Gas phase catalytic hydrodechlorination of chlorobenzene over cobalt phosphide catalysts with different P contents

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HIGHLIGHTS

- CoP catalysts are active in the gas phase hydrodechlorination of chlorobenzene.
- The amount of P incorporated determines the catalytic response.
- The catalytic activity followed the trend: $CoP > Co_2P > Co$.
- Conversion, H-spillover species, weak acidity and dispersion are correlated.

GRAPHICAL ABSTRACT
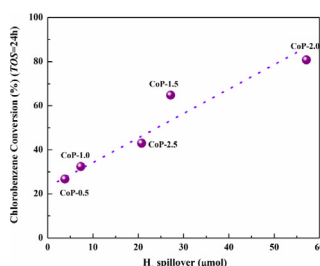
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ABSTRACT

The gas phase catalytic hydrodechlorination (HDC) of chlorobenzene (CB) at atmospheric pressure was investigated over silica-supported cobalt and cobalt phosphide catalysts containing different P loading and a fixed amount of cobalt (5 wt.%). The effect of the initial P/Co molar ratio on the stoichiometry of the cobalt phosphide phase, the acidity and the hydrogen activation capability were discussed and these properties correlated with the catalytic activity. Catalytic results indicated that the cobalt phosphide phase is much more active than the monometallic cobalt one. The activity raised with the P content present in the sample due to the formation of the CoP phase instead of the Co_2P one, which favored the formation of hydrogen spillover species, increased the amount of weak acid sites and the number of exposed superficial cobalt atoms probably related to a better dispersion of the active phase. All the catalysts gave rise benzene as the main reaction product.

1. Introduction

Chlorinated hydrocarbons compounds (CHCs) are largely used as raw materials, intermediates and solvents in chemical, agro-chemical and pharmaceutical industries [1,2]. Owing to their tremendous utilities in numerous commercial applications, large quantities of toxic wastes are released into the environment constituting a very important environmental hazard. CHCs are known for their high resilient in the environment and high toxicity, being many of them mutagenic and carcinogenic. CHCs have recently gained attention for their contribution to ozone layer depletion, the formation of acid rain and the greenhouse effect [3–5]. Conventionally, abatement of the CHCs involves destructive technologies like incineration and thermal degradation that have lower energy demands and reduced NO_x emissions [6], however significant quantities of CO_2 and products such as CO, Cl_2 and $COCl_2$ are released that are difficult to trap together with carcinogenic byproducts [7]. Thus, safe conversion of CHCs into value added products is still an intriguing goal of research. Catalytic hydrodechlorination (HDC) has been identified as a promising non-destructive process and a low-energy treatment whereby the chlorinated wastes are transformed into recyclable products with negligible associated toxic emissions [8]. Additionally, liquid-phase

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HDC is not suitable for environmental protection purpose owing to the involvement of additional solvents and many types of toxic wastes such as chlorofluorocarbons, chlorobenzenes, chlorophenols, polychlorinated biphenyls, insecticides and dioxins [9]. This fact is minimized in the gas-phase operation leading to a sustainable method for the chlorine removal. Gas-phase HDC reaction takes place at mild reaction conditions; however, one critical issue associated with this reaction is the deactivation of the catalyst which is caused by halogen adsorption on the catalyst surface and the modification of their electronic properties leading to sintering and leaching of active sites [10].

In the last years, many efforts have been devoted to the heterogeneous catalytic HDC of chlorobenzene (CB) and its derivatives with non-noble-metal catalysts, like Ni [11–14] Co [15] and Fe [16], bulk or supported, under liquid and gas phase conditions. Nevertheless, the presence of HCl as a by-product provokes a fast deactivation of these catalysts. Cobalt based catalysts have only been studied in bimetallic systems such as Ni–Co [15] and Pt–Co [17] where a synergic metallic effect contributes to the activation of the C—Cl bond. Furthermore, precious metals such as Pd [10,18–20], Pt [21,22], Rh [21,23], and Ru [21,24] have been developed as HDC catalysts. These catalytic systems have shown higher stability than non-noble-metal catalysts; however, the high cost of these catalysts greatly limits large-scale practical applications.

In the last decade, transition metal phosphides have shown an excellent performance in hydrotreating reactions such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) [25–32]. Recently, nickel phosphide has been claimed to be a promising new high-activity catalyst for hydrodechlorination reactions [33–36]. Previous researches have established that HDC reaction is promoted by the presence of spillover hydrogen, i.e. the migration of atomic hydrogen to the catalyst support after H_2 dissociation on the metallic surface. There is some evidence that spillover hydrogen is evolved in hydrogenation and hydrogenolysis processes due to the generation of reactive hydrogen atoms that facilitate de C—Cl scission for a range of metals as Ni, Pd, Pt, and Rh [37,38] and transition metal phosphides as Ni_2P [33]. It is generally accepted that the catalytic deactivation in the HDC reaction is related to the increase in the metal particle size by agglomeration or sintering during the HDC reaction, ascribed to metal–chlorine reaction [39,40]. Therefore, the active phase dispersion, acid–base properties of the support and the electronic interactions support-active phase will contribute to the overall catalytic response [37,37].

As far as we are concerned, no work has been devoted to the catalytic activity of cobalt phosphide catalysts in hydrodechlorination reactions. It should be stated that the activity of the cobalt phosphide strongly depends on the stoichiometry of the phosphide [27] and therefore determined by the phosphorous–support interaction [29] and the P/Co initial ratio of the catalytic precursor [27,41].

The present work describes the formation, activity and catalytic stability of supported cobalt and cobalt phosphide catalysts in the HDC reaction of chlorobenzene exposed to prolonged concentrated chlorinated aromatic gas streams.

2. Experimental

2.1. Materials

The reagents used to prepare the catalysts were cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$ Aldrich 98%), phosphorus acid (H_2PO_3H, Aldrich, 99%), cobalt(II) hydroxide ($Co(OH)_2$, Aldrich 99%). The chemical products utilized in the catalytic study were chlorobenzene (Aldrich 99.8%) in hexane (Sigma–Aldrich 99.99%). The gases employed were He (Air Liquide 99.99%), H_2 (Air Liquide 99.999%), N_2 (Air Liquide 99.9999%), Ar (Air Liquide 99.999%) and NH