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In situ characterisation of carbon-containing species formed on chromia/alumina during propane dehydrogenation

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Abstract

The formation of carbon-containing species was studied during propane dehydrogenation on a chromia/alumina catalyst with 13.5 wt% chromium. The deposition was monitored by in situ DRIFT spectroscopy combined with mass spectrometry, and by in situ Raman spectroscopy combined with gas chromatography. The reduction of chromates by propane resulted in the formation of adsorbed acetone, formates, and acetates. Acetates/carboxylates and hydrocarbon species—aliphatic, unsaturated/aromatic, and graphite-like species—were present under dehydrogenation conditions. The deposition of the hydrocarbon species was gradual, consistent with the continuous deactivation of the catalyst observed during the measurements. Hydrogen prereduction of the chromia/alumina catalyst slowed the formation of acetates/carboxylates, but it had no detectable effect on the deposition of the hydrocarbon species.

Keywords: Dehydrogenation; Chromia/alumina; Carbon-containing deposits; In situ spectroscopy

1. Introduction

Chromia supported on alumina is widely used as a catalyst in the dehydrogenation of light alkanes to alkenes [1]. Oxidised chromia/alumina contains chromium mainly as Cr^{3+} and Cr^{6+}, and in trace amounts as Cr^{5+} [1,2]. Under dehydrogenation conditions the higher oxidation states reduce to Cr^{3+}, which is generally considered to be the active species in the reaction [1,3].

One problem related to the supported chromia catalysts is their rapid deactivation during dehydrogenation, which is most likely due to coke formation. Consequently, the catalyst must be regenerated at frequent intervals. In a study by ex situ infrared spectroscopy of coked chromia/alumina catalysts used in the dehydrogenation of butene to butadiene, Ibarra et al. [4] concluded that the carbon-containing deposits consisted of both aliphatic and aromatic hydrocarbons. Recently, operando and in situ Raman spectroscopic studies have provided further information on the hydrocarbon species formed during alkane dehydrogenation. Nijhuis et al. [5] investigated propane dehydrogenation on a catalyst with 13 wt% chromium by operando UV–vis/Raman spectroscopy and concluded that formation of (poly)aromatic hydrocarbon deposits took place at 550 °C. Sullivan et al. [6], on the other hand, using in situ UV-Raman spectroscopy to study chromia/alumina with 0.7 wt% chromium, observed the formation of polyolefinic, or both polyolefinic and polyaromatic species, depending on the reaction temperature and on whether the catalyst had been oxidised or hydrogen-prereduced before the dehydrogenation.

The purpose of our study was to investigate the nature of the carbon-containing deposits formed during propane dehydrogenation on a chromia/alumina catalyst with 13.5 wt% chromium. Neither Nijhuis et al. [5] nor Sullivan et al. [6] reported the formation of carbonate or carboxylate deposits during propane dehydrogenation. In the present study, in situ infrared spectroscopy was used to explore this matter further. Hakuli et al. [7] observed, moreover, that hydrogen-

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prereduced chromia/alumina catalyst is less active in dehydrogenation than an alkane-reduced chromia/alumina catalyst. Another aim was to determine whether, on a catalyst with high chromium loading, hydrogen prereduction affects the nature of the carbon-containing species. Sullivan et al. [6] observed such an effect for a low-loaded chromia/alumina catalyst.

Propane dehydrogenation was investigated by in situ spectroscopic methods. The reduction of Cr^{6+}, present as chromates, and the formation of hydroxyl and carbon-containing species were studied by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). In situ Raman spectroscopy was used to study further the reduction of chromates and the formation of carbon-containing deposits. The effects of both temperature and time on stream on the carbon-containing deposits were evaluated.

