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Preparation and characterization of SBA-1–supported chromium oxide catalysts for CO_2 assisted dehydrogenation of propane

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ABSTRACT

A series of Crx/SBA-1 cubic mesoporous catalysts with 1, 3, 5, 7, 10, and 15 wt.% content of Cr (Cr_{total}) were obtained by incipient wetness impregnation of SBA-1. The obtained catalysts were characterized with various physicochemical techniques (chemical composition, low-temperature adsorption of N_2, H_2–TPR, XRD, UV–vis DRS, Raman, and EPR) and tested in dehydrogenation of propane to propene in the presence of CO_2. Various chromium species including Cr^{6+}, dispersed Cr^{5+}, and crystalline Cr_2O_3 were found in the calcined Crx/SBA-1 samples. Cr^{6+} species were present mainly in the form of mono- and dichromates, despite the Cr loading. The presence of dispersed Cr^{5+} species and crystalline α-Cr_2O_3 in the calcined catalysts depended on the total Cr_{total} content. Cr^{5+} species were found in the samples containing below 7 wt.% of Cr_{total}, while particles of crystalline α-Cr_2O_3 were detected in the catalyst with Cr_{total} content above 5 wt.%. All of the Crx/SBA-1 catalysts exhibited excellent catalytic activity and high selectivity in the dehydrogenation of propane to propene in the presence of CO_2 with the maximum propane conversion (37.7% at 550 °C) for ~7 wt.% of Cr_{total}. For higher Cr contents the conversion of propane remained almost constant which was connected with the formation of crystalline Cr_2O_3 which was inactive in the test reaction. *Operando* UV–vis DRS measurements performed during the dehydrogenation of propane, both in the presence and absence of CO_2 at 550 °C, indicated that the Cr^{6+} species (main redox sites) were reduced rapidly to Cr^{2+}/Cr^{3+} species already at the beginning of the process. The dispersed Cr^{2+}/Cr^{3+} ions were the main sites available to the reactants under the dehydrogenation conditions in all of the studied feed compositions.

1. Introduction

Supported-chromium oxide materials are widely applied as the catalysts in ethene polymerization (Phillips process) [1–3], oxidation of various organic compounds [3], hydrogenation-dehydrogenation of hydrocarbons [3–5] and to a lesser degree in many other processes such as: dehydroisomerization of n-butane [6], selective catalytic reduction of NO_x with ammonia [7]. Recently, it has been found that chromium oxide-based catalysts also exhibit excellent catalytic performances in the oxidative dehydrogenation (ODH) of various hydrocarbons in the presence of CO_2, including ethane [8–11], propane [12–21], isobutane [22], and ethylbenzene [23,24]. The ODH process is considered as an improvement of the traditional dehydrogenation as well as a new attractive pathway for CO_2 utilization. Because of the fact that in reaction conditions CO_2 is reduced to CO, together with hydrogen (synthesis gas) or separately, it has many applications in the chemical industry.

The role of CO_2 in the dehydrogenation of hydrocarbons such as propane, over chromium oxide-based catalysts, is to enhance the yield of propene and the stability of the catalyst. The promoting role of CO_2 is attributed mainly to its weak oxidative properties. CO_2 participates in the process as an oxidant and allows for regeneration of the reduced chromium sites generated during the dehydrogenation of propane (1) as well as a consecutive reduction with H_2 (2). CrO_x and CrO_{x-1} stand for the oxidized and reduced form of the catalyst, respectively.

$$\begin{aligned} &C_3H_8 + CrO_x \rightleftharpoons CrO_{x-1} + C_3H_6 + H_2O \\ &CO_2 + CrO_{x-1} \rightleftharpoons CO + CrO_x \end{aligned} \qquad (1)$$

$$\begin{aligned} &H_2 + CrO_x \rightleftharpoons CrO_{x-1} + H_2O \\ &CO_2 + CrO_{x-1} \rightleftharpoons CO + CrO_x \end{aligned} \qquad (2)$$

Up to now several cycles between various redox Cr species including Cr^{6+}/Cr^{3+} [8,10,13], Cr^{5+}/Cr^{3+} [9], and Cr^{3+}/Cr^{2+} [18,23,24] have been proposed. All of these investigations indicate that CO_2 exhibits very weak oxidative properties mainly because it is thermodynamically stable and is a kinetically inert molecule.

