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Lanthanide compounds as catalysts for the one-step synthesis of vinyl chloride from ethylene

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ABSTRACT

The industrial manufacture of vinyl chloride relies on a two-step process involving $CuCl_2$-catalyzed ethylene oxychlorination to ethylene dichloride followed by thermal cracking of the latter to vinyl chloride. This work evaluates a wide range of commercial and self-prepared lanthanide (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er) compounds for the one-step production of vinyl chloride from ethylene in a fixed-bed reactor at 623–773 K and 1 bar using feed ratios of C_2H_4:HCl:O_2:Ar:He = 3–6:1–9.6:1–7:3:80–92 and space times of 6–252 g h mol^{-1} (based on ethylene). *Ex situ* characterization by X-ray diffraction, electron microscopy, and X-ray photoelectron spectroscopy reveals that the oxide forms of all compounds, except CeO_2, transform into their respective (oxy)chloride. Among all studied systems, CeO_2 shows the highest activity but suffers from combustion forming CO_x, while europium oxychloride (EuOCl) leads to the best vinyl chloride selectivity of 96% at 20% C_2H_4 conversion for over 100 h on stream. Temperature-programmed reduction with H_2, temperature-programmed desorption of NH_3, and oxidation tests (C_2H_4, CO, and HCl oxidation) unravel the unique balance of mild redox and enhanced acid properties of EuOCl compared to CeO_2, which suppress over-oxidation and boost ethylene dichloride dehydrochlorination. Strategies to couple the excellent selectivity of EuOCl with the high activity of CeO_2 are demonstrated through the synthesis of homogeneous europium-cerium mixed oxides, combining two functions on a single surface. In addition, the engineering of a dual-bed reactor, integrating a CeO_2 bed first to produce ethylene dichloride in high yield which is subsequently transformed to vinyl chloride over EuOCl leads to vinyl chloride yields of up to 30% per pass. These very promising findings constitute a crucial step for process intensification of polyvinyl chloride production and exploring the potential of rare-earth compounds in industrially-relevant reactions.

1. Introduction

Polyvinyl chloride (PVC, 44 Mton, annual global growth rate of 3.2%) is an integral part of modern society owing to its widespread applications that improve our everyday life [1,2]. Its monomer, chloroethene (commonly known as vinyl chloride and hereafter denoted as VCM), was first produced on a commercial scale in the 1920s through acetylene hydrochlorination over mercuric chloride catalysts, which still is the main production method in countries such as China, due to cheap availability of coal from which acetylene is produced [3,4]. However, the increasing demand for PVC and rising price of acetylene in the late 1950s prompted a shift in the feedstock to the more economical ethylene in the United States and Europe [3]. Since then, VCM is predominantly produced *via* a two-step process involving the selective oxychlorination of ethene (commonly known as ethylene) to 1,2-dichloroethane (commonly known as ethylene dichloride and hereafter denoted as EDC) over promoted $CuCl_2/\gamma$-Al_2O_3 catalysts in fluidized-bed reactors (T = 473–573 K, P = 10 bar) and the subsequent thermal cracking of EDC to VCM (T = 773–873 K, P = 25–35 bar) [3–5]. The greatest limitations of the current process are the stability issues faced by the copper catalyst, and the limited per pass conversion (50–60% with VCM selectivity >98%) and high energy demand of the thermal cracking [3]. Despite continued efforts to optimize the robustness of the catalyst by doping with additives such as alkali (Li, Na, K), alkaline earth (Mg, Ca), and rare earth metals (La, Ce), the copper chloride phase is still prone to volatilization and particle agglomeration [6–10]. Besides, the possible intensification of VCM production by integration of the oxychlorination and dehydrochlorination reactions as a one-step process requires a novel catalyst which can combine two functions.