2. Experimental

2.1. Sample preparation

The chromia/alumina catalyst used in the study was prepared by the atomic layer deposition (ALD) technique, in which the precursor of the metal oxide is deposited on the support from the gas phase through saturating gas–solid reactions, as described in detail elsewhere [3,8]. The γ-alumina support, AKZO 000–1.5E, was crushed and sieved to a particle size of 0.25–0.50 mm and calcined with air at 600 °C for 16 h. Chromium(III) acetylacetonate, $Cr(acac)_3$ (Riedel–de Haën, 99%), was used as the chromium precursor. After the ALD preparation, the catalyst was calcined with air at 600 °C for 4 h. According to earlier analyses [8], the catalyst contained 13.5 wt% chromium and 3.0 wt% Cr^{6+} and had a surface area of 166 $m^2\,g^{-1}$. No crystalline Cr_2O_3 was detected by X-ray diffraction or Raman spectroscopy, indicating that the surface chromia species were well dispersed. X-ray photoelectron spectroscopic measurements indicated that the catalyst contained Cr^{3+} and Cr^{6+} after oxidation, and mainly Cr^{3+} after reduction with hydrogen or alkane (butane); the treatments were done in a reactor connected directly to the spectrometer system, permitting sample transfer in vacuum.

For comparison, the alumina support and a bulk chromia sample (Cr_2O_3, Aldrich, 98+) were also investigated. The chromia sample was calcined with air at 600 °C for 4 h before use.

2.2. In situ spectroscopic measurements

The reduction of chromates and the formation of hydroxyl and carbon-containing species were studied by in situ DRIFTS combined with mass spectrometry (MS) and by in situ Raman spectroscopy combined with gas chromatography (GC). Two types of experiments were made with the two methods: (i) temperature-programmed (TP) measurements from 25 to 580 °C and (ii) time-dependent measurements at a constant temperature of 580 °C.

2.2.1. In situ DRIFTS–MS measurements

The DRIFTS measurements were performed with a Nicolet Nexus FTIR spectrometer and a Spectra-Tech high-temperature/high-pressure chamber. The gaseous products were monitored on-line with a Pfeiffer Vacuum OmniStar mass spectrometer. A fresh catalyst sample was used in each experiment and was pretreated by in situ oxidisation with 10% O_2/N_2 at 580 °C for 2 h before study. The total gas flow rate was kept at 50 $cm^3\,min^{-1}$ during the entire experiment.

The TP-DRIFTS measurement was done for the chromia/alumina catalyst and for the pure chromia and alumina samples. A flow of 5% C_3H_8/N_2 was directed to the sample cell at 25 °C, after which the temperature was increased stepwise to 100 °C. Spectra were recorded every 25 °C (4 cm^{-1}, 100 scans), with the spectrum of an aluminum mirror measured under nitrogen flow as the background. The product gas was analysed continuously by MS. At 100 °C, the sample cell was flushed with nitrogen, and the spectrum of the sample without the contribution of gas-phase propane was recorded. Thereafter, the propane flow was resumed and the temperature was increased. Spectra were collected every 25 up to 550 °C, and then at 580 °C. The nitrogen flush of the reaction chamber was repeated at 200, 300, 400, 500, and 580 °C.

The time-dependent measurement at 580 °C was made for the chromia/alumina catalyst after oxidation of the catalyst, and after a 15-min hydrogen prereduction with 5% H_2/N_2. Spectra were collected once every minute (4 cm^{-1}, 30 scans), and the product gas was analysed continuously by MS. After 3 min on propane stream (5% C_3H_8/N_2), the sample cell was flushed with nitrogen to obtain a spectrum without the contribution by gas-phase propane. Thereafter, the propane flow was continued for another 3 min, making the total time on propane stream 6 min; the sample cell was flushed with nitrogen; and the spectrum was recorded under inert flow. This was repeated after a total of 10, 15, 20, 30, and 40 min on propane stream.

2.2.2. In situ Raman–GC measurements

The Raman spectra were measured with a Renishaw Micro-Raman System-1000 equipped with a cooled CCD detector and a holographic super-Notch filter for removing the elastic scattering. An Ar^+ laser (514 nm) was used as the exciting source. The experiments were performed in a home-made quartz reaction cell. The catalyst (0.2 g) was loaded between two layers of silicon carbide and was kept in place with quartz wool plugs at both ends of the reactor. In this way, there was no void volume in the reactor. The reaction products were analysed with a Varian 3800 gas chromatograph equipped with a thermal conductivity detector. A fresh catalyst sample was used in each experiment and was pretreated by in situ oxidisation with 20% O_2/He at 580 °C for 1 h. The total gas flow rate was 20 $cm^3\,min^{-1}$ during the whole experiment.

