



Performance of platinum and gold catalysts supported on ceria–zirconia mixed oxide in the oxidation of chlorobenzene



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ABSTRACT

Monometallic noble metal catalysts supported on ceria–zirconia mixed oxide were prepared by impregnation and tested in the oxidation of chlorobenzene (100 ppm in air). With the pure ceria–zirconia support, 27% conversion was achieved at 400 °C and only incomplete oxidation to carbon monoxide was evidenced. The introduction of gold and especially platinum significantly improved the efficiency of the catalyst. The catalytic performance increased with increasing noble metal content. The catalyst with 1 wt.% of Pt achieved 97% conversion of chlorobenzene already at 350 °C and complete oxidation to CO₂ with only traces of by-products was detected. Platinum catalysts were more efficient than gold ones, which was ascribed to their superior redox properties. On the other hand, the lower acidity of platinum catalysts was not detrimental for their catalytic performance.

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1. Introduction

Low-temperature catalytic oxidation is one of the most effective technologies for the abatement of chlorinated hydrocarbons, which are harmful due to their toxicity and high stability [1]. Chlorobenzene is used as a model compound for the catalytic combustion of dioxins, which present serious health and environmental issue. In industrial applications, vanadia catalysts are typically employed along with Mn-based catalysts or noble metals, mostly platinum and/or palladium, supported on alumina [2]. Main drawbacks of noble metal catalysts are the formation of polychlorinated by-products [3] and deactivation of the catalyst due to chlorination of metal active sites [4]. Nevertheless, Pt-based commercial catalysts were reported to be more resistant to poisoning than vanadia-based commercial catalysts [5]. Moreover, deactivation of some Pt-based catalysts was attributed to the support (usually Al₂O₃) but not to the platinum. Generally, the nature of the support can widely affect the performance of the catalysts in chlorobenzene oxidation [6].

Recently, catalysts based on CeO₂ showed promising results in the oxidation of chlorinated compounds due to the combination of acidic and oxidizing properties, thermal stability, and resistance to poisoning by chlorine [7]. Doping of V₂O₅-TiO₂ catalysts with

ceria increased their activity in chlorobenzene oxidation, which was related to the redox properties of ceria [8]. Similarly, the addition of ceria to Pt/Al₂O₃ and Pd/Al₂O₃ catalysts increased their performance in the oxidation of perchloroethylene and such catalysts were superior to that based on Rh and V₂O₅ [9]. Fe, Co, Cu, Ni, Mn, and especially Ru-doped ceria catalysts were highly active and stable in the oxidation of chlorobenzene. Dai et al. [10] have proposed the mechanism of chlorobenzene oxidation over Ru catalyst supported on ceria. The C–Cl bond in chlorobenzene is dissociated easily on Ce³⁺/Ce⁴⁺ active sites, which is followed by its oxidation to CO₂ and H₂O by surface reactive oxygen or lattice oxygen. However, the adsorption of chlorine species on the active sites resulted in rapid deactivation of the catalyst due to blocking or occupying the active sites. On the other hand, such deactivation can be prevented by the addition of Ru, which catalyzes the removal of adsorbed chlorine species via the Deacon reaction [10]. At higher temperatures, this reaction can be catalyzed also by CeO₂ itself.

Ceria–zirconia catalysts exhibited better performance in the oxidation of chlorinated aliphatic hydrocarbons than pure ceria due to a large population of acid sites, easily accessible oxygen species and hydrophobic nature [11]. In chlorobenzene oxidation, the addition of 1 wt.% of gold to ceria or ceria–zirconia caused the decrease of light-off temperature of over 100 °C; however, such catalyst suffered from rapid deactivation [12]. We have shown that ceria–zirconia mixed oxide is an efficient catalyst for dichloromethane oxidation and that the selectivity to CO₂ can be improved by introduction of gold and especially platinum [13].

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The aim of this study was to investigate the performance of ceria–zirconia mixed oxide and ceria–zirconia mixed oxide supported Au and Pt catalysts in chlorobenzene oxidation. Moreover, the prepared catalysts were compared with the commercial catalyst for the oxidation of chlorinated volatile organic compounds—Envicat[®] HHC-5557.

2. Experimental

2.1. Catalyst preparation

Ceria–zirconia mixed oxide with Ce:Zr weight ratio 1:1 (labeled as CeZr) was synthesized using sol–gel method and used as a support for platinum and gold catalysts prepared by impregnation with gold(III) acetate or platinum(II) tetraaminehydroxide solutions, respectively. Details are given elsewhere [14]. The catalysts were labeled according to the actual contents of Au (0.3 and 2.8 wt.%) and Pt (0.2 and 1.5 wt.%) determined by chemical analysis as 0.3Au/CeZr, 2.8Au/CeZr, 0.2Pt/CeZr, and 1.5Pt/CeZr, respectively. For the matter of comparison, commercial alumina-supported catalyst EnviCat[®] HHC-5557 (labeled as HHC-5557) containing 0.11 wt.% Pd and 0.13 wt.% Pt was purchased from Süd-Chemie, Germany. Detailed characterization of this catalyst can be found in Ref. [15].

2.2. Characterization

The prepared samples were characterized by chemical analysis (ICP), powder X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), N₂ physisorption, and temperature programmed techniques (TPR and TPD).

Chemical analysis of samples was performed on the ICP OES instrument Intrepid II DUO and GBC Avanta instrument. The concentration of elements was quantified in solutions obtained after decomposition of samples by melting in KHSO₄ in porcelain crucibles, filtration, and dissolution in water.

