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Dehydrogenation of Propane with CO_2 on Supported CrO_x/SiO_2 Catalysts

M. A. Tedeeva^a, A. L. Kustov^{a,b}, P. V. Pribytkov^{a,*}, A. V. Leonov^a, and S. F. Dunaev^a

^aDepartment of Chemistry, Moscow State University, Moscow, 119991 Russia ^bZelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia *e-mail: pribytkov@general.chem.msu.ru Received May 21, 2018

Abstract—A systematic analysis was performed of the physicochemical properties of amorphous silicas (Acros, Degussa, KSKG) and CrO_x/SiO_2 catalysts prepared from them with 2, 3, 5, 7, and 10 wt % chromium. The supports and catalysts were characterized by BET, XRD, and UV–Vis diffuse reflectance spectroscopy. In the oxidative dehydrogenation of propane with carbon dioxide, the highest propylene selectivity (95%) was observed for the 5% CrO_x/SiO_2 (Degussa) sample, and the highest propane conversion (53%) was reported on the 5% CrO_x/SiO_2 (Acros) catalyst. The structure of chromium oxide particles on the support surface was studied by UV–Vis spectroscopy. The catalytic properties were correlated with the state of chromium.

Keywords: chromium oxides, silica gel, oxidative dehydrogenation of propane, propylene, carbon dioxide, XRD, UV diffuse reflectance spectroscopy, specific surface area **DOI:** 10.1134/S0036024418120403

The search for alternative sources of chemical raw materials and new methods for the synthesis of valuable chemical compounds is currently one of the priorities in scientific research. One such compound is propylene, which serves as the starting substance for the preparation of a number of valuable monomers and polymers: acrolein, acrylic acid, acrylonitrile, propylene oxide, cumene, polypropylene, and polyacrylonitrile. The conventional methods for the industrial production of propylene are the thermal and catalytic cracking of oil and natural gas and liquid-phase catalytic cracking of gasolines. The oxidative dehydrogenation of propane in the presence of oxygen has recently been recognized as a promising method for the production of propylene. The problem with this method is coke deposition on the catalyst surface and decreased activity after prolonged work.

In the dehydrogenation of propane on MO_x/sup port catalysts (M = Cr, Ga, Fe, In, W, V, and other metals; support = SiO₂, Al₂O₃, ZrO₂, TiO₂, ZSM-5, MCM-41, SBA-15, etc.), carbon dioxide was often used as the oxidizing agent [1–6]. At the same time, the involvement of CO₂ in propane dehydrogenation is a solution to another important problem: greenhouse gas utilization. When carbon dioxide was used, the catalysts containing chromium, gallium, and tungsten showed the best catalytic properties [1–6].

Chromium oxide catalysts on different supports were compared in [1, 2, 7, 8], but there were few pub-

lications that compared these catalysts on supports of the same chemical nature but with different physical properties. In [9], chromium oxide catalysts supported on ordinary amorphous silicas SiO₂ ($S_{BET} = 477 \text{ m}^2/\text{g}$) and SiO₂ ($S_{BET} = 261 \text{ m}^2/\text{g}$) were compared with those on mesoporous silicas SBA-1 ($S_{BET} = 1181 \text{ m}^2/\text{g}$) and SBA-15 ($S_{BET} = 750 \text{ m}^2/\text{g}$). It was shown that the rate of propylene formation increased almost proportionally to the concentration of chromium in the form of Cr⁶⁺, which was higher on catalysts with a larger specific surface area.

The aim of the present study was the synthesis of the catalysts of propane dehydrogenation in the presence of CO_2 , containing chromium oxide deposited on amorphous SiO₂ of different grades (Acros, Degussa, KSKG), and a comparative study of their physicochemical and catalytic properties.