The TP measurement was performed for the chromia/alumina catalyst by stepwise heating from 25 to 580 °C under 5% C_3H_8/He. The weight hourly space velocity (WHSV) of propane was 0.8 h^{-1}. GC samples and Raman spectra were taken at 25, 100, 200, 300, 400, 500, and 580 °C. At each temperature, after the GC sample was taken, the propane flow was stopped temporarily and the Raman spectrum was recorded under helium flow. Thereafter the alkane flow and heating were continued. This was done to enable a better comparison with the DRIFTS results. Each spectrum was measured for approximately 40 min.

The time-dependent measurement at 580 °C was made with an oxidised sample and with a sample that had been prereduced for 15 min with 1% H_2/Ar. After 10 min on a propane stream (5% C_3H_8/He), a GC sample was taken, the reactor was flushed with helium, and the spectrum of the catalyst sample was measured under helium flow. Thereafter the propane flow was continued for another 10 min, making the total time on propane stream 20 min; a GC sample was taken, and the spectrum was again recorded under helium flow. This was repeated after 30 and 40 min on propane stream.

3. Results and discussion

3.1. *Effect of temperature on the carbon-containing species*

3.1.1. *In situ DRIFTS–MS measurement*

The TP-DRIFTS experiment was performed for the chromia/alumina catalyst between 25 and 580 °C to investigate the reduction of the chromia phase by propane. Selected spectra obtained are shown in Fig. 1. Although spectra were measured after every 25 °C rise in temperature, only the spectra obtained after the sample cell was flushed with nitrogen are shown. Thus the strong C–H stretching band of gas-phase propane does not dominate the C–H area, allowing the changes between 3100 and 2800 cm^{-1} to be observed. Since the nitrogen flush could result in desorption of deposited species, we made some reference measurements without stopping the alkane feed. The results were not noticeably different from those reported below.

The room-temperature spectrum of the oxidised catalyst showed absorption bands at 3730, 3620, and 1600 cm^{-1} due to Al–OH [9], Cr–OH [3], and adsorbed water [10], respectively. The sharp peak at 2340 cm^{-1} is characteristic for the γ-alumina used as the support and belongs to carbon dioxide species trapped inside the material, possibly during its preparation [11]. The broad band near 2000 cm^{-1} is assigned to the chromate overtone vibrations [8] and was observable even at 580 °C during heating under air or nitrogen.

After the start of the propane feed, the spectrum measured at 100 °C exhibited two bands at 1670 and 1250 cm^{-1} attributed to the $\nu(C{=}O)$ and ν_{as}(C–C–C) vibrations of adsorbed acetone, respectively [12]. These had appeared already at room temperature and were observable up to 175 °C. Other bands were present at 3620, 3480–3450, 2970, 2880, 1555–1535, 1440–1430, 1380, and 1355–1350 cm^{-1} between about 100 and 450 °C. The first two bands are due to Cr–OH species and hydrogen-bonded hydroxyls [10], respectively, whereas the bands at 2970, 2880, 1555, 1380, and 1355 cm^{-1} can be assigned to formates (ν_s(COO) + ν_{as}(COO), ν(CH), ν_{as}(COO), δ(CH), and ν_s(COO), respectively) [12,13]. The bands at 1535 and 1440–1430 cm^{-1} are due to acetates [12] or carboxylate species in general [14] (ν_{as}(COO), ν_s(COO), respectively). However, the weak $\delta_s(CH_3)$ band at 1350 cm^{-1} present at 500–580 °C seems to belong to the same species and supports the acetate assignment [12]. The absence of the acetate/carboxylate peaks at 1535 and 1350 cm^{-1} below 400 °C is explained by the overlapping of the acetate and formate bands. Carbonate groups may also be contributing to the acetate peaks since they have been observed on chromia at similar wavenumbers [14]. Chromate overtones were not seen above about 300 °C, and above 450 °C the amounts of hydrogen and propene detected by MS increased. Therefore, the catalyst was reduced before dehydrogenation started. The formates were not stable above this temperature, whereas the acetate/carboxylate bands were clearly observed up to 580 °C, indicating that they were thermally more stable. At 500 °C, aliphatic C–H bands [10] were present at 2985

