RESEARCH NOTE

Monitoring Chromia/Alumina Catalysts *in Situ* during Propane Dehydrogenation by Optical Fiber UV–Visible Diffuse Reflectance Spectroscopy

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A continuous-flow reactor system with *in situ* monitoring of the catalyst was developed. The catalyst surface was analyzed by collecting UV–visible diffuse reflectance spectra through an optical fiber placed in the catalyst bed. The system was tested with a series of chromia/alumina catalysts (1 wt% Cr) under the conditions of propane dehydrogenation. The fast reduction of Cr^{6+} to Cr^{3+} under propane stream could be detected. Increase in the catalytic activity with the alumina pretreatment temperature was tentatively ascribed to the presence of θ-alumina, and decrease in the activity during calcination to incorporation of Cr^{3+} inside the alumina support. © 2001 Academic Press

Key Words: **alkane dehydrogenation; catalyst deactivation; chromium; diffuse reflectance spectroscopy; fiber optics.**

INTRODUCTION

Monitoring the events taking place in solid catalysts under operating conditions is crucial for understanding the reaction mechanism of many important chemical processes (1–3). Techniques have been developed which allow the studying of catalysts truly *in situ*, i.e., at high temperatures and pressures in a stream of reactants. The most used techniques have been infrared spectroscopy (4), Raman spectroscopy (5, 6), Mössbauer spectroscopy (7), nuclear magnetic resonance spectroscopy (8, 9), X-ray absorption spectroscopy (10–12), and UV–visible (vis) spectroscopy (13–15). A challenge often remaining is the implementation of the techniques without changing the catalytic properties of the system under study.

The current note introduces a new approach for measuring UV–vis diffuse reflectance (DR) spectra of an operating catalyst. The technique is based on the use of optical fiber technology, by which the state of solid transition metal oxide catalysts can be probed while they are positioned as a fixed bed in a catalytic reactor. Fiberoptic DR spectroscopy has been used for a variety of applications, such as pigment analysis (16), clinical diagnosis (17), and powder blend quality control (18); but to our best knowledge, the current work presents the first application in the field of heterogeneous catalysis. As an example, the changes taking place in chromia/alumina catalysts during alkane dehydrogenation are monitored by UV–vis DR spectroscopy. Alkane dehydrogenation is an industrially important process that is a viable route, for example, for the production of high-purity propene used for the production of polymer materials (19). The effect of alumina pretreatment temperature for the catalytic activity is studied. In addition, the differences in activity caused by a deactivating thermal treatment of chromia/alumina catalysts are investigated by *in situ* UV–vis DR measurements. Finally, the performance of the current setup as an *in situ* tool is compared with that of a system reported earlier (13, 15), and differences are pointed out.

METHODS

Chromia/alumina catalysts with about 1 wt% Cr were prepared by incipient wetness impregnation. An aqueous solution of CrO_3 (UCB Chemicals) was impregnated onto a commercial AKZO 001–1.5E alumina material that had been pretreated in ambient air at 600, 800, or 1000°C for 16 h. BET surface areas of 235, 177, and 154 m^2/g were measured for the alumina supports, respectively. The catalysts were aged and dried at 60 and 120°C for 4 h, after which they were calcined at 600°C for 16 h or at temperatures up to 1200°C for 24 h. The higher calcination temperatures were used to deliberately deactivate the catalysts.
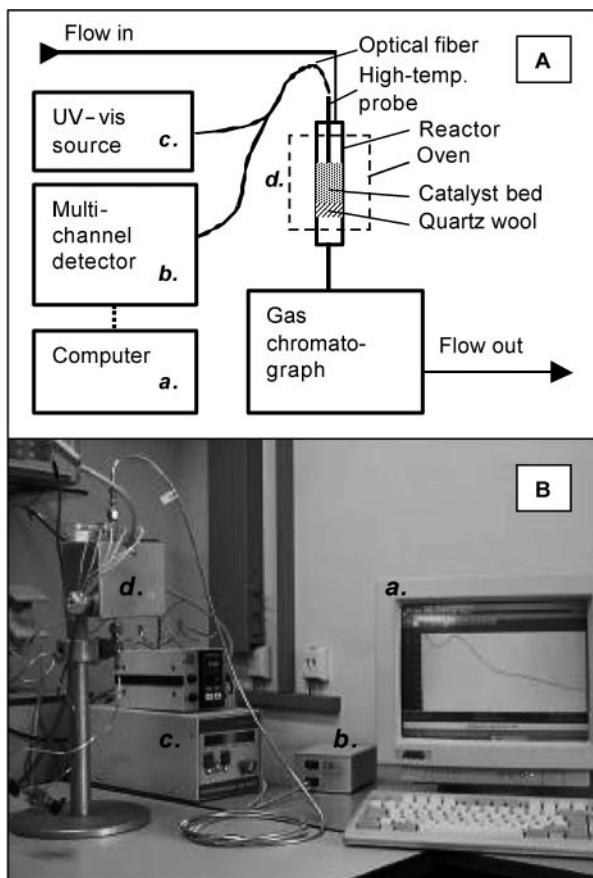
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FIG. 1. The fiber-optic UV–visible(vis) spectrometer–reactor setup: (A) a schematic representation and (B) a photographic illustration.

