Silica is preferred over various single and mixed oxides as support for CO_2-assisted cobalt-catalyzed oxidative dehydrogenation of ethane

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A B S T R A C T

Catalysts containing 4.5 wt% cobalt supported on single oxides of SiO_2, Al_2O_3, TiO_2 and ZrO_2 and on mixed ones of SiO_2-Al_2O_3, SiO_2-TiO_2, SiO_2-ZrO_2 and TiO_2-ZrO_2 were produced in a single step by flame spray pyrolysis and tested in the CO_2-assisted oxidative dehydrogenation of ethane in a continuous fixed-bed microreactor. Structural and chemical properties of the nonporous catalysts were characterized by nitrogen adsorption, XRD, HR-TEM, EDXS, NH_3-TPD, H_2-TPR, TGA, DRIFTS, XPS and Raman and UV–vis spectroscopy. Depending on the supporting oxides the reducibility of the cobalt species varied in a broad range, indicating vastly different interaction of the cobalt species with the oxidic support. For catalysts supported on Al_2O_3 and SiO_2-Al_2O_3 no significant H_2 consumption was observed up to 840 °C, while ZrO_2-supported CoO_x was already reduced at T <500 °C. The silica-supported catalysts showed a broad reduction peak at ~780 °C attributed to well dispersed CoO_x embedded in the SiO_2 matrix forming cobalt silicate, consistent with HR-TEM, XPS and UV–vis analyses. Among all catalysts, silica-supported cobalt showed the best catalytic performance under the test conditions used (700 °C with CO_2/C_2H_6 = 2.5). Admixing Al_2O_3, TiO_2 and ZrO_2 to SiO_2 did not result in improved catalytic performance. Reducibility of the CoO_x species as well as the strength and surface density of acidic sites were identified as crucial catalyst properties for optimal ethene yield. Control of the surface acidity seems particularly important to avoid undesired side reactions (cracking, coking) impairing activity and selectivity. Parametric sensitivity studies of the silica supported cobalt catalyst, including reaction temperature, CO_2/C_2H_6 feed ratio and space velocity, revealed the important role of CO_2. In the absence of CO_2, only low C_2H_6 conversion was observed and change of the oxidant to O_2 resulted in poorer catalytic performance.

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1. Introduction

Increasing demand for ethene (C_2H_4) derivatives such as polyethene, ethene oxide, ethylbenzene and many more has made ethene one of the main chemical feedstocks in the chemical industry [1,2]. Conventionally, ethene is made by naphtha and ethane (C_2H_6) cracking, both energy intensive processes that promote high rate of coke deposition, a continuous operation hurdle, apart from high CO_2 emission [3,4]. Recently, ethane cracking has significantly picked up the pace, due to current growth in discoveries of natural gas, especially shale gas in the US, making it a cheap feed for ethene production [5]. The aforementioned inherent problems of these processes can be tackled by developing a relatively low temperature catalytic process. Oxidative dehydrogenation of ethane (ODHE) [6] takes place at lower temperatures where oxidants such as oxygen [7], carbon dioxide [8] and nitrous oxide [9] are utilized. However, O_2 results in an exothermic reaction requiring efficient heat removal and it also easily oxidizes ethane, whereas utilizing N_2O in large scale, is rather challenging due to its limited availability. Therefore, CO_2, a greenhouse gas, comes as an obvious choice due to its high availability and relatively low cost [10].

Studies on ODHE employing CO_2 have been reported over Cr_2O_3- [11,12] and Ga_2O_3-based [13–15] catalysts, where the former showed superior activity. However, the use of Cr_2O_3 is problematic due to toxicity issues while Ga_2O_3 is relatively expensive and shows severe sintering and coking. The latter metal oxide has been reported to exhibit higher activity compared to that of the former [16]. But when supported on generic supports (e.g. Al_2O_3, SiO_2 etc) [8,17], the observed activity was reversed, i.e. the Cr-based catalyst was superior. One of the issues that crippled the performance of Ga_3O_3-based catalyst is high rate of coke deposition resulting in gradual and early deactivation [17], requiring frequent regen-