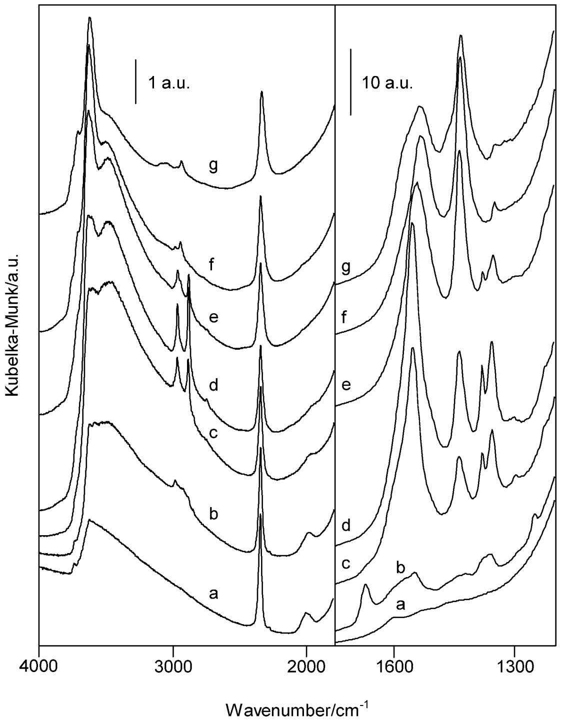

Fig. 1. DRIFT spectra measured for the chromia/alumina catalyst (a) at room temperature after oxidation, and during the TP measurement at (b) 100, (c) 200, (d) 300, (e) 400, (f) 500, and (g) 580 °C. Spectra measured under nitrogen flow.

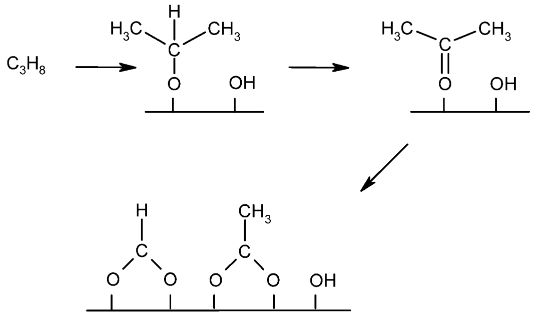

Fig. 2. Evolution of the oxygen and carbon-containing species formed from propane.

and 2940 cm^{-1}. At 500–580 °C a broad band at 3060 and a shoulder at 1585 cm^{-1} increased, which have generally been attributed to unsaturated or aromatic species, or both, strongly bonded to the catalyst surface [4,10,15].

Similar TP-DRIFTS experiments were also carried out for bulk chromia and the alumina support. Bulk chromia, which contained a small amount of Cr^{6+} after oxidation [8], exhibited bands due to acetone, formates, and acetates/carboxylates at wavenumbers and temperatures similar to those of the chromia/alumina catalyst, whereas for alumina only weak bands due to acetates/carboxylates were observed at high temperatures. This suggests that the oxidised carbon species, especially acetone and formates, were formed in the reaction of propane with the chromia phase of the catalyst. The interaction of propane with Cr^{6+}-containing MgCr$_2$O$_4$ at different temperatures has been studied by Finocchio et al. [12,16] and Busca et al. [17]. They suggested the activation of propane to take place through reaction with the chromate groups present on the oxidised MgCr$_2$O$_4$, resulting in reduction of chromium and formation of isopropoxide and hydroxyl species. With increasing temperature the isopropoxide species would react further to adsorbed acetone, formates, and acetates. According to our TP-DRIFTS measurements, the pathway presented in Fig. 2 may therefore be operational on chromia surfaces too, with reduction of the chromates taking place simultaneously with the formation of the isopropoxide species. Since acetates/carboxylates were observed on alumina, these species formed also in other reactions in addition to the reduction of the chromia phase. Oxidised species may have formed, for example, via reaction of propane with the surface OH groups, as was proposed by Ermini et al. [18] for alumina under propane atmosphere. The reduced chromia/alumina catalyst was active in dehydrogenation, resulting in formation of aliphatic and unsaturated/aromatic hydrocarbon deposits, in accordance with studies performed with other methods [4–6]. The formation of the hydrocarbon deposits only when propene was present in the product supports the earlier proposal [19] that the coke species on chromia/alumina are mainly formed from the alkene rather than the alkane.

