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Catalysis Today 112 (2006) 37–39
CATALYSIS TODAY
www.elsevier.com/locate/cattod

In situ characterization of carbonaceous deposits formed on chromia/zirconia during isobutane dehydrogenation

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Abstract

The formation of carbonaceous species during isobutane dehydrogenation on chromia/zirconia was studied by in situ diffuse reflectance Fourier transform infrared spectroscopy combined with mass spectrometry for on-line product gas analysis. The reactions of the hydroxyl groups of zirconia support with the hydrocarbons and the reduction of the chromates resulted in the formation of adsorbed acetone, formate and acetate. However, they were suspected not be involved in the dehydrogenation. The reduced chromia/zirconia catalysts were active in the dehydrogenation of isobutane but deactivated due to formation of coke. These unsaturated/aromatic hydrocarbon species were suggested to form through the adsorbed dehydrogenation intermediates or products.

Keywords: FTIR; Chromia; Zirconia; Dehydrogenation; Isobutane

1. Introduction

Chromia/alumina is used as a catalyst in the commercial dehydrogenation (DH) of light alkanes [1]. However, De Rossi et al. [2] reported a higher activity of chromia/zirconia per Cr atom compared with chromia/alumina. Despite this, the carbonaceous deposits formed during the DH on chromia/zirconia have not been investigated thoroughly.

The aim of this study was to characterize by in situ measurements the carbonaceous species formed during isobutane DH on chromia/zirconia. In addition, the effect of hydrogen prereduction on the formed surface species was studied. The measurements were performed by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) combined with mass spectrometry (MS) in temperatures between 25 and 580 °C and at constant temperature of 580 °C to elucidate the reduction of the catalysts, the stability of the formed species and their effect on the behavior of the catalysts.

2. Experimental

2.1. Sample preparation and characterization

The samples used in the study were chromia/zirconia (0.4, 0.8 and 2.7 wt% Cr, X-ray fluorescence (XRF)), zirconia support (MEL EC 0100E 1/8 in., surface area 47 m^2/g) and bulk chromia (α-Cr_2O_3, Aldrich >98%). The chromia/zirconia samples will be referred to as *x*CrZr where *x* indicates the Cr loading in wt%. The 0.4CrZr and 0.8CrZr samples were prepared by the Atomic Layer Deposition (ALD) technique in which the metal precursor ($Cr(acac)_3$, Riedel-de Haën 99%) is deposited on the support from the gas phase through gas–solid reactions [3]. The sample 2.7CrZr was prepared by incipient wetness impregnation using $Cr(NO_3)_3 \cdot 9H_2O$ (Aldrich 99%) as the precursor.

2.2. In situ spectroscopic measurements

The formation of carbonaceous deposits on all samples was studied by in situ DRIFTS (Nicolet Nexus Fourier transform infrared spectrometer and a Spectra-Tech high temperature/high pressure chamber) combined with MS (Pfeiffer Vacuums OmniStar mass spectrometer). Two types of experiments with 5% isobutane in nitrogen were performed: (i) temperature-

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doi:10.1016/j.cattod.2005.11.053

programmed measurements (TP) from 25 to 580 °C and (ii) time-dependent DH at 580 °C. Similar experiments with 5% H_2, CO or isobutene in nitrogen were performed to identify the surface species formed during the DH. The samples were calcined in situ with 10% O_2/N_2 at 580 °C for 2 h. After experiment the samples were reoxidized (2–10% O_2/N_2) at 580 °C for 30 min.

The TP experiment was started by increasing the temperature stepwise from 25 to 100 °C under isobutane flow. The spectra were recorded every 25 °C (4 cm^{-1}, 100 scans) and the product gas was analyzed by MS. At 100 °C the sample was flushed with nitrogen to obtain a spectrum without the contribution of gaseous isobutane, after which the isobutane flow was redirected to the sample cell and the temperature was again raised stepwise. The sequence was repeated by recording the spectra under nitrogen flow at 200, 300, 400, 500 and 580 °C.

The time-dependent DH measurements were performed with calcined and prereduced (5% H_2/N_2, 15 min) samples at 580 °C. The spectra were recorded every minute (4 cm^{-1}, 30 scans) and the gaseous products were analyzed by MS. The experiments were performed using sequences of isobutane feed and nitrogen flushes (after 3, 6, 10, 15, 20 and 30 min on isobutane stream).