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In order to achieve this goal, new materials such as non-halide copper containing catalysts [11] and lanthanide (oxy)chlorides [12], particularly lanthanum oxychlorides, have been reported in the patent literature. However, none of these systems is realized on an industrial scale, most likely due to the low per pass VCM yields and/or stability hurdles faced by these catalysts. Recently, we have uncovered the high stability and remarkable yield of chlorinated compounds (25% VCM, 25% EDC) over CeO_2. This outstanding performance was attributed to the integration of both redox sites, which catalyze the ethylene oxychlorination to EDC, and acid sites, responsible for the dehydrochlorination of EDC to VCM, on the same catalyst surface.

In spite of these encouraging results, CeO_2 offers significant margins for improvement. In particular, a considerable amount of over-chlorinated compounds (1,2-dichloroethene, commonly known as 1,2-dichloroethylene and hereafter denoted as 1,2-DCE) and combustion products (CO_x) were also formed, decreasing the overall selectivity of EDC and VCM. Moreover, only moderate dehydrochlorination activity was observed. Thus, it can be anticipated that materials exhibiting milder oxidative properties and higher density of strong cites than ceria could lead to enhanced performance. Surprisingly, despite their extensive use as dopants of the $CuCl_2/\gamma\text{-}Al_2O_3$ catalysts, lanthanide compounds were never systematically investigated as the main active phase for the conversion of ethylene to VCM. Besides, they were investigated in several other catalyst formulations mainly as dopants and supports [14–18], with the exception of cerium oxide and lanthanum oxide (or (oxy)chloride) which are also studied as the primary catalytic phase in oxidative processes, including CO oxidation [19,20], isobutane oxidation [21], HCl oxidation [22,23], methane oxidative coupling [24], selective reduction of nitrogen oxides [19,25], and methane oxychlorination [26,27].

Herein, the comparison of the performance of a broad set of the most abundant rare-earth compounds leads to the discovery of the exceptional performance of europium oxychloride, exhibiting 96% VCM selectivity at 20% conversion for over 100 h on stream. Structural, redox, and acidic properties are investigated to rationalize the superior performance of europium oxychloride with respect to other lanthanides and parametric studies give insight to the distribution of products. In order to attain superior VCM yields, this novel active phase is combined with the high activity of CeO_2 by synthesis of mixed oxides and through dual-bed reactor concepts. This study comprises the first practically-relevant application of europium in heterogeneous catalysis and the materials presented here have great potential to be explored in challenging catalyzed reactions, particularly toward the functionalization of hydrocarbons.

2. Experimental methods

2.1. Catalyst preparation

Commercial La_2O_3 (Alfa Aesar, 99.99%), Pr_2O_3 (Alfa Aesar, 99.9%), Nd_2O_3 (Sigma–Aldrich, 99.9%), Sm_2O_3 (Sigma–Aldrich, 99.9%), Eu_2O_3 (Sigma–Aldrich, 99.5%), Gd_2O_3 (Alfa Aesar, 99.99%), Tb_2O_3 (Strem Chemicals, 99.9%), Dy_2O_3 (ABCR, 99.99%), Ho_2O_3 (Fluka Chemie, 99.9%), and Er_2O_3 (Fluka Chemie, 99.9%) were calcined at 773 K, and CeO_2 (Sigma–Aldrich, 99.9%) at 773 K and 1173 K in static air using a heating rate of 5 K min^{-1} and an isothermal step of 5 h prior to their use in catalytic studies. Analysis by X-ray diffraction revealed that the commercial praseodymium oxide actually consisted of Pr_4O_7 and thus it is denoted as such hereafter. Europium oxide (Eu_2O_3-p-T_{cal}, where T_{cal} denotes the calcination temperature in K), cerium oxide (CeO_2-p-T_{cal}), and mixed europium-cerium oxides ($Eu_xCe_{1-x}O_{2-0.5x}$-cp-T_{cal}, where x represents the molar fraction of Eu in the range of 0.3–0.9) were synthesized by precipitation (p, single oxides) and coprecipitation (cp, mixed oxides) following a protocol reported elsewhere [13]. Briefly, the metal nitrates ($Eu_2(NO_3)_3{\cdot}6H_2O$ (ABCR, 99.9%) for Eu_2O_3-p, $Ce(NO_3)_3{\cdot}6H_2O$ (ABCR, 99.9%) for CeO_2-p, or mixtures for $Eu_xCe_{1-x}O_{2-0.5x}$-cp) were dissolved in deionized water under stirring and H_2O_2 (Acros Organics, 35%) was added to the solution to obtain a molar H_2O_2:M ratio of 3 (M = Eu, Ce, or Eu + Ce). The coprecipitation was achieved by the dropwise addition of aqueous NH_4OH (Sigma–Aldrich, 30%) until a pH of 10.5 was reached. The slurry was stirred for 4 h and washed with deionized water. Upon filtration, the precipitate was dried at 393 K for 12 h and calcined at 773 K for CeO_2-p, 773–1173 K for Eu_2O_3-p, and 773 K for $Eu_xCe_{1-x}O_{2-0.5x}$-cp in flowing air using a heating rate of 5 K min^{-1} and an isothermal step of 5 h.