3.1.2. In situ Raman–GC measurement

The reduction of the catalyst by propane was further investigated by TP-Raman. Fig. 3 presents spectra measured during this experiment. The sample was flushed with inert gas before the Raman spectra were acquired, to enable better comparison with the DRIFTS results. The oxidised sample showed Raman bands centered at about 1020 and 830 cm^{-1}, corresponding to the stretching modes of terminal Cr=O and bridging Cr–O–Cr units of surface chromate species, respectively [2,20]. Upon introduction of propane, these bands decreased in intensity with increasing temperature and were no longer observed above 300 °C, in agreement with the TP-DRIFTS results, indicating that the surface chromate species had been reduced. The amount of propene detected by GC in the product stream started to increase at 500 °C. At 500–580 °C two bands were present at about 1600 and 1390 cm^{-1}. These were assigned to graphite-like carbon species [21,22] in accordance with the results of Mul et al. [23] and Espinat et al. [24], who investigated propane oxidative dehydrogenation on vanadia/alumina and coked platinum-based reforming catalysts, respectively. The assignment was based on the similarities between the Raman spectra of coked catalysts and of disordered graphitic materials. Disordered graphitic materials show Raman bands at about 1580 and 1360 cm^{-1} that are referred to as the G and D bands, respectively [21,22]. Single-crystal graphite exhibits only the G (graphite) band, whereas the D (distorted) band appears with increasing disorder of the material [21]. At 580 °C, in addition to the bands of the graphite-like deposits, a broad band was observed at 2890 cm^{-1}, where C–H species typically appear [25]. The band at 800 cm^{-1} is caused by the quartz reactor. The C–H band indicates the presence of hydrocarbon-type species, possibly the unsaturated and/or aromatic species that were observed by DRIFTS. The presence of aromatic deposits causes fluorescence and may explain the increasing background in the spectra. The graphite-like species were most likely formed

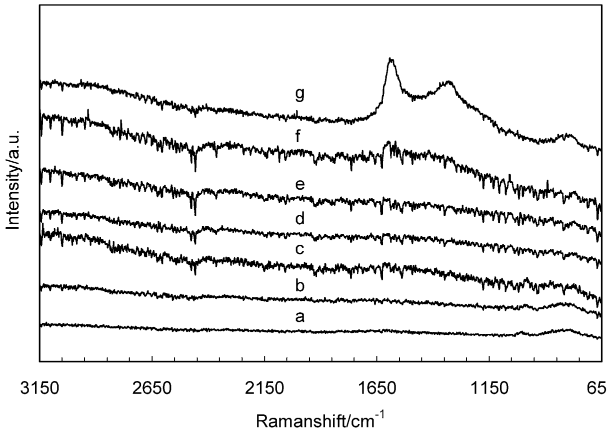

Fig. 3. Raman spectra measured for the chromia/alumina catalyst (a) at room temperature after oxidation, and during the TP measurement at (b) 100, (c) 200, (d) 300, (e) 400, (f) 500, and (g) 580 °C. Spectra measured under helium flow.

by dehydrogenation of the unsaturated/aromatic hydrocarbon deposits.

3.2. Effect of time on stream on the carbon-containing species

3.2.1. In situ DRIFTS–MS measurements

The effect of time on propane stream on the carbon-containing species was investigated at 580 °C for oxidised and hydrogen-prereduced chromia/alumina. Fig. 4A presents DRIFT spectra obtained for the oxidised catalyst. Spectra (b) and (c) were measured under propane flow during the first 2 min on stream, and spectra (d)–(j) were measured up to 40 min on stream after the sample cell was flushed with nitrogen. Fig. 4B shows the change in the MS signal intensity for m/e 42 characteristic for propene. The regularly occurring drop in the signal is due to the nitrogen flushes.