3. Results and discussion

3.1. Characterization of the samples

The support zirconia was assumed to be monoclinic based on the high intensity of its terminal (3774 cm^{-1}) and tribridged (3674 cm^{-1}) hydroxyl groups [4]. On all calcined chromia/zirconia samples the chromium loading was below the monolayer coverage and the chromates were observed at 2069, 2021 (overtones of $Cr^{6+}{=}O$ stretching vibrations [5]), 1040 and 1018 cm^{-1} ($Cr^{6+}{=}O$ stretching vibrations [6]).

3.2. Temperature-programmed measurements

Fig. 1 presents the spectra obtained during the TP on 2.7CrZr. Acetone (1678 and 1248 cm^{-1}) [7] and water (1621 cm^{-1}) [7] were observed already close to room temperature. At 100 °C bands were observed at 2980, 2880, 1562 and 1365 cm^{-1} assigned to the formate $\nu_s(COO) + \nu_{as}(COO)$, $\nu(CH)$, $\nu_{as}(COO)$ and $\nu_s(COO)$ vibrations [7–9]. Aliphatic hydrocarbon species (2937 cm^{-1}) [10] were also detected. At 200 °C the acetone bands disappeared and a band at 1438 cm^{-1} ($\nu_s(COO)$ [7,8]) indicated the formation of acetate. New formate bands were detected at 2750 and 1380 cm^{-1} $\delta(CH)$ [7–9]. The formates were observed up to 400 °C, indicating that they were stable at low temperatures. At 325 °C the chromate bands disappeared suggesting that Cr^{6+} was reduced. At 350 °C a band at 1536 cm^{-1} appeared, as the intensity of the formate bands decreased, and was assigned to acetate ($\nu_{as}(COO)$ [7,8]). The acetate bands were still observed at 580 °C indicating the stability of the species at high temperatures. At 400 °C new bands, disappearing immediately after temperature rise, were observed at 3101, 1636, 1472 and 1239 cm^{-1}. These were assigned to adsorbed isobutene based on the experiments with isobutene. The start of DH reaction was also confirmed by MS. At 500–580 °C a band appeared at 3060 cm^{-1}, assigned to unsaturated/aromatic hydrocarbon species [10]. Oxidation at 580 °C restored the chromate bands and removed the bands of the carbonaceous species. All of the chromia/zirconia samples were observed to behave similarly.

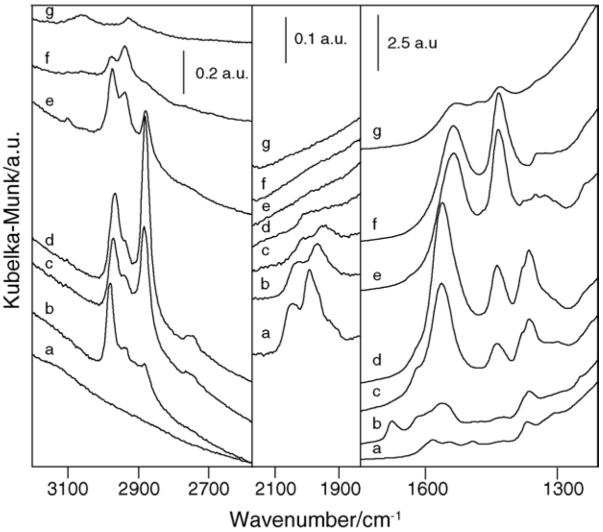

Fig. 1. In situ TP-DRIFTS on 2.7CrZr. (a) Calcined sample at 25 °C. Spectra recorded during the TP at (b) 100, (c) 200, (d) 300, (e) 400, (f) 500 and (g) 580 °C. Spectra were recorded under nitrogen flow.

Isobutane reduction of Cr^{6+} on $MgCr_2O_4$ proceeds through the formation of isobutoxide species, which react to acetone and further to formate and acetate [8]. On pure alumina the formates and acetates form in a reaction, not directly involved in the DH, between the hydroxyl groups and hydrocarbons below 527 °C [11]. Chromia behaved similarly to the chromia/zirconia samples whereas the formation of acetates on zirconia was first observed at 500–580 °C. On the chromia/zirconia samples the oxygenated species formed probably through the reduction of chromates and as the hydroxyl groups of the support reacted with the hydrocarbons while on pure zirconia they formed similarly as on alumina. Airaksinen et al. [12] have also reported similar performance of chromia/alumina. After the start of the DH reaction unsaturated/aromatic hydrocarbon species were observed on all chromia/zirconia samples.