Propane dehydrogenation was carried out at $580°C$ with a 25 ml/min feed of 10 vol% propane (Alphagas, 99.95 vol%) in helium (Air Liquide, 99.995 vol%) and 0.2 g of catalyst for 20 min. The catalysts were regenerated for 40 min by a 25 ml/min stream of 5% oxygen (Air Liquide, 99.5 vol%) in helium. A helium flush of 30 min separated the dehydrogenation and regeneration steps. Three dehydrogenation cycles were carried out. The outlet gases were analyzed on line by a gas chromatograph (GC) (HP 5830A) equipped with a flame ionization detector and a packed column (n-octane/Porasil C). The reported activities correspond to the second cycle after 17.1 min of propane on stream unless otherwise stated. Yields and selectivities were calculated on a molar basis.

The catalysts were continuously monitored by optical fiber UV–vis DR spectroscopy. A schematic representation of the current setup is shown in Fig. 1A and a photographic illustration in Fig. 1B. The setup consists of a tubular fixed-bed reactor fitted inside a furnace, a UV–vis (deuterium–halogen) light source (Top Sensor Systems DH-2000) and a photodiode array detector (Ocean Optics SD-2000) connected to the catalyst bed via optical fiber technology (Top Sensor Systems FCB-UV400-ME cable and FCB-UV400G-

0.1-XHT high-temperature probe). The high-temperature probe is separated by a few millimeters from the hot catalyst particles placed in the fixed-bed reactor. A spectrum of the catalyst in the 200 to 800 nm region can be collected in less than a second.

X-ray diffractograms were measured for some samples with a Siemens D5000 X-ray Diffractometer. To investigate whether Na diffuses to the surfaces of samples during the heat treatment, alumina samples pretreated in air at 600, 800, 1000, and $1200°C$ were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS data were obtained with a Vacuum Generators XPS system, using a CLAM-2 hemispherical analyzer for electron detection. Non-monochromatic Al$K\alpha$ X-ray radiation was used for exciting the photoelectron spectra using an anode current of 20 mA at 10 keV. The pass energy of the analyzer was set at 50 eV, and data were collected at intervals of 0.1 eV. Survey spectra were taken with a pass energy of 100 eV at intervals of 0.5 eV.