2.2. Characterization

The metal content was determined by X-ray fluorescence (XRF) spectroscopy using an Orbis PC Micro-EDXRF analyzer with a Rh source (15 kV, 500 μA) and a silicon drift detector. Powder X-ray diffraction (XRD) was measured using a PANalytical X'Pert PRO-MPD diffractometer and Cu Kα radiation (λ = 0.15418 nm). The data were recorded in the 10–70° 2θ range with an angular step size of 0.017° and a continuing time of 0.26 s per step. N_2 sorption at 77 K was measured in a Quantachrome Quadrasorb-SI analyzer. Prior to the measurements, the samples were outgassed to 50 mbar at 573 K for 3 h. The Brunauer-Emmett-Teller (BET) method [28] was applied to calculate the total surface area, S_{BET}, in $m^2\,g^{-1}$. High-resolution transmission electron microscopy (HRTEM) and elemental mapping using energy-dispersive X-ray spectroscopy (EDX) were conducted on a FEI Talos microscope operated at 200 kV. All samples were dispersed as dry powders onto lacey carbon coated nickel or molybdenum grids. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Physical Electronics Quantum 2000 X-ray photoelectron spectrometer using monochromatic Al Kα radiation generated from an electron beam operated at 15 kV, and equipped with a hemispherical capacitor electron-energy analyzer. The powdered sample was firmly pressed onto the foil. The area analyzed was 150 μm in diameter and the electron take-off angle was 45°. The pass energy used for the detailed spectra of the C 1*s*, O 1*s*, Cl 2*p*, Eu 3*d*, Eu 4*d*, and Ce 3*d* core levels was 46.95 eV to yield a total analyzer energy resolution of 0.95 eV. The spectrometer energy scale was calibrated for the Au 4*f* electrons to be at 84.0 ± 0.1 eV. Partial compensation of surface charging during spectra acquisition was obtained by the simultaneous operation of electron and argon ion neutralizers. Elemental concentrations are given in atomic percent using the measured photoelectron peak areas after Shirley background subtraction and the built-in sensitivity factors for calculation. Temperature-programmed desorption of ammonia (NH_3-TPD) and temperature-programmed reduction with hydrogen (H_2-TPR) were performed using a Micromeritics Autochem II 2920 unit equipped with a thermal conductivity detector coupled to a MKS Cirrus 2 mass spectrometer. The powder sample (0.1 g) was loaded into a U-shaped quartz micro-reactor, pretreated in He (20 cm^3 STP min^{-1}) at 573 K for 3 h, and cooled to 373 K in He. For NH_3-TPD experiments, ammonia was chemisorbed at 473 K in three consecutive cycles of saturation with 5 vol.% NH_3/He (20 cm^3 STP min^{-1}) for 30 min followed by purging with He (20 cm^3 STP min^{-1}) at the same temperature for 30 min. Desorption of NH_3 was monitored in the range of 473–1273 K using a heating rate of 20 K min^{-1} and a He flow of 20 cm^3 STP min^{-1}. For H_2-TPR experiments, the sample was pretreated in He (20 cm^3 STP min^{-1}) at 423 K for 1 h, and cooled to room