The oxidised catalyst showed at 580 °C weak Al–OH and Cr–OH bands at 3720 and 3610 cm^{-1}, respectively, and the chromate overtone band at 1985 cm^{-1}. The chromates were reduced at the start of the propane feed, resulting in formation of gaseous carbon dioxide (increase in the 2340 cm^{-1} band, MS). The band of gaseous propane (2970 cm^{-1}) exhibited a shoulder at 2880 cm^{-1} due to formates. Acetates/carboxylates appeared at 1530, 1430, and 1340 cm^{-1} and hydroxyls at 3710, 3620, and 3490 cm^{-1}. The aliphatic C–H species at 2935 cm^{-1} were formed at the beginning of the propane feed, whereas the band of the unsaturated/aromatic species at 3050 cm^{-1} appeared after 6 min on stream and increased thereafter. A shoulder at 1590 cm^{-1} attributed to the same species was seen as well. The amount of propene detected in the product stream by MS decreased during the measurement, indicating deactivation of the catalyst.

Fig. 5 presents DRIFT spectra measured for the hydrogen-prereduced catalyst during the first 2 min (spectra (c) and (d)) and up to 40 min on propane stream (spectra (e)–(k)). Hydrogen prereduction removed the chromates and resulted in the formation of hydroxyl species similar to those produced by reduction by propane. Formates were not seen, whereas acetate/carboxylate species were formed (1530, 1430, and 1350 cm^{-1}), although not as rapidly as after oxidation. This result supports the conclusion that these species may also form in other reactions in addition to the reduction, although it has been reported [26] that some Cr^{5+} ions

