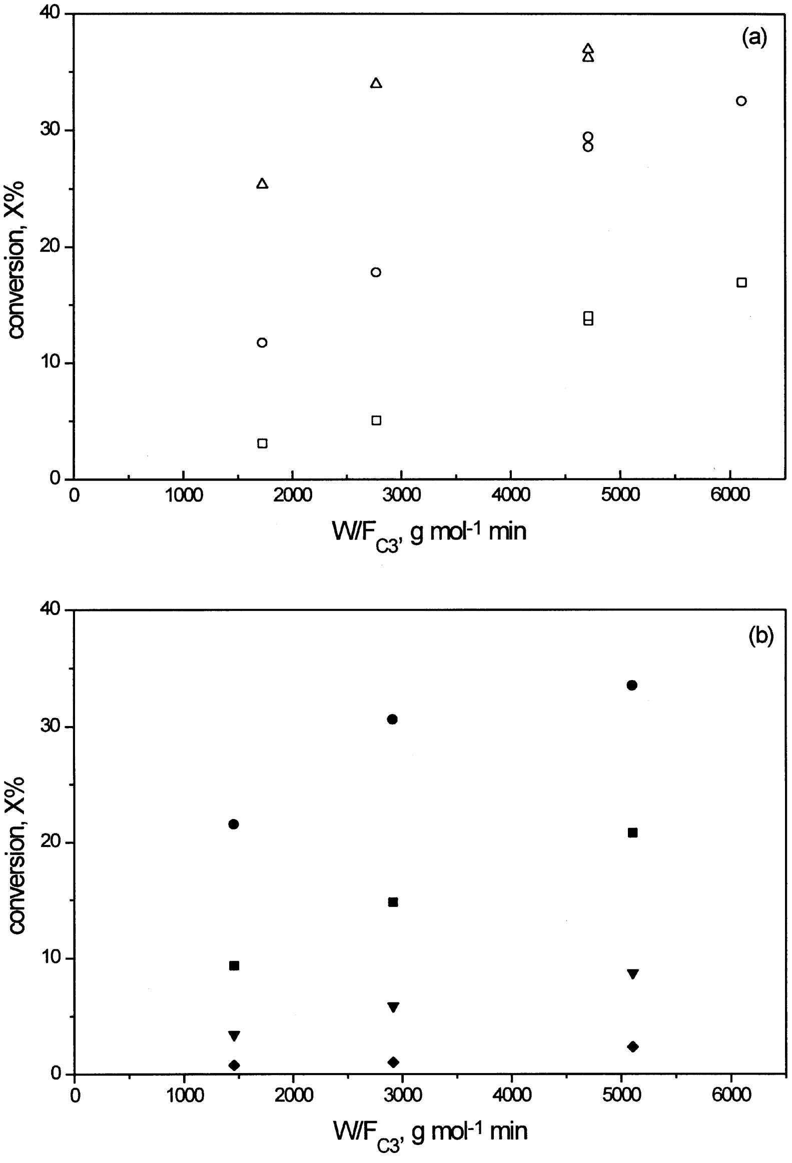

Figure 1. Propane conversion as a function of W/F_{C3}: (a) Mo/γ-Al_2O_3; (b) 5CrMo/γ-Al_2O_3. △, 823 K, ◄, 793 K; ●, ○, 773 K; ■, □, 723 K; ▼, 673 K; ◆, 623 K.

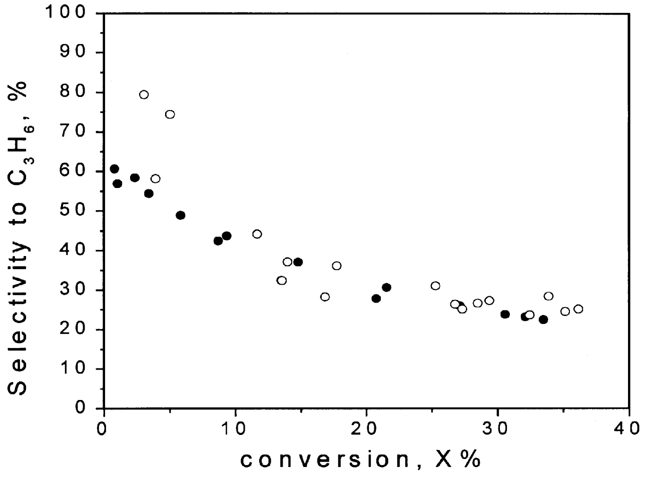

Figure 2. Selectivity to propene as a function of propane conversion: ○, Mo/γ-Al_2O_3; ●, 5CrMo/γ-Al_2O_3.

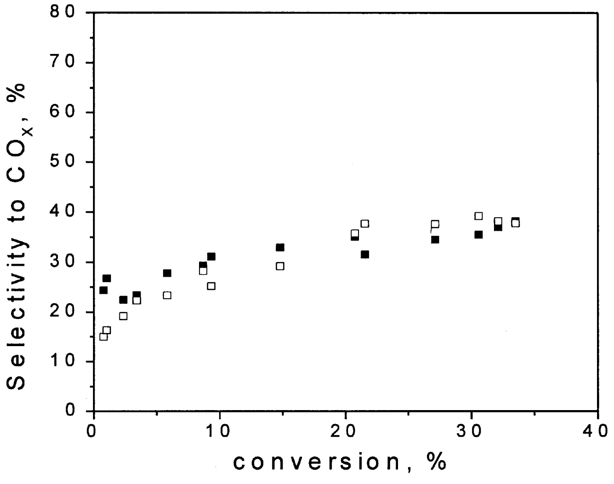

Figure 3. Selectivity to CO_x as a function of propane conversion on 5CrMo/γ-Al_2O_3: □, CO; ■, CO_2.