3.3. Time-dependent DH measurements

Fig. 2 presents the spectra obtained during DH at 580 °C on calcined 2.7CrZr. Immediately after the start of the isobutane feed the Cr^{6+} species reduced. After 3 min on stream bands at 2930, 1530 and 1430 cm^{-1}, assigned to aliphatic hydrocarbon species and acetates were detected. After 6 min on stream the intensity of the acetate bands decreased and bands at 3060 and 1480 cm^{-1} were observed simultaneously as the DH activity decreased. The band at 3060 cm^{-1} was assigned to unsaturated/aromatic hydrocarbon species and the decrease in the DH activity indicated that the deactivation occurred through coke

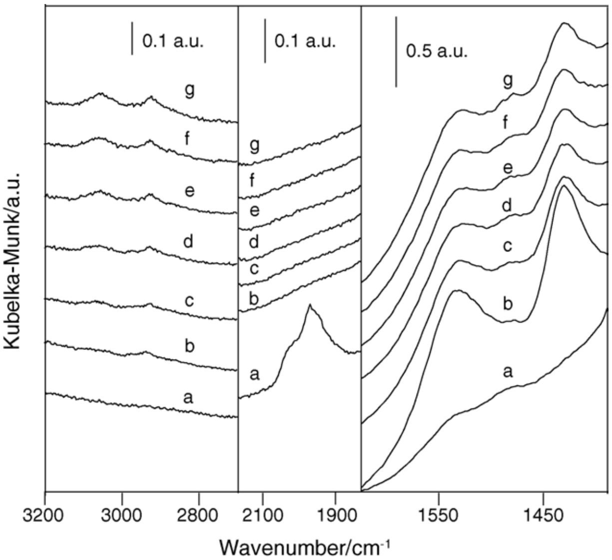

Fig. 2. In situ DRIFTS on 2.7CrZr. (a) Calcined sample at 580 °C. Spectra recorded during the DH at 580 °C after (b) 3, (c) 6, (d) 10, (e) 15, (f) 20 and (g) 30 min on isobutane stream. Spectra were recorded under nitrogen flow.

formation. Experiments with CO implied that the band at 1480 cm^{-1} belonged to a hydrocarbon-like species. After 30 min on stream unsaturated/aromatic, aliphatic and hydrocarbon-like species as well as acetates were observed. Oxidation at 580 °C restored the chromate bands and removed the carbonaceous species. All of the chromia/zirconia samples behaved similarly.

All the chromia/zirconia samples were active in the DH of isobutane but zirconia and chromia showed negligible DH activity. The oxygenated species are suspected not to be involved in the DH reaction based on the TP results and because the acetate band intensities were highest on pure zirconia. On zirconia no unsaturated/aromatic hydrocarbon species were detected implying that their formation occurred through adsorbed DH intermediates or isobutene. Prereduction with hydrogen reduced the chromates and decreased the DH activity but did not affect the adsorbed carbonaceous species significantly.

4. Conclusions

The formation of carbonaceous species during DH of isobutane was studied on chromia/zirconia, zirconia and chromia. The chromia/zirconia samples behaved similarly irrespective to the chromium loading. At low temperatures the formation of oxygen-containing carbonaceous species was observed during the reduction of the chromates and as the hydroxyl groups of the support reacted with the hydrocarbons. Based on the TP results and since the intensity of the acetates was highest on pure zirconia, which had a negligible DH activity, the species possibly were not involved in the DH reaction. In the time-dependent DH experiments deactivation of chromia/zirconia occurred through coke formation. These unsaturated/aromatic species were observed only on samples having a high DH activity indicating that their formation occurred through intermediates in the DH reaction.

Acknowledgements

We thank Olli Jylhä and Sami Juutilainen for the preparation of the chromia/zirconia samples. The authors gratefully acknowledge the financial support received from the Academy of Finland and Fortum Oil Oy.

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