



Synergy effect between Zr and Cr active sites in binary CrZrO_x or supported CrO_x/LaZrO_x: Consequences for catalyst activity, selectivity and durability in non-oxidative propane dehydrogenation



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ABSTRACT

Bulk CrZrO_x, supported CrO_x/LaZrO_x, and CrO_x/Al₂O₃ catalysts were prepared with Cr surface site density varying between 0.04 and 2.3 nm⁻². They were characterized by BET, XRD, temperature-programmed reduction with H₂, and NH₃ temperature-programmed desorption. Their activity, selectivity, and durability in non-oxidative propane dehydrogenation (PDH) were determined under industrially relevant conditions. The catalysts on the basis of ZrO₂ outperform their Al₂O₃-based counterparts in terms of PDH activity. This was explained by the presence of two catalytically active sites, i.e. CrO_x and coordinatively unsaturated Zr⁴⁺ (Zr_{cus}) sites. The former species promote formation of Zr_{cus} under reaction conditions or upon reductive catalyst treatment.

Practical relevance of CrZrO_x and CrO_x/LaZrO_x catalysts was checked in a series of 10 PDH/regeneration cycles performed at 550 °C. The catalysts possessing up to 40 times lower chromium content performed superior to an analogue of commercial K-CrO_x/Al₂O₃ with respect to space time yield of propene and the amount of propene formed within one PDH cycle. In terms of durability, bulk promoting of ZrO₂ with Cr was found to be advantageous over simple deposition of CrO_x on the surface of LaZrO_x.

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1. Introduction

Since the 1930s, chromium-based catalysts have been used for large-scale non-oxidative dehydrogenation of light alkanes [1]. The industrial Al₂O₃-supported catalysts contain between 10 and 20 wt.% of chromium oxide and about 2 wt.% of potassium as a promoter [2–4]. A lot of research work has been performed to understand the nature of active sites and factors influencing catalytic performance [3,5–7]. Nowadays, it is generally accepted that coordinatively unsaturated Cr³⁺ sites are catalytically active in alkane dehydrogenation [7,8]. Neighboring O²⁻ ions are involved in the reaction as well [9]. The presence of an alkali promoter influences both activity and selectivity of the catalysts. On the one hand, the promoter increases dispersion of active sites by provoking formation of Cr⁶⁺O_x under oxidizing conditions with the latter being transformed into highly dispersed catalytically active Cr³⁺O_x under reducing conditions. On the other hand, potassium reduces surface acidity of alumina and thus suppresses undesired reactions such as coke formation and cracking [7]. Although alumina is a primary

support for chromium-based catalysts, other materials such as SiO₂, SiO₂-Al₂O₃, SiO₂-ZrO₂, and ZrO₂ were also investigated. They are considered to be suitable or even better candidates because they possess lower surface acidity [2,10–13]. It should be noted that the dehydrogenation activity of ZrO₂-supported chromium catalysts is higher than those of Al₂O₃ or SiO₂-supported ones [10]. This was explained by stabilization of highly dispersed CrO_x species on the surface of ZrO₂ [10,11]. For example, Rossi et al. [10] found that freshly prepared zirconia-based materials contain higher concentration of mononuclear Cr⁵⁺ species in comparison with their counterparts on the basis of γ-Al₂O₃ or SiO₂. Such Cr species are easily reduced to the active mononuclear Cr³⁺ species under reaction conditions.

In comparison with supported catalysts, studies on alkane dehydrogenation with bulk binary CrZrO_x catalysts are rather scarce. Wu et al. used mixed Cr₂O₃-ZrO₂ oxide catalysts for propane dehydrogenation in the presence of CO₂ [14]. Those authors determined that calcined catalysts possessed high amount of Cr⁶⁺ species positively influencing catalyst activity. Thus, it was concluded that the presence of such species in mixed Cr₂O₃-ZrO₂ oxide catalysts is the key factor determining their high activity. The role of ZrO₂ was not discussed.