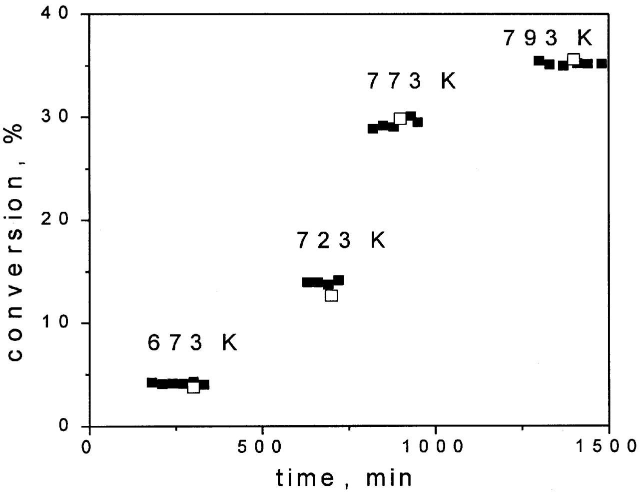

Figure 4. Propane conversion as a function of time on stream over Mo/γ-Al_2O_3 at different temperatures: ■, first run; □, second run.

773 K they are the same as those obtained on fresh catalyst. Product distribution is also the same with the exception of the results at 673 K. An explanation could be found if it is assumed that coke formation occurs at higher temperature which is burned to CO_2 (near 673 K) when the reaction atmosphere is rich in oxygen. Carbon deposit formation was verified by the TPO experiment. Two distinct weight losses are observed in TGA experiments. The first weight loss was characteristic for physical desorption of water (360 K) and the second one corresponds to the burning of coke ($T_{\text{maximum}} = 757$ K). The amount of coke is near 1 wt%. It is determined by DSC that the first peak is endothermic and the second exothermic in total agreement with the above interpretation. Since 1% of coke represents quite a high C/Mo ratio and the deactivation process is not significant in the reaction, it can be assumed that the coke formed has migrated on the support surface such as in other catalytic systems supported on γ-Al_2O_3 [22]. Another less plausible explanation is that all the coke can be deposited at the beginning of the reaction to operate as a stable active phase. In this case, the deactivation could not be detected.

A similar test was carried out on 3CrMo/γ-Al_2O_3 and the results are shown in table 4. A significant loss of activity is not observed and the behavior is similar to

Table 3
Stability test on Mo/γ-Al_2O_3

Sample state	T (K)	X (%)	Selectivity (%)				Y_{C3} (%)
			CO	CO_2	C_2	C_3H_6	
Fresh	673	4.1	26.1	22.7	–	51.2	2.1
	723	14.0	35.6	26.3	0.6	37.5	5.2
	773	29.4	44.0	27.3	1.3	27.4	8.1
	793	35.2	48.2	25.9	1.4	24.5	8.6
Used	673	3.7	22.6	43.4	–	34.0	1.3
	723	12.6	35.3	23.9	0.6	40.3	5.1
	773	29.8	46.6	26.5	1.3	25.5	7.6
	793	35.6	48.2	26.2	1.8	23.9	8.5

Table 4
Stability test on 3CrMo/γ-Al_2O_3

Sample state	T (K)	X (%)	Selectivity (%)				Y_{C3} (%)
			CO	CO_2	C_2	C_3H_6	
Fresh	623	1.1	22.0	21.5	–	56.5	0.6
	673	5.2	29.0	29.0	–	41.9	2.2
	723	15.1	29.8	33.3	1.4	35.4	5.4
	773	31.9	42.2	33.0	1.4	23.4	7.5
	793	34.7	41.8	32.7	2.0	23.5	8.1
Used	623	1.0	18.4	26.7	–	54.8	0.5
	673	3.5	35.3	34.7	–	30.0	1.0
	723	14.5	34.2	30.0	0.8	34.9	5.1
	773	31.0	42.8	33.5	1.4	22.3	6.9
	793	34.3	42.5	32.5	1.9	23.0	7.9

Table 5
Combustion temperature and wt% of coke on CrMo/γ-Al_2O_3 by TPO

Sample	C (%)	T (K)
Mo/γ-Al_2O_3	1.0	757
3CrMo/γ-Al_2O_3	1.5	766
5CrMo/γ-Al_2O_3	1.1 [a]	756

[a] This value corresponds to the first run on fresh catalyst.

the base catalyst. TPO results for 3CrMo/γ-Al_2O_3 and 5CrMo/γ-Al_2O_3 are shown in table 5. It can be observed that coke formation is higher on Cr-doped catalysts but deactivation is not so important under the operation conditions used. These results confirm that Mo sublimation can also be discharged.

From the very good yield of propene at lower temperatures and the marked catalytic stability, an in-depth characterization of surface active phases is needed for these catalysts especially for determining the role of Cr.

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