RESULTS AND DISCUSSION

The yield of propene for the series of chromia/alumina catalysts, where the alumina pretreatment temperature and the catalyst calcination temperature were varied, is shown in Fig. 2. The data points (17.1 min on stream) represent a "stable" situation of the catalysts, where all the Cr^{6+} has been converted to Cr^{3+} and the initial CO_2, CO, and H_2O formation (20) no longer affects the product distribution. Increasing the alumina pretreatment temperature had a positive effect on the dehydrogenation activity of the catalysts. This possibly was caused by the increased formation of the θ-alumina phase during the pretreatment, as was observed by X-ray diffraction. α-alumina had not yet been formed in the pretreatment at $1000°C$. Increasing the calcination temperature of the chromia/alumina catalysts above $600°C$ resulted in loss of dehydrogenation activity.
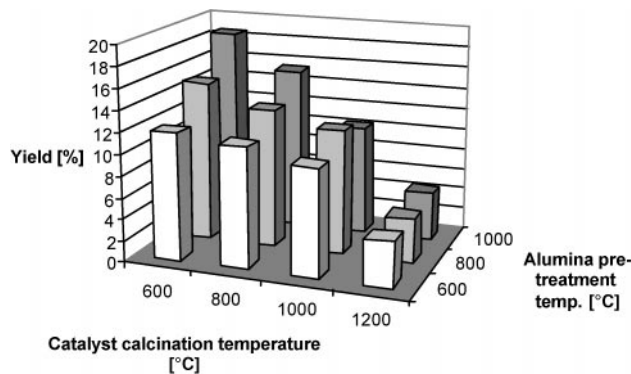

FIG. 2. Yield of propene during the second cycle of propane dehydrogenation by a series of 1 wt% Cr chromia/alumina catalysts in which the alumina pretreatment and catalyst calcination temperature were varied.

Calcination at $1200°C$ strongly deactivated all the catalysts (propene yield of approximately 4%), but some activity remained, since pure alumina pretreated at $1200°C$ gave a propene yield of 0.5%. XPS investigation showed that the amount of Na present in the samples was close to the detection limit and no accumulation had occurred onto the sample surface during the heat treatment. Loss of activity thus cannot be explained by diffusion of Na to block the active sites. Conversionwise there was practically no difference between the catalysts prepared on different aluminas; selectivity was generally higher (up to about 80%) the higher the alumina pretreatment temperature. The catalyst prepared on alumina pretreated at $600°C$ suffered the least deactivation when calcined at temperatures up to $1000°C$. This could be due to the fact that chromium inhibits the transformation of alumina from γ to α phase (21). Indeed, peaks of α-alumina were observed in the X-ray diffractograms of catalysts calcined at $1200°C$, but their intensity was smaller the lower the alumina pretreatment temperature.