eration [13]. By tuning the acidity and basicity of the catalyst, to some extent, the coke deposition has been minimized [15], however, the necessity of catalyst regeneration seemed to be inevitable. The reported initial ethane conversion and ethene selectivity over Ga_2O_3-based catalysts are in the range of 20–30% and 80–90%, respectively, which gradually decrease, primarily ethane conversion, with time [17,18]. In contrast, relatively high and stable ethane conversion of around 50% and ethene selectivity of >90% were obtained over SiO_2-supported Cr_2O_3 compared to that of other supported catalysts (e.g. Al_2O_3, TiO_2, and ZrO_2) [8]. The observed high activity was attributed to the redox property and acidity/basicity of the Cr_2O_3/SiO_2. Some improvement on the Cr_2O_3/SiO_2 activity has been achieved by addition of acidic and basic oxide promoters [19].

Cobalt oxide based catalysts are attractive for oxidative dehydrogenation of ethane [20–22], propane [23,24] and isobutene [25] using O_2 and also for dry reforming of methane [26,27]. Li et al. [28] used 3%Co-MCM-41 with CO_2 as oxidant and reported ethane conversion of about 40% with a selectivity of 99%. Zhang et al. [29] found 7% Co loading on $BaCO_3$ to be optimal with a very stable (>5 h) ethane conversion of 48% at a C_2H_4 selectivity of 92%. The high activity and the stable performance was attributed to the redox property of CoO_x as well as synergism between $BaCO_3$ and $BaCoO_3$.

The support characteristics have major influence on the performance in ODHE, as has been shown for Cr_2O_3- [8] and Ga_2O_3-based [17] catalysts. To our knowledge, there exists no systematic study of the catalytic performance of single and mixed oxide supported cobalt catalysts on CO_2-assisted ODHE. With this in mind, we investigated the influence of single and mixed-oxide supports on the performance of Co-based ODHE catalysts. A scalable single-step flame spray pyrolysis (FSP) method was used for their preparation [30]. This synthesis technique is flexible, easily operable and offers high possibility of metastable phase formation due to which rapid growth in its utilization for catalyst synthesis is observed in recent years [31].

In this comparative study we report the physicochemical properties of flame-made single and mixed-oxide supported Co catalysts and their performance in ODHE using CO_2 as a mild oxidant. The physicochemical properties of the catalysts were analyzed by nitrogen adsorption, XRD, HR-TEM, EDXS, NH_3-TPD, TPR, DRIFTS, XPS and Raman- and UV–vis spectroscopy and crucial properties for optimal catalytic performance were identified.

2. Experimental

2.1. Catalyst preparation

All catalysts were made by FSP [13]. Briefly, precursor solutions were prepared by mixing appropriate amounts of metal-precursors in toluene (Sigma Aldrich), except for catalysts containing (a) Al_2O_3, where diethylene glycol monobutyl ether (Sigma–Aldrich) and acetic anhydride (Sigma-Aldrich) (vol. ratio of 2:1) and (b) ZrO_2, where a mixture of toluene, 2-ethylhexanoate (Sigma-Aldrich, purity >99%) and acetonitrile (Sigma-Aldrich, purity >99.5%) at vol. ratio of 3:1:1 were used. All the metal precursors, cobalt (III) acetylacetonate (98%), hexamethyldisiloxane (≥98%), titanium iso-propoxide (>97% purity) and aluminum tri-sec-butoxide (97% purity) from Sigma-Aldrich and zirconium 2-ethylhexanoate (~6% Zr) from Strem chemicals, were used as received. The total molar concentration of metal (i.e. Co + metal in support(s)) was set to 0.45 M except for Zr-containing catalysts where the molarity was set to 0.31 M due to solubility limitation. When preparing mixed-oxide supports, both oxides were of equivalent weight (i.e. 1:1 ratio of 95.5 wt%). The cobalt content was always 4.5 wt%. During FSP, the precursor solution was pumped at 5 mL/min into the flame reac-

tor nozzle using a syringe pump (Lambda, VIT-FIT). The feed was dispersed into fine droplets by co-flowed O_2 of 5 L/min (>99.9% PanGas) and immediately ignited by a pilot flame fed by CH_4/O_2 of 1/2 L/min (>99.9% PanGas). The pressure drop at the nozzle-tip was maintained at 2 bar. Product powders were collected on glass fiber filter (ALBET GF 6, 25.7 cm in diameter) with the aid of a vacuum pump (Busch, Seco SV 1040C). All gas flow rates were regulated by mass flow controllers (Bronkhorst).