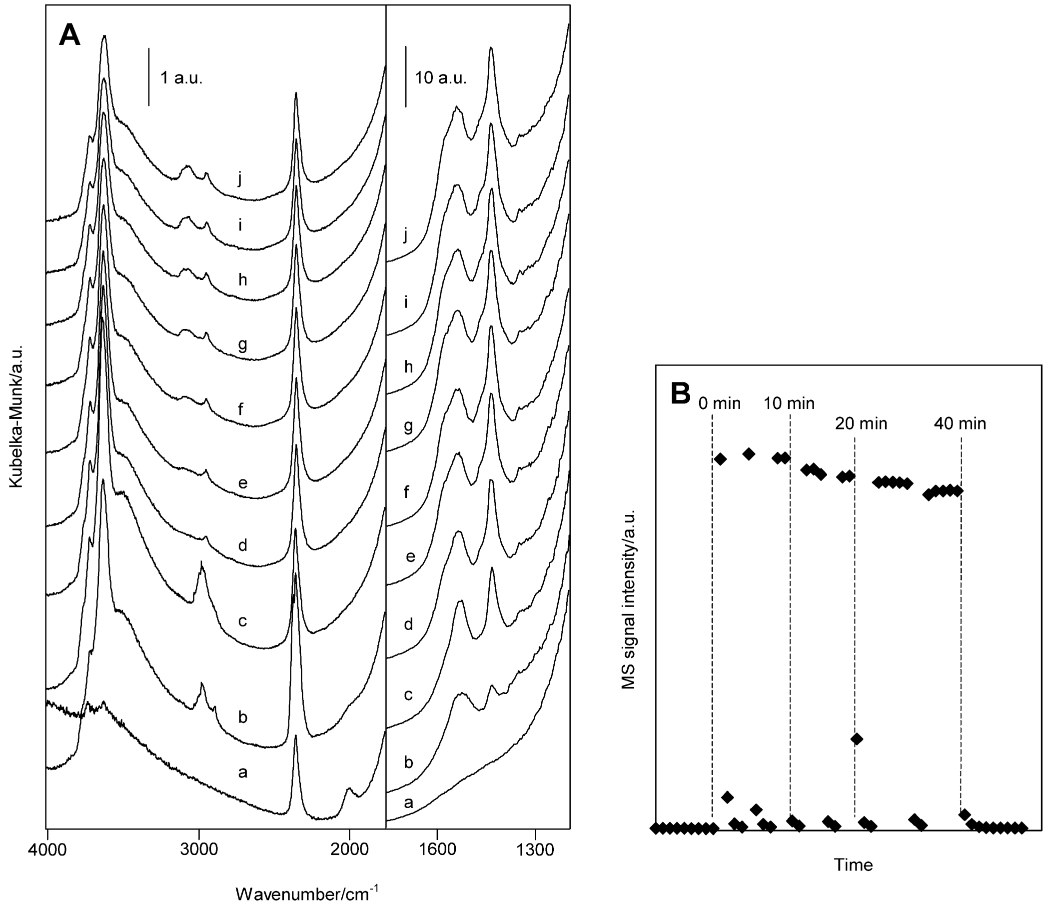

Fig. 4. (A) DRIFT spectra measured for the chromia/alumina catalyst at 580 °C (a) after oxidation, and during the time-dependent measurement after (b) 10 s, (c) 1 min 10 s, (d) 3, (e) 6, (f) 10, (g) 15, (h) 20, (i) 30, and (j) 40 min on propane stream. Spectra (b) and (c) measured under propane flow, spectra (d)–(j) after nitrogen flush. (B) MS signal intensity for m/e 42 characteristic for propene.

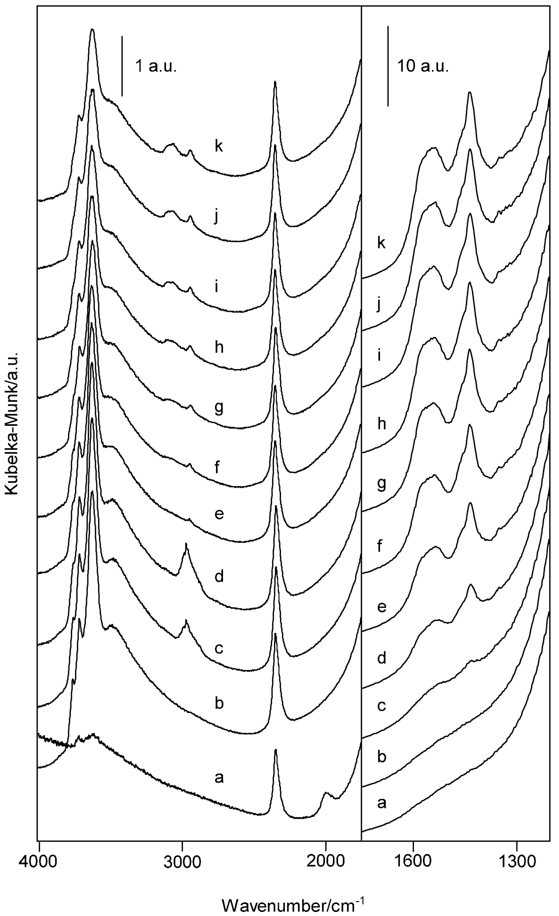

Fig. 5. DRIFT spectra measured for the chromia/alumina catalyst at 580 °C (a) after oxidation, (b) after hydrogen prereduction, and during the time-dependent measurement after (c) 10 s, (d) 1 min 10 s, (e) 3, (f) 6, (g) 10, (h) 15, (i) 20, (j) 30, and (k) 40 min on propane stream. Spectra (c) and (d) measured under propane flow, spectra (e)–(k) after nitrogen flush.

on supported chromia catalysts can be stable under hydrogen and are reduced by alkane. With increasing time on stream, hydrocarbon species appeared that were similar to those that appeared with the oxidised catalyst: first the aliphatic species (2930 cm^{-1}) and then the unsaturated/aromatic deposits (3060 and 1590 cm^{-1}). The dehydrogenation activity of the sample also decreased in this experiment (MS).

3.2.2. *In situ Raman–GC measurements*

The Raman spectra obtained for the oxidised chromia/alumina catalyst during the time-dependent measurement at 580 °C are shown in Fig. 6. The disappearance of the chromate bands at 1025 and 850 cm^{-1} cannot be observed clearly from these spectra because of the overlapping by the quartz reactor band at 800 cm^{-1}. However, a change in the colour of the sample from brown to green, characteristic for Cr^{3+} oxide [27], indicated that the catalyst was reduced at the beginning of the experiment. After 20 min, peaks attributed to graphite-like species appeared at 1580 and 1340 cm^{-1}. These became more apparent with time. In addition, the spectra measured after 30 and 40 min showed the Raman band at 2870 cm^{-1} due to C–H species indicating, along with the increased fluorescence background, the presence of hydrocarbon species, in accordance with the DRIFTS results. The dehydrogenation activity of the sample decreased during the experiment (GC).