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In our recent short communication, bulk binary CrZrO_x catalysts were reported to be active for isobutane dehydrogenation to isobutylene [15]. Their high activity was partially related to the presence of surface coordinatively unsaturated zirconium cations (Zr_{CUS}), which are responsible for alkane activation [15–18]. The objective of the present study was to investigate if there is a synergy effect between two types (Cr and Zr) of active sites in bulk binary CrZrO_x or supported CrO_x/LaZrO_x catalysts in terms of their activity in propane dehydrogenation (PDH). Other important questions were as follows. Does product selectivity depend on the type of catalyst (bulk vs. supported)? How and whether does the kind of catalytically active species affect catalyst on-stream stability within one PDH cycle and durability over several cycles of PDH and oxidative catalyst regeneration? How do ZrO₂-based catalysts perform in comparison with an industrial analogue K-CrO_x/Al₂O₃? To this end, XRD, NH₃-TPD and H₂-TPR were used to characterize phase composition, acidic and redox properties of both bulk and supported catalysts as a function of Cr content. Catalytic tests were instrumental in determining the rate of propene formation, catalyst on-stream performance and durability at industrially relevant degrees of propane conversion and establishing primary and secondary reaction pathways in the course of PDH.

2. Experimental section

2.1. Catalyst preparation

ZrOCl₂·8H₂O (>95%, Fluka), Cr(NO₃)₃·9H₂O (99%, Aldrich), NH₃ (25% aqueous solution, Roth), KOH (Merck), CrO₃ (99.9%, Sigma Aldrich), LaZrO_x (ZrO₂ doped with 10 wt.% La₂O₃, MelChemicals), Al₂O₃ (Chempur, basic), and Al₂O₃ (Saint-Gobain NorPro) were used as starting materials. Bare ZrO₂ was prepared according to the below protocol. Required amount of ZrOCl₂·8H₂O was dissolved in deionized water to obtain solution with Zr⁴⁺ concentration of 1.0 M. An aqueous solution of ammonia was then added dropwise under stirring until pH value of 9 was reached. The precipitate formed was aged overnight, filtered, and washed several times with deionized water until chloride ions were not identified in filtrate (reaction with AgNO₃). The solid was dried at 110 °C overnight and calcined at 550 °C for 4 h. Binary CrZrO_x materials with different Zr to Cr ratio were prepared in a similar way with an exception that required amounts of Cr(NO₃)₃·9H₂O and ZrO(NO₃)₂·xH₂O were initially dissolved in deionized water to obtain solution with a total concentration of Zr⁴⁺ and Cr³⁺ of 1.0 M. The samples were denoted as Cr_{0.5}Zr_{99.5}O_x, Cr₂Zr₉₈O_x, Cr₅Zr₉₅O_x and Cr₁₀Zr₉₀O_x with the numbers standing for molar fraction of each metal.

Supported CrO_x/LaZrO_x and CrO_x/Al₂O₃ (Al₂O₃ was provided by Chempur) catalysts were prepared by simple impregnation of the support with a required amount of an aqueous solution of chromium nitrate to yield desired concentration of Cr₂O₃ in the resulting catalyst precursors. They were dried at 110 °C overnight and calcined at 550 °C for 4 h. The final catalysts are abbreviated as 0.05CrO_x/LaZrO_x, 0.15CrO_x/LaZrO_x, 0.5CrO_x/LaZrO_x, 1.5CrO_x/LaZrO_x, 3.2CrO_x/LaZrO_x, 0.08CrO_x/Al₂O₃, 0.8CrO_x/Al₂O₃, and 5.1CrO_x/Al₂O₃ with the numbers standing for weight percentage (wt.%) of Cr₂O₃.

An analogue of industrial K-CrO_x/Al₂O₃ catalyst was prepared according to the protocol described in a patent of SüdChemie [19]. Briefly, two aqueous solutions with the required amounts of CrO₃ and KOH were separately prepared and then mixed together. Hereafter, Al₂O₃ (Al₂O₃ was provided by Saint-Gobain NorPro) was impregnated with the resulting solution. The catalyst precursor was dried at 120 °C overnight and calcined at 760 °C for 4 h. The nominal concentration of Cr₂O₃ and K₂O in the resulting catalyst was 19.7 wt.% and 0.93 wt.% respectively.