2.2. Catalyst characterization

X-ray diffractograms were recorded on a Bruker D8 Advance diffractometer (40 kV, 20 mA, Cu Kα) over the 2θ range of 10–70° with a step size of 0.019° and scan speed of 0.1 s/step. Nitrogen adsorption-desorption isotherms were measured on a Micromeritics Tristar instrument and the specific surface area (SSA) of both fresh and spent catalyst powders was determined by applying the Brunauer-Emmett-Teller (BET) method at 77 K. All samples were kept at 150 °C in N_2-atmosphere for 1 h prior to measurements.

Micromeritics Autochem 2920 was used for H_2-temperature programmed reduction (H_2-TPR) and NH_3-temperature programmed desorption (NH_3-TPD). For all measurements, a sample mass of ca. 100 mg, a temperature ramp rate of 10 °C/min and total gas flow rate of 20 mL/min were applied. The NH_3-TPD was performed by heating the sample from room temperature to 400 °C in 5% O_2 in He and maintaining it at this temperature for 2 h before cooling down to 50 °C in helium. Then, the gas flow was switched to 10% NH_3 in Ar, which was passed over the sample for 90 min. Temperature was increased to 100 °C and the gas flow switched back to helium to remove physisorbed NH_3 from the surface of the sample. Finally, the temperature was ramped to 840 °C and the desorbed NH_3 was monitored by a mass spectrometer (m/z = 15). For H_2-TPR measurements, the samples were heated from room temperature to 200 °C in helium and held at this temperature for 2 h before cooling down to 50 °C. Then the gas flow was switched to 5%H_2/Ar before ramping to 840 °C. The H_2-consumption was monitored by a mass spectrometer (m/z = 2).

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of all fresh catalysts was performed on a Vertex 70 v spectrometer (Bruker Optics). The powder samples were placed in an in-situ DRIFTS cell that was heated to 400 °C in 5%O_2 in He at 20 mL/min and held at this temperature for 30 min. After cooling down to 40 °C in helium at 20 mL/min, background (sample + KBr) was taken and then the gas was switched to 10% NH_3/Ar, which was passed over the sample for 15 min. Afterward the weakly adsorbed NH_3 was flushed by helium for 15 min before measuring the spectra.

UV–vis diffuse reflectance spectra (Cary 500 UV–vis-NIR Spectrophotometer) were recorded from 300 to 800 nm for the fresh supported Co-catalysts and bare single metal oxides. The samples were diluted with $BaSO_4$ keeping constant the mass ratio of the sample and $BaSO_4$ and spectra were measured against a $BaSO_4$ background. Raman (Renishaw InVia Raman microscope) spectra of both fresh and spent catalysts were obtained using a 785 nm laser with 5% of the laser power (500 mW) and an exposure time of 10 s. Accumulation of spectra was set to 20 for better resolution.

XPS measurements were performed using a VG ESCALAB 220iXL spectrometer (Thermo Fisher Scientific) with monochromatic Al Kα source (spot size: 500 μm, power: 150 W). The powder samples were placed on an adhesive copper tape which was mounted on a stainless steel holder that was later transferred to the instrument chamber and kept under vacuum. In built electron and ion neutralizers were used to compensate the charge generated from the samples. The spectra were recorded in constant analyzer energy of 30 eV. The XPS system was calibrated using the Ag $3d_{5/2}$, the Cu $2p_{3/2}$ and the Au $4f_{7/2}$ peaks.