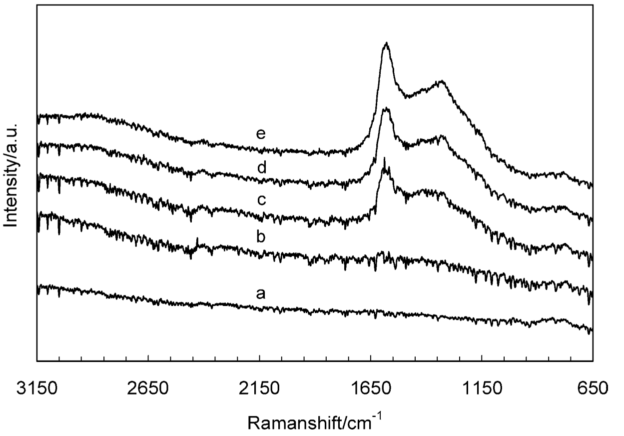

Fig. 6. Raman spectra measured for the chromia/alumina catalyst at 580 °C (a) after oxidation, and during the time-dependent measurement after (b) 10, (c) 20, (d) 30, and (e) 40 min on propane stream. Spectra measured under helium flow.

The prereduction of the oxidised catalyst resulted in the disappearance of the chromate bands present after oxidation. The spectra measured during the dehydrogenation (not shown for brevity) were similar to those for the non-prereduced catalyst, showing between 20 and 40 min the formation of graphite-like species, indicated by the Raman bands at 1580 and 1340 cm^{-1}, and C–H species at 2870 cm^{-1}.

The steady deposition of the carbon-containing species on both the oxidised and hydrogen-prereduced chromia/alumina catalysts with time on stream was consistent with the deactivation of the samples observed during the DRIFTS and Raman experiments. The results of the TP and time-dependent measurements suggest that the hydrocarbon deposits were formed sequentially from adsorbed propene or from intermediate species formed in the dehydrogenation of propane. The propene may first form adsorbed polymeric species on the surface, which react further to aromatic species and then, by loss of hydrogen, to the graphite-like deposits. The carbon deposits deactivate the catalyst most likely by blocking the active chromium sites.

Aside from the difference observed in the initial formation of acetates/carboxylates, the deposition of carbon-containing species was similar on the oxidised and on the hydrogen-prereduced catalyst. Sullivan et al. [6], however, found a difference between the pretreatments. During propane dehydrogenation on chromia/alumina they observed by in situ UV-Raman that, after oxidation, both polyolefins and polyaromatics formed at 400 °C, and only polyolefins formed at 500 °C. The hydrogen-prereduced catalyst produced only polyolefins at 400 °C, and both polyolefins and polyaromatics at 500 °C. In fact, our DRIFT results may not be in contradiction with their results, since the IR bands at 3050 and 1590 cm^{-1} due to strongly bonded carbon-containing species may be assigned to either unsaturated or aromatic hydrocarbons. Since the chromium content of the catalyst of Sullivan et al. (0.7 wt%) was lower than the chromium content of our catalyst (13.5 wt%), some qualitative difference may have existed between the carbon-containing species on their and our catalysts. For instance, more alumina support was exposed on their catalyst, owing to the lower chromium content, and this could have contributed to the formation of the deposits.

4. Conclusions

The formation of carbon-containing species during propane dehydrogenation was studied for a chromia/alumina catalyst with 13.5 wt% chromium. The reduction of chromates by propane may proceed through the formation of isopropoxide species, which react further first to adsorbed acetone and then to formates and acetates. Acetates/carboxylates may also form in other reactions, for example, through reaction of propane with surface OH groups. Dehydrogenation of propane resulted in sequential formation of aliphatic, unsaturated/aromatic, and graphite-like hydrocarbon deposits, which deactivated the catalyst. Hydrogen prereduction slowed the formation of the oxidised species, but it did not have a detectable effect on the hydrocarbon species formed during dehydrogenation.

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