The powder X-ray diffraction (XRD) data were collected on a PANalytical X'Pert PRO diffractometer in Bragg–Brentano reflecting geometry with fixed slits using Co K α radiation. The patterns were acquired in the diffraction angle range $2\theta = 20\text{--}80^\circ$ with a step size of 0.02° . The crystallite-size was calculated according to the Scherrer equation [16].

The field-emission scanning electron microscopy (FE-SEM) images were taken using JSM-6700F scanning electron microscope. The samples for FE-SEM measurements were prepared by the powder depositing on a graphite tape.

X-ray photoelectron spectroscopy (XPS) analyses were performed on a SSX 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized micro focused Al X-ray K α source (powered at 20 mA and 10 kV), a 30° solid angle acceptance lens, a hemispherical analyzer, and a position sensitive detector. The sample was pressed in small stainless steel troughs of 4 mm diameter and placed on a multi-specimen holder. The pressure in the analysis chamber was around 10^{-6} Pa. The angle between the surface normal and the axis of the analyzer lens was 55° . The analyzed area was approximately 1.4 mm^2 and the pass energy was set at 150 eV. Atomic concentration ratios were calculated by normalizing surface area ratios with sensitivity factors based on Scofield cross sections. In addition, all binding energies were calculated taking as reference the C–(C, H) component of the C 1s peak fixed at 284.8 eV. Peak decomposition was performed using the CasaXPS program (Casa Software Ltd., UK) with a Gaussian/Lorentzian (85/15) product function and a Shirley nonlinear sigmoid-type baseline.

Nitrogen physisorption was performed using ASAP 2020 Micromeritics instrument after degassing at 105°C for 24 h under 1 Pa vacuum. The adsorption–desorption isotherms of nitrogen at -196°C were treated by the standard Brunauer–Emmett–Teller (BET) procedure [17] for the p/p_0 range 0.05–0.25 to calculate the specific surface area S_{BET} . The total pore volume, V_{total} , was determined from nitrogen adsorption isotherm at maximum p/p_0 (~ 0.995).

Temperature-programmed reduction (TPR) of the catalysts (0.300 g) was performed with a H₂/N₂ mixture (10 mol% H₂), flow rate 50 ml min^{-1} , and linear temperature increase $20^\circ\text{C min}^{-1}$ up to 1000°C . A change in H₂ concentration was detected with a mass spectrometer Omnistar 300 (Pfeiffer Vacuum). Reduction of the grained CuO (0.16–0.32 mm) was performed in each experiment to calculate absolute values of hydrogen consumed during reduction.

Temperature-programmed desorption (TPD) of NH₃ was carried out to examine acid properties of the catalysts surface. The measurements were accomplished with 0.300 g of a sample in the temperature range $20\text{--}1000^\circ\text{C}$, with helium as a carrier gas and NH₃ as adsorbing gas. Prior to the measurement, each sample was calcined in helium at 500°C , then cooled to 30°C , and an excess of NH₃ (10 doses, 840 μl each) was applied on the sample. Then, the sample was flushed with helium for 1 h to remove physically adsorbed ammonia and after that heating rate of $20^\circ\text{C min}^{-1}$ was applied. A change in NH₃ concentration was detected with a mass spectrometer Omnistar 300 (Pfeiffer Vacuum). During the experiments, the mass contribution $m/z = 16$ was collected.

2.3. Catalytic experiments

The catalytic tests were performed in a metallic fixed-bed microreactor operating at atmospheric pressure. The reactor was made of an inconel tube of 1 cm internal diameter. The catalytic bed was composed of 200 mg of grained catalyst (0.16–0.32 mm) and 800 mg of inactive glass spheres (diameter in the range 315–500 μm). The gas stream contained 100 ppmv of chlorobenzene in He (Praxair), 20% of O₂ (Praxair; 99.995%), and He (Praxair; 99.996%) as diluting gas to obtain total flow of 200 ml min^{-1} ($\text{GHSV} = 37,000\text{ h}^{-1}$). The reaction was run from 100 to 400°C in a step mode, the catalysts being stabilized for 150 min at each temperature. The analysis of reactants and products (CO₂ and CO) was continuously performed by on-line gas chromatography (Varian CP 3800 GC). This equipment allowed to detect potential reaction intermediates like hydrocarbons and (poly-) chlorinated hydrocarbons. The conversion is defined as the molar ratio reactant transformed/reactant in the inlet (in %). Temperature T_{50} (the temperature at which 50% conversion of chlorobenzene was observed) was chosen as a measure of catalyst performance; the T_{50} was interpolated from the conversions achieved at constant temperatures. No conversion was observed in the blank experiment without catalyst.

3. Results and discussion

3.1. Characterization

X-ray diffraction patterns of the support and selected catalysts are shown in Fig. 1. The diffraction lines at 34.1 , 39.0 , 56.7 , and 67.4° (2θ) correspond to hkl reflections of cubic fluorite structure of CeO₂ (please note that the diffractograms were recorded using Co K α radiation). The diffraction lines of ZrO₂ crystalline phase are missing in XRD patterns, which indicate that Zr ions are incorporated into the CeO₂ lattice, forming a ceria–zirconia solid solution while maintaining its fluorite structure with cubic symmetry [18,19]. Based on the Scherrer equation, the mean crystallite

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