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ZrO_2-based unconventional catalysts for non-oxidative propane dehydrogenation: Factors determining catalytic activity

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ABSTRACT

Non-oxidative propane dehydrogenation (PDH) was investigated over unconventional catalysts, i.e. binary La_2O_3-ZrO_2 and Y_2O_3-ZrO_2 materials with or without tiny amounts (0.005 or 0.05 wt.%) of Ru in form of nanoparticles with the size of about 1.1 nm. The results of catalytic tests and catalyst characterization with complementary techniques enabled us to conclude that coordinatively unsaturated zirconium cations (Zr_{cus}) and neighboring lattice oxygen are catalytically active sites responsible for C_3H_6 formation. Supported Ru species contribute to a minor extent to PDH but promote generation of Zr_{cus} sites upon catalyst reductive treatment or in situ under PDH conditions. The concentration of Zr_{cus} sites can also be increased through doping of ZrO_2 with La_2O_3 or Y_2O_3 with the latter being a more efficient dopant. High activity, selectivity, and durability of our catalysts were verified by comparing their performance under industrially relevant conditions with that of a conventional K-CrO_x/Al_2O_3 reference material in a series of 60 PDH/oxidative regeneration cycles at 550, 600, and 625 °C.

1. Introduction

Propene is one of the most important petrochemicals mainly used in polymer production [1]. The most common processes for synthesis of this olefin are steam cracking of naphtha and fluidized catalytic cracking of heavy oil fractions [2]. Since they cannot match the continuously increasing demand for propene, other processes have been commercialized for on-purpose large-scale production, which are metathesis of ethylene and 2-butenes as well as non-oxidative propane dehydrogenation (PDH) [3,4]. The latter process is performed over supported CrO_x- and Pt-based catalysts [4–6]. Cr-containing compounds are, however, toxic and lead to health and environmental concerns. On the other hand, Pt-based catalysts are environmentally friendly. To ensure high dispersion of Pt species, which is important for high activity and selectivity, such catalysts, however, have to be treated under chlorine atmosphere after removal of carbon deposits [5]. High price of Pt is another shortcoming of Pt-based catalysts.

Stimulated by the drawbacks mentioned above, various research groups in both industry and academia have attempted to improve available commercial catalysts or to develop suitable alternatives. Among the latter materials, those containing supported GaO_x, VO_x, or InO_x species have been identified to be the most suitable candidates [5–15]. Isolated ions of Zn^{2+}, Co^{2+}, or Fe^{2+} on the surface of SiO_2 were also reported to be active in the PDH reaction [16–18].

In our recent short communications, we introduced alternative type of alkane dehydrogenation catalysts, which have typically been used as supports, i.e. Al_2O_3 [19] and ZrO_2 promoted with La_2O_3 [20]. In comparison with usually applied supported materials, surface defects such as coordinatively unsaturated surface metal cations (Al_{cus} or Zr_{cus}) were suggested to play an important role in alkane dehydrogenation over the above unconventional catalysts. We also reported that PDH activity of ZrO_2 promoted with La_2O_3 could be increased after depositing hydrogenation-active metals such as Ru, Cu, Ni, and Co [20]. The metals were not assumed to be directly responsible for the increase in the activity but helped to increase the concentration of Zr_{cus} sites through reaction-induced reduction of ZrO_2. Further comprehensive studies are required to prove the dehydrogenation role of Zr_{cus} and to understand how its concentration can be tuned to affect the catalyst activity.

From a structural viewpoint, such surface sites are located at anion vacancies. The latter can be created upon doping of ZrO_2 with oxides of metal with oxidation state of lower than 4+ as a result of charge compensation [21]. It is also well known that

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the ability of dopants for the substitution of Zr cations and formation of homogeneous binary solid solutions strongly depend on the ionic radius of dopant metal cation, which should be close to that of Zr^{4+} (0.79 Å). Not only the radius but also the kind of dopant influence structural and mechanical properties of zirconia as well as the concentration of oxygen vacancies [22]. Concentration of such defect sites and, therefore that of Zr_{cus} sites, can also be increased through high-temperature reduction of zirconia, e.g. by H_2. The higher the reduction temperature, the higher the number of oxygen vacancies [23]. Reducibility of ZrO_2 can also be improved when depositing hydrogenation-active metals on the surface of zirconia. As documented in several previous studies [24–26], the role of supported metals was to dissociate gaseous hydrogen to highly reactive atomic hydrogen species. The latter can leave the metal surface and spillover onto the support surface, where they react with lattice oxygen yielding water and anion vacancies [27,28].

In comparison with our previous short communication [20], the purpose of the current work was to elucidate the fundamentals of propane dehydrogenation over ZrO_2-based catalysts, which are required for tailored catalyst design. In particular, we focused on (i) the kind of catalytically active sites as well as (ii) factors affecting their formation and, in particular, activity. To investigate the effect of dopant on catalytic activity, ZrO_2 was promoted by either La_2O_3 or Y_2O_3. In addition, these both binary oxides were impregnated with tiny amounts (0.005 or 0.05 wt.%) of Ru in form of well-defined (about 1.1 nm in diameter) Ru nanoparticles. In situ UV–vis analysis was used to monitor the effects of promoter and reduction conditions on formation of anion vacancies (indirectly Zr_{cus} sites). Their concentration as a function of the type of dopant, the presence of Ru, and reduction temperature in an H_2 flow was determined from O_2-pulse titration experiments in the temporal analysis of product (TAP) reactor. Catalytic tests were performed after different reduction treatments to correlate the activity with the amount of Zr_{cus} sites in the samples. Finally, the catalysts were tested under alternating C_3H_8 and O_2 feeds in the temperature range from 550 to 625 °C to check their activity, selectivity, and durability in comparison with an industrially relevant K-CrO_x/Al_2O_3 material.