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Regardless of the oxidation state of Cr species which participate in the redox mechanism, it is clear from the above that for the activation of CO_2 in the oxidative pathway, high-valent redox chromium species (Cr^{6+}, Cr^{5+} and Cr^{3+}) are needed. As it has already been established, several factors influence the concentration of these species on the surface of supports. They include the type of the Cr precursor, preparation conditions (e.g., calcination temperature), Cr content and properties of the support (e.g. isoelectric point, specific surface area). The high-surface-area supports provide more adsorption sites which may stabilize the redox Cr species. Therefore, more attention has been recently dedicated to various Cr-containing mesoporous catalysts. Up to now, a number of mesoporous catalysts with different pore architecture prepared by one-pot and post synthesis techniques have been investigated as the potential catalysts for dehydrogenation of propane to propene in the presence of CO_2 [12,13,15,17–20,22,23].

In a recent study, we have explored SBA-1 mesoporous silica as a support for a Cr-containing catalyst obtained by one-pot method (direct synthesis) for propane dehydrogenation with CO_2 [19]. The study showed that due to the strongly acidic conditions needed for SBA-1 preparation, the dispersion of the Cr species in the SBA-1 matrix is limited and has a negative impact on the catalytic performance of the resultant system. This observation remains in agreement with the results obtained by Zhao and Wang [12], who concluded that during the direct synthesis of the Cr/SBA-1 catalysts the pH was low enough to convert $[Cr_2O_7]^{2-}$ (precursor) into the more polymerized chromium oxide species, e.g. $[Cr_4O_{13}]^{2-}$, resulting in poor chromium dispersion in the SBA-1 matrix.

In the present work, we report the strategy for preparation of the very efficient Cr/SBA-1 catalyst. A series of Cr*x*/SBA-1 catalysts with Cr content in the range of 1–15 wt.% were obtained by the incipient wetness impregnation, characterized with various physicochemical techniques and tested in the dehydrogenation of propane in the presence of CO_2. In particular, the catalyst behavior during the process, both in the presence and absence of CO_2, was investigated using *in situ* UV–vis diffuse reflectance probe.

2. Experimental

2.1. Preparation of support and catalysts

Parent, unmodified SBA-1 was prepared under acidic conditions using cetyltriethylammonium bromide (CTEABr) as the surfactant and tetraethyl orthosilicate (TEOS) as the silica source. In a typical synthesis, 10 g of CTEABr, 1157 cm^3 of distilled water and 566 cm^3 of hydrochloric acid (37%, Chempur) were combined to form a homogeneous solution, which was cooled to 0 °C and stirred (400 rpm) for 30 min. Finally, 27.90 cm^3 of TEOS, (98%, Aldrich) precooled to 0 °C was added while vigorous stirring. The molar composition of the reaction mixture was TEOS:CTEABr:HCL:H_2O = 1:0.2:56:700. Stirring was continued for 5 h until the precipitation of the silica-surfactant assemblies was completed. After that percipient formed at 0 °C was aged in the reaction mixture for 1 h at 100 °C to improve cross-linking of the silica framework. The resultant precipitate was filtered off and dried (without washing) at 60 °C overnight. The dried material was than calcined in air by rising temperature from ambient to 550 °C over 9 h and keeping it at 550 °C for another 12 h.