2.2. Catalyst characterization

Nitrogen physisorption experiments at 77 K were carried out using a Belsorp mini II setup (Bel Japan) to determine specific surface areas (S_{BET}) of the samples. 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 CuKα radiation (λ = 1.5418 Å, 40 kV, 40 mA) and an X'Celerator RTMS detector. Phase composition of the samples was identified using the program suite WinXPOW (Stoe & Cie) with inclusion of the powder diffraction file PDF2 of the international center for diffraction data.

To quantify acidic sites, temperature-programmed desorption of ammonia (NH₃-TPD) tests were carried out in a set-up containing eight individually heated continuous-flow fixed-bed quartz reactors. Before ammonia adsorption at 120 °C, the catalysts (50 mg for each sample) were calcined in air at 550 °C for 1 h, purged with Ar for 15 min and then reduced in a flow of H₂ (57 vol.% in Ar) Ar at 550 °C for 1 h. Hereafter, they were cooled to 120 °C in a flow of Ar. So treated catalysts were exposed to a flow of ammonia (1 vol.% NH₃ in Ar) at 120 °C for 1 h, then purged with Ar flow for 5 h to remove weakly bound NH₃, cooled to 80 °C, and finally heated up to 900 °C with a heating rate of 10 K·min⁻¹ in Ar flow. An on-line mass spectrometer (Pfeiffer Vacuum OmniStar GSD 320) was used for quantifying desorbed ammonia. Signals at atomic mass units of 15 (NH₃) and 40 (Ar) were recorded in these tests.

Temperature-programmed reduction (TPR) experiments were carried out in the same set-up as for NH₃-TPD tests. The samples (200 mg for each sample) were heated in a flow of 5 vol.% H₂ in Ar (10 ml·min⁻¹) up to 900 °C with a heating rate of 10 K·min⁻¹. The H₂ consumption was quantified with an on-line mass spectrometer (Pfeiffer Vacuum OmniStar GSD 320). Signals at atomic mass units of 2 (H₂) and 40 (Ar) were recorded in these tests. Prior to the experiment, all samples were *in situ* calcined in air flow at 550 °C for 1 h.

Temperature-programmed oxidation (TPO) experiments were carried out by heating the spent catalysts (after the 10th cycle of a long-term stability test described in section 2.3) in a flow of 5 vol.% O₂ in Ar (10 ml·min⁻¹) up to 900 °C with a heating rate of 10 K·min⁻¹. The release of CO₂ and CO was detected using the above-mentioned on-line mass spectrometer. Signals at atomic mass units of 44 (CO₂), 28 (CO, CO₂) and 40 (Ar) were recorded in these tests.

2.3. Catalytic tests

Catalytic tests were performed at 1 bar in an in-house developed setup consisting of 15 continuous-flow fixed-bed quartz reactors. To determine the rate of propene formation, the tests were carried out at a degree of propane conversion below 10%. In this case, coke formation is insignificant and the catalytic reactor can be considered as differential. Before the tests, the catalysts were initially heated in an N₂ flow up to 550 °C and then calcined in an air flow at the same temperature for 1 h. Then, they were purged with N₂ for 15 min, treated with H₂ (57 vol.% H₂ in N₂) for 1 h and purged again with N₂ for 15 min. Finally, the catalysts were exposed to a flow of C₃H₈-N₂ mixture (40 vol.% C₃H₈). The initial rate of propene formation was measured after 190 s on stream.

To determine the dependence of product selectivity on propane conversion, we performed catalytic tests at 550 °C with the catalysts reduced in a flow of H₂ (57 vol.% H₂ in N₂) for 1 h at 550 °C. Both, total flow (10, 20, 40 and 60 ml·min⁻¹) of the reaction feed and catalyst amount (0.01–1.2 g) were varied to achieve different contact times and accordingly different degrees of propane conversion.

Long-term stability tests were performed at 550 °C with a C₃H₈/N₂ = 40/60 feed with a total flow of 10 ml·min⁻¹. Catalyst amount

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