2. Experimental

2.1. Catalyst preparation

$RuCl_3{\cdot}nH_2O$ (37.2 wt.% Ru, Merck), ethylene glycol (99.8%, Aldrich), NaOH (99%, Merck), acetone (>99%, Roth), toluene (99.99%, Acros), and ethanol (absolute, J.T. Baker) were used for synthesis of Ru nanoparticles (Ru NP) as described in Ref. [29]. Catalysts were synthesized by impregnation of commercial supports ($LaZrO_x$ (ZrO_2 doped with 10 wt.% La_2O_3, MelChemicals) and $YZrO_x$ (ZrO_2 doped with 8 wt.% Y_2O_3, MelChemicals)) with colloidal solution of Ru NP. The samples were denoted according to the weight percentage of ruthenium: 0.005Ru/$LaZrO_x$, 0.005Ru/$YZrO_x$, 0.05Ru/$LaZrO_x$ and 0.05Ru/$YZrO_x$. They were calcined in flowing air directly before starting catalytic tests.

A reference catalyst (K-CrO_x/Al_2O_3) was prepared according to the protocol described in a patent of Süd-Chemie [30]. KOH (Merck), CrO_3 (99.9%, Sigma Aldrich), and Al_2O_3 (Saint-Gobain NorPro) were used as starting materials. Briefly, two aqueous solutions with the required amounts of CrO_3 and KOH were separately prepared and then mixed together. Hereafter, Al_2O_3 was impregnated with the resulting solution. The catalyst precursor was dried at 120 °C overnight and finally calcined at 760 °C for 4 h. The nominal concentration of Cr_2O_3 and K_2O in the resulting catalyst was 19.7 and 0.93 wt.%, respectively.

2.2. Catalyst characterization

Specific surface areas (S_{BET}) of the samples were determined from nitrogen physisorption experiments at 77 K using a Belsorp mini II setup (Bel Japan). Desorption isotherms were evaluated according to the BET method.

X-ray diffraction (XRD) measurements were performed on a Theta/Theta diffractometer X'Pert Pro (Panalytical) with Cu Kα radiation (α = 1.5418 Å, 40 kV, 40 mA) and an X'Celerator RTMS detector. Phase composition of the samples was determined using the program suite WinXPOW (Stoe & Cie) with inclusion of the powder diffraction file PDF2 of the international center for diffraction data.

Transmission electron microscopy (JEM-ARM200F, E = 200 kV) was used to determine size distribution of Ru NP after their deposition from ethylene glycol solution onto copper grid.

Inductively coupled plasma optical emission spectrometry (ICP-OES, Varian 715-ES) was applied to ascertain Ru concentration.

In situ UV–vis measurements were carried out using an Avantes spectrometer (AvaSpec-2048-USB2-RM) equipped with a high-temperature reflection UV–vis probe, an Ava-Light-DH-S-BAL deuterium-halogen light source, and a CCD array detector. The probe consisting of six radiating optical fibers and one reading fiber was threaded through the furnace to face the wall of the quartz tube reactor at the position where the catalyst (250 mg) was located [31]. Before recording UV–vis spectra, the sample was heated up to a certain temperature (550, 600, or 650 °C) in Ar and then treated in 20 vol.% O_2 in Ar flow for 1 h. After the oxidative treatment, the catalyst was purged with Ar followed by treatment in an H_2 flow (57 vol.% H_2 in Ar) for 1 h. UV–vis spectra were recorded in the range from 225 to 800 nm every 1 min during the reduction stage. Barium sulfate (99.998%, Aldrich) was used as a white standard.

For visualizing the progress of reduction process, a relative reflectance (R_{rel}) was defined as the ratio of the reflectance of sample treated in H_2 to that of the fully oxidized one as given in Eq. (1). From this relative reflectance, we calculated the relative Kubelka-Munk function $F(R_{rel})$ according to Eq. (2).

$$R_{rel} = \frac{R_{in\ H_2\ flow}}{R_{oxidized}} \tag{1}$$

$$F(R_{rel}) = \frac{(1 - R_{rel})^2}{2 \cdot R_{rel}} \tag{2}$$

The concentration of anion vacancies in the catalysts reduced at 550, 600, or 650 °C was determined by O_2-pulse experiments performed at 550 °C in the temporal analysis of products (TAP) reactor [32,33]. The catalyst (50 mg, particle size: 250–710 μm) was placed in a quartz-tube microreactor between two layers of quartz (particle size: 250–350 μm). Before starting transient experiments, the catalyst was treated in the following way. It was initially heated in an O_2 flow (10 ml/min) up to 550 °C with a heating rate of 10 K/min. Hereafter, the catalyst was either flushed with N_2 at 550 °C for 5 min, or further heated in N_2 flow (10 ml/min) up to 600 or 650 °C. At 550, 600, or 650 °C it was exposed to an H_2 flow (57 vol.% H_2 in N_2) for 1 h. After finishing the reductive treatment, the catalyst was either cooled down to 550 °C (for reduction at 600 and 650 °C) during evacuation to ca. 70 Pa or directly evacuated (for reduction at 550 °C). Then it was exposed to high vacuum of approximately 10^{-5} Pa.

The pulse experiments were performed using an O_2:Ar = 1:1 mixture. Ar (5.0) and O_2 (4.5) were applied without additional purification. The pulsing was continued until no changes were observed in the intensity of O_2 pulses during the last 30–40 pulses. Such experiment was repeated at least 3 times for each reduction