EXPERIMENTAL

Synthesis of the Samples

The catalysts were prepared by incipient wetness impregnation from aqueous solutions of chromium nitrate. As supports, granular silica gels SiO_2 (Acros, Degussa, and KSKG) were used. The previously ground silica gel (0.25–0.5 mm fraction) was dried in air at 120°C for 6 h. The active component was then deposited by incipient wetness impregnation of silica

Sample	$S_{\rm sp},{\rm m^2/g}$
SiO ₂ (Degussa)	156
5% Cr/SiO ₂ (Degussa)	155
SiO ₂ (KSKG)	231
5% Cr/SiO ₂ (KSKG)	231
SiO ₂ (Acros)	532
3% Cr/SiO ₂ (Acros)	520
3% Cr/SiO ₂ (Acros) after catalysis	511
5% Cr/SiO ₂ (Acros)	460
7% Cr/SiO ₂ (Acros)	433
10% Cr/SiO ₂ (Acros)	414
20% Cr/SiO ₂ (Acros)	410

Table 1. Specific surface areas of the CrO_x/SiO_2 catalysts and the starting SiO_2

gel with aqueous $Cr(NO_3)_3 \cdot 9H_2O$ (Acros). The dried samples were calcinated in air at 500°C for 4 h. The resulting catalysts contained 2, 3, 5, 7, and 10 wt % chromium.

Methods

The texture characteristics of the catalysts were determined from the nitrogen adsorption isotherms measured at 77 K. The specific surface area was calculated by the BET method; the pore size distribution was determined from the desorption branch of the isotherm by the Barrett–Joyner–Halenda (BJH) method.

The X-ray diffraction (XRD) analysis was performed on a DRON-3 diffractometer using CuK_{α} radiation (35 kV, 25 mA, scanning at $2\theta = 10^{\circ}-60^{\circ}$ at a step of 0.1°).

The UV–Vis spectra were recorded on a Shimadzu UV-3600 Plus spectrophotometer equipped with ISR-603 integrating sphere. The spectra were recorded in the wavelength range 185-850 nm at room temperature using BaSO₄ as a standard and diluent of the samples. The resulting spectra were treated with the UVProbe program.

Catalytic Tests

Dehydrogenation of propane into propylene in the presence of CO_2 was studied at atmospheric pressure in a flow type steel reactor with an inner diameter of 4 mm. The $C_3H_8 + CO_2$ gas mixture was fed in the reactor in a ratio of 1 : 2 v/v; the total flow rate of the gas mixture was 30 mL/min. The catalyst load was 1 g. The catalyst volume was 0.9 cm³ for SiO₂ (Acros), 0.48 cm³ for SiO₂ (Degussa), and 0.45 cm³ for SiO₂ (KSKG). The gas flow space velocity was 2000 h⁻¹ for the Acros sample, 3750 h⁻¹ for Degussa, and 4000 h⁻¹

for KSKG, respectively. The on-line analysis of the reaction products was performed using a Chromatec Crystal 5000 gas chromatograph with a thermal conductivity detector and an Mss316 column (3 m \times 2 mm, Hayesep Q 80/100 mesh). The column temperature was varied according to the following program: 40°C for 1.5 min, and then the temperature was raised to 100°C at a rate of 15°C/min. The product contents were calculated by the absolute calibration method.

RESULTS AND DISCUSSION

Physicochemical Properties of Supports and Catalysts

Table 1 presents the specific surface areas of the starting SiO_2 of different grades (Acros, Degussa, and KSKG) and the catalysis prepared from it.

According to Table 1, the specific surface areas did not change after the deposition of 5 wt % chromium on SiO₂ (Degussa, KSKG). For SiO₂ (Acros), whose starting surface area is two or three times larger than that of SiO₂ (Degussa, KSKG), the surface area decreased slightly (by $\sim 2\%$) when 3% chromium was deposited and by $\sim 13\%$ when chromium load was 5%. When the chromium concentration on the support increased further, the specific surface area decreased more slowly; the deposition of more than 10 wt %chromium did not lead to a decrease in the surface area. This is apparently due to the blocking of the narrowest pores by chromium particles for SiO_2 (Acros). A similar decrease in the specific surface area during the chromium deposition on SiO₂ (KSKG) was also observed in [10], where $S_{\rm sp} = 346 \text{ m}^2/\text{g}$ for the initial SiO₂ (KSKG); when 5% Cr was deposited, $S_{\rm sp}$ decreased to 307 m²/g, i.e., by ~11%. Note that for 3%Cr/SiO₂ (Acros), the surface area slightly decreased after the catalytic propane dehydrogenation in the presence of carbon dioxide due to the insignificant coke deposition on its surface.

The crystalline structure of the synthesized $Cr(5\%)O_x/SiO_2$ catalysts (Acros, Degussa, KSKG) was studied by XRD. The diffraction pattern of the $Cr(5\%)O_x/SiO_2$ (Degussa) sample shows the peaks belonging to Cr_2O_3 ; for the $Cr(5\%)O_x/SiO_2$ (KSCG) sample, there are peaks belonging to Cr_2O_3 , which are much less intense; for the $Cr(5\%)O_x/SiO_2$ (Acros) sample, these peaks are not observed (Fig. 1).

Based on these data, we can conclude that chromium is mainly in the form of Cr_2O_3 in the SiO₂ (Degussa) sample, some chromium is present as Cr_2O_3 in CrO_x/SiO_2 (KSKG), and is not observed at all in the form of Cr_2O_3 in SiO₂ (Acros).

Additional information that confirms the structure of chromium oxide particles on the support surface was obtained by measuring the UV–Vis diffuse reflectance spectra. Figure 2 shows these UV–Vis spectra of



Fig. 1. X-ray diffraction patterns of the samples: (a) $Cr(5\%)O_x/SiO_2$ (Degussa), (b) $Cr(5\%)O_x/SiO_2$ (KSKG), and (c) $Cr(5\%)O_x/SiO_2$ (Acros); for comparison, the peak positions of Cr_2O_3 are given (JCPDS 04-312).

the $Cr(5\%)O_x/SiO_2$ (Acros, Degussa, KSKG) catalysts measured before and after the catalytic tests.

Before catalysis, all the three samples showed four bands in the range 200–700 nm. The UV bands at 270 and 360 nm relate to the $O^{2-} \rightarrow Cr^{6+}$ charge transfer for chromium ions in the tetrahedral environment [11–16]. The bands at 455 and 600 nm correspond to the octahedral coordination of Cr^{3+} in Cr_2O_3 or CrO_x clusters [11–16]. The UV–Vis spectra indicate that the



Fig. 2. UV–Vis diffuse reflectance spectra (a) before and (b) after catalysis of the samples: (*1*) $Cr(5\%)O_x/SiO_2$ (KSKG), (*2*) $Cr(5\%)O_x/SiO_2$ (Acros), and (*3*) $Cr(5\%)O_x/SiO_2$ (Degussa); *A* is absorption.

Cr(VI) and Cr(III) forms coexist in the samples. In the 5% Cr/SiO₂ (Degussa) sample, however, Cr(III) predominates; in 5% Cr/SiO₂ (Acros), chromium is mainly in the form of Cr(VI). After catalysis, the concentration of chromium in the form of Cr(VI) and Cr(III) decreased in all the samples, especially in 5% Cr/SiO₂ (Acros); this may be due to coke formation on the surface of chromium oxide particles. Figure 3 shows the UV–Vis spectra of the fresh CrO_x/SiO₂ (Acros) catalysts with 2–10 wt % chromium.

Even with 2% Cr in the catalyst, chromium is mainly in the form of Cr(VI), which does not change when the chromium content increases to 10%. This tendency is consistent with the data of [9], where the 2–7% Cr/SiO₂-a ($S_{\text{BET}} = 477 \text{ m}^2/\text{g}$) and 2– 7% Cr/SiO₂-p ($S_{\text{BET}} = 261 \text{ m}^2/\text{g}$) samples were studied.

Oxidative Dehydrogenation of Propane on the CrO_x/SiO₂ Catalyst in the Presence of CO₂

To compare the support effects on the catalyst activity, the CrO_x/SiO_2 catalysts were prepared using SiO_2 Acros, Degussa, and KSKG.

Propane is dehydrogenated in the presence of CO_2 by the reaction

$$C_3H_8 + CO_2 \rightarrow C_3H_6 + CO + H_2O.$$

In addition to propylene, by-products such as methane, ethane, and ethylene formed. The results of the catalytic tests are shown in Figs. 4 and 5.



Fig. 3. UV–Vis diffuse reflectance spectra of fresh samples: (a) $Cr(2\%)O_x/SiO_2$ (Acros), (b) $Cr(5\%)O_x/SiO_2$ (Acros), (c) $Cr(7\%)O_x/SiO_2$ (Acros), and (d) $Cr(10\%)O_x/SiO_2$ (Acros); *A* is absorption.



Fig. 5. Temperature dependences of propylene selectivity (δ) on the catalysts: (1) Cr(5%)O_x/SiO₂ (Acros), (2) Cr(5%)O_x/SiO₂ (KSKG), and (3) Cr(5%)O_x/SiO₂ (Degussa).

The highest propylene selectivity of 95% was observed for 5% Cr/SiO₂ (Degussa) at $T = 600^{\circ}$ C; the highest propane conversion of 53% and propylene yield of 34% were determined for 5% Cr/SiO₂ (Acros) at $T = 700^{\circ}$ C.

For further studies, the $(3, 5, 7\%)Cr/SiO_2$ (Acros) catalyst samples were prepared. The dependences of



Fig. 4. Temperature dependences of propane conversion on the catalysts: (1) $Cr(5\%)O_x/SiO_2$ (Acros), (2) $Cr(5\%)O_x/SiO_2$ (KSKG), and (3) $Cr(5\%)O_x/SiO_2$ (Degussa); σ is conversion.



Fig. 6. Temperature dependences of propane conversion (σ) on the catalysts: (1) Cr(3%)O_x/SiO₂ (Acros), (2) Cr(5%)O_x/SiO₂ (Acros), and (3) Cr(7%)O_x/SiO₂ (Acros).

propane conversion and propylene selectivity are shown in Figs. 6 and 7.

The highest conversion of propane (67%) was observed for the catalyst with 3 wt % Cr at T = 700 °C. The highest propylene selectivity (83%) was found for the catalyst with 7 wt % Cr at T = 600 °C.

Thus, the oxidative dehydrogenation of propane in the presence of carbon dioxide on chromium oxide



Fig. 7. Temperature dependences of propylene selectivity on the catalysts: (1) $Cr(3\%)O_x/SiO_2$ (Acros), (2) $Cr(5\%)O_x/SiO_2$ (Acros), and (3) $Cr(7\%)O_x/SiO_2$ (Acros).

catalysts with different contents of chromium deposited on amorphous silica of different grades was studied. The highest propylene selectivity was observed for the 5% Cr/SiO₂ Degussa sample, in which chromium was in the form of Cr(III) in the freshly prepared sample. The highest propane conversion was observed on the 5% Cr/SiO₂ Acros catalyst. Chromium in this freshly prepared catalyst is mainly in the form of Cr(VI).

In all the samples, the concentration of chromium in the form of Cr(VI) and Cr(III) decreased after catalysis, especially in the 5% Cr/SiO₂ (Acros) sample, which may be due to coke formation on the surface of chromium particles.

In the case of the CrO_x/SiO_2 (Acros) catalysts, the highest propane conversion was observed for the catalyst with 3 wt % Cr; the highest propylene selectivity, for the catalyst containing 7 wt % Cr.

Further progress in the development of catalysts for propane dehydrogenation with CO_2 can be achieved using more complex catalytic systems and hybrid nanomaterials as supports and catalysts [17–24].

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