In a next step, a series of Cr*x*/SBA-1 catalysts were prepared by the incipient wetness method using $Cr(NO_3)_3{\cdot}9H_2O$ (99.6% Polish Chemical Reagents, POCH) as a chromium source. Before the impregnation the SBA-1 support was dried for 12 h at 120 °C. Typically, 1 g of the mesoporous support was treated with 4.0 cm^3 of an aqueous solution containing the desired amount of $Cr(NO_3)_3$. The concentration of $Cr(NO_3)_3$ in solution was matched so as to obtain 1, 2, 3, 5, 7, 10, and 15 wt.% of total Cr content (Cr_{total}) in the final catalysts. The impregnated samples were dried at room temperature overnight, then for 6 h at 60 °C and finally all dry materials were calcined at 550 °C for 6 h in air. The catalysts were denoted as Cr*x*/SBA-1, where *x* stands for nominal Cr_{total} given in wt.% of Cr.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) patterns of mesoporous materials were collected on a Panalytical X'Pert Pro instrument operated at 40 kV and 30 mA, equipped with a Cu Kα X-ray (λ = 0.154 nm) radiation source. The diffractograms were recorded in the 2θ range between 0.5° and 70° with a 2θ step size 0.0167°.

Nitrogen adsorption–desorption isotherms were measured at −196 °C using a Quantachrome Autosorb-1 instrument. The samples were degassed at 250 °C before measurements for 12 h in the degas port of the sorption analyzer. Specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method within the relative pressure P/P_0 = 0.05–0.15. Pore size distributions were calculated from the branch of the adsorption curve using the Barrett-Joyner-Halenda (BJH) method taking into account corrected form of Kelvin equation proposed by Kruk et al. [25]. Total pore volumes were obtained from the volumes of nitrogen adsorbed at P/P_0 = 0.95 or in vicinity.

Total Cr content (Cr_{tot}) in the catalysts was determined by ICP spectrometry (Perkin Elmer ELAN 6100). The catalysts samples were dissolved in a mixture of HF and HNO_3.

Diffuse reflectance UV–vis (UV–vis DR) spectra were measured with an Ocean Optics HR2000 + instrument (integration time 400 ms) equipped with an Ocean Optics DH-2000 BAL halogen-deuterium light source. The spectra were recorded at room temperature within the wavelength range of 200–850 nm. In all cases 40 scans were accumulated to ensure a sufficient signal-to-noise ratio. $BaSO_4$ was used as a standard.

The Raman spectra were recorded with a resolution of 2 cm^{-1} at room temperature using a Renishaw InVia dispersive spectrometer. The system is equipped with a 360 mW laser operating at the wavelength of 785 nm, a Leica DMLM confocal microscope, and a CCD detector. Depending on the sample, the spectra were recorded using 0.5–10% of total power of laser at a sample position. The Raman scattered light was collected in the spectral range 150–1200 cm^{-1}. Nine scans were accumulated to ensure a sufficient signal-to-noise ratio.

Electron paramagnetic resonance (EPR) spectra were recorded at room temperature with a X-band Bruker ELEXSYS-580 spectrometer operating at 100 kHz field modulation with 1–5 G modulation amplitude. The samples were sealed in quartz tubes and were not evacuated prior the measurements.

Operando measurements combining temperature-programmed reduction with hydrogen (H_2-TPR) coupled with *in situ* UV–vis DR spectroscopy were carried out in a modified gas chromatograph with a thermal conductivity detector (TCD). Purified mixture of N_2/H_2 (95/5 vol.%, Air Liquide) served as a simultaneous carrier and reducing gas at a total flow rate of 40 cm^3min^{-1}. Before experiment a catalyst sample (100 mg) was preheated in air for 30 min at 550 °C and then in dry He stream for another 30 min. After that the sample was cooled down to room temperature and TPR experiment was started. The sample was heated at 10 °C·min^{-1} to the final temperature of 650 °C. The H_2 consumption was measured by a TCD against NiO (99.999%, Aldrich) used for calibration of H_2 consumption. During reduction the UV–vis DR spectra were collected in the range of 225–1050 nm (integration time 20 ms, 20 scans) with a high temperature reflection probe (FCR-7UV400–2-ME-HTX, 7 x 400 μm fibers). The probe was attached at the top of