UV–vis DR spectra were recorded continuously *in situ* during the catalytic experiments. As an example, we discuss the spectra of two chromia/alumina catalysts, which were both prepared on alumina pretreated at $600°C$, but the calcination temperatures were 600 and $1200°C$. The former is here referred to as the "fresh catalyst" and the latter as the "deactivated catalyst." The spectra of these catalysts measured during three consecutive dehydrogenation–oxidation cycles are shown in Fig. 3. A common feature of all the spectra measured at the end of oxidation was that there was an absorption band centered at $25,000–26,000\ cm^{-1}$, which was due to Cr^{6+} (22). The Cr^{6+} present in the fresh catalyst was readily reduced to Cr^{3+} during the first 30 s of propane on stream, in accord with the observations of Hakuli *et al.* (20) which were made by a rapid Fourier transfer infrared analysis of the gas phase products. For the deactivated catalyst in all cycles and for the fresh catalysts in the second and third cycles, Cr^{6+} was not stable during the helium flush but converted to Cr^{3+}. This was evidenced by the appearance of two absorption bands at about 16,000 and $23,000\ cm^{-1}$ (23). During the propane feed, coke was formed on the fresh catalyst, as evidenced by increasing intensity in the whole wavenumber range of the spectrum, and by that the yield of propane decreased from 13% to 12% during 13.1 min on stream. The presence of coke can be seen in UV–vis DR spectra because polycyclic aromatic structures have wide absorption bands in the UV–vis region (24, 25). Darkening of the sample through coke formation also may increase the overall intensity, leading to poorer resolution of the spectra. On the deactivated catalyst, coke
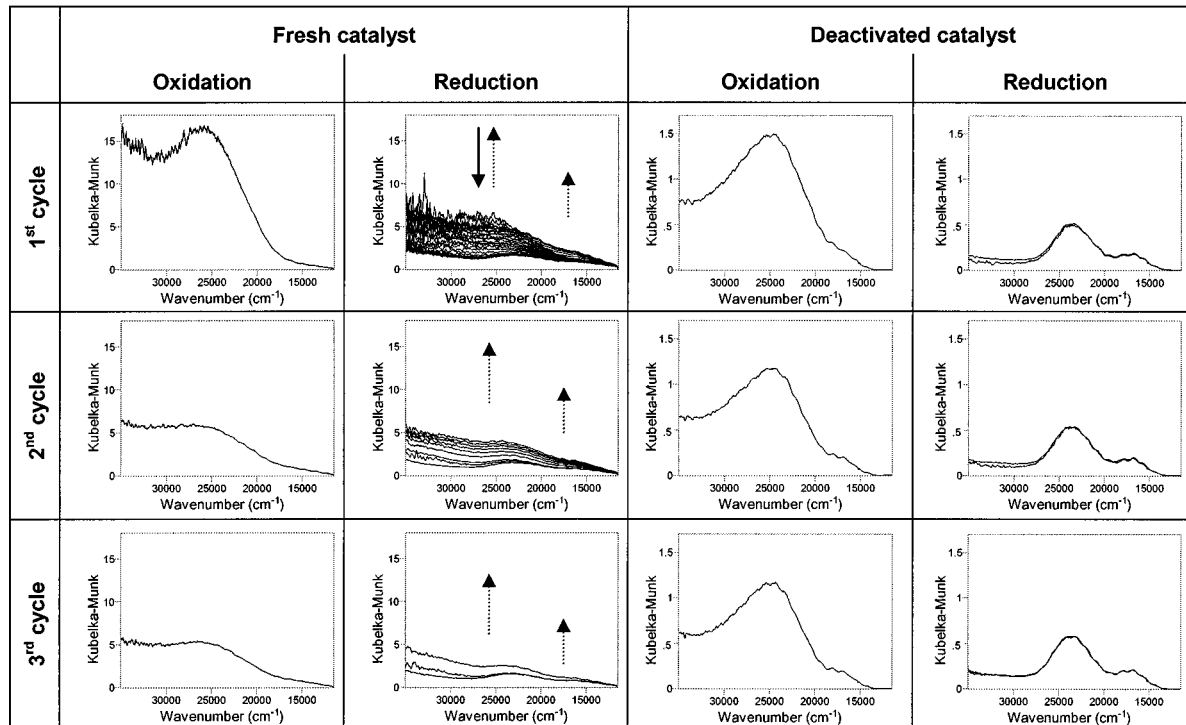

FIG. 3. UV–vis diffuse reflectance spectra of a fresh and a deactivated chromia/alumina catalyst (alumina pretreatment and catalyst calcination temperatures $600°C/600°C$ and $600°C/1200°C$, respectively) measured for three successive oxidation–dehydrogenation cycles ($580°C$, 1 atm) after calcination and during a 20 min propane feed. The solid-line arrow indicates the fast changes taking place during the reduction of Cr^{6+} to Cr^{3+} during the first 30 s on stream, and the dotted-line arrow indicates slower changes caused by coke formation. (Note that the y scales differ for the fresh and deactivated catalyst.)

formation as seen by UV–vis was almost negligible. During the following oxidative regeneration, the overall intensity decreased as a result of coke burn-off, and the Cr^{6+} signal reappeared. However, it never reached its original intensity during the 40-min oxidation. Oxidation of Cr^{3+} to Cr^{6+} thus seems to be a considerably slower process than reduction of Cr^{6+} to Cr^{3+}.

The UV–vis DR spectra can be used to investigate the changes that have taken place during the deactivation procedure. The positions of the absorption bands are characteristic of the coordination environment of Cr^{3+} (23). For spectra measured at room temperature, Cr^{3+} located inside an α-alumina structure (i.e., ruby) has d–d transitions at 18,150 and 24,700 cm^{-1} (23), whereas Cr^{3+} in Cr_2O_3 has bands at 16,600 (26) and 21,700 cm^{-1} (27). According to our measurements, increasing the measurement temperature from room temperature to 580°C shifts the maximum position of the bands at about 17,000 and 22,000 cm^{-1} to lower energy by about 700 and 200 cm^{-1}, respectively. The apparent band maxima at the start of the propane feed for the different catalysts are shown in Fig. 4. The energy of the d–d transitions of Cr^{3+} increased with increasing calcination temperature. Taking into account the effect of temperature on the band maxima, the shift in absorption band maxima indicates that most of the Cr^{3+} present in the catalyst deactivated at 1200°C had been incorporated in alumina, which explains the low activity observed. We propose that the Cr^{3+} species with bands at about 16,000 and 23,000 cm^{-1} (as measured at 580°C) were active dehydrogenation sites. It needs to be noted that the UV–vis DR results did not provide an explanation for the high activity of catalysts prepared on alumina pretreated at 1000°C.

Previously, the activity of supported chromia catalysts were investigated in isobutane dehydrogenation at 350 to 500°C (15). The catalysts were monitored *in situ* by UV–vis DR spectroscopy in a Praying Mantis DR attachment (Harrick) equipped with a photomultiplier detector. The performances and requirements of the two setups are compared in Table 1. The main advantage of the current fiberoptic setup compared with the Praying Mantis setup is the speed of data collection: fast processes with the time scale
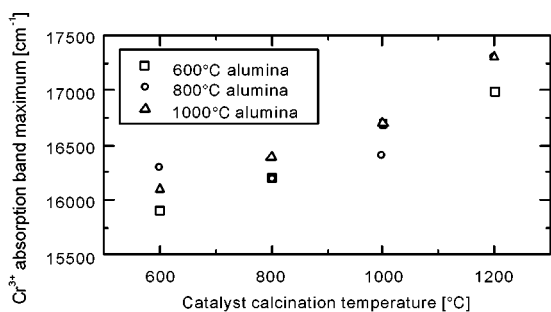
TABLE 1

Comparison of the Performances and Requirements of Different Setups for Measuring UV–Vis DR Spectra *in situ* During Catalysis

	Fiberoptic setup[a]	Praying Mantis setup (13, 15)
Time needed to acquire a spectrum (200–800 nm)	<1s	~60 s
Different parts of the spectrum represent the same time	Yes	No[b]
Reactor requirements	Catalytic fixed-bed reactor	Optical *in situ* cell
Temperature limitation	580°C[c]	500°C[d]

[a] This work.
[b] A photomultiplier detector records one wavelength at a time.
[c] Degradation of probe quality was observed after use of some months.
[d] Maximum reported temperature.

of seconds can be followed through the use of a photo diode array detector. Note also that through the use of a catalytic fixed-bed reactor the conversion level is not limited because of the spectroscopic requirements; high dehydrogenation conversions could be obtained in this work (conversion up to 24% in this study vs typically below 2% in (15)).

CONCLUSIONS

The activity and selectivity of chromia/alumina catalysts increased when alumina pretreatment temperature was increased from 600 to 1000°C, perhaps because of the increased amount of θ-alumina in the samples. Calcination of the catalysts at 1200°C resulted in severe deactivation. Optical fiber UV–vis DR spectroscopy indicated that Cr^{6+} reduced to Cr^{3+} during the first 30 s of propane on stream, and this was followed by coke formation. The Cr^{6+} formed during oxidative regeneration was not stable during an inert flush of the system but converted to Cr^{3+} even before the start of the propane feed. A correlation was observed between the dehydrogenation activity and Cr^{3+} absorption maxima for catalysts prepared on alumina pretreated at a constant temperature.

Monitoring the changes taking place in the coordination environment and oxidation state of supported metal oxides under reaction conditions was successful by optical fiber UV–vis DR spectroscopy. This technique is generally applicable to transition metal ions, which possess absorption bands in the UV–vis region. Its strength lies in the possibility of using a simple catalytic fixed-bed reactor. Moreover, a photo diode array detector enables a data collection speed in the range of seconds.

FIG. 4. Apparent absorption maximum of Cr^{3+} at the start of the second dehydrogenation cycle for the series of alumina pretreated at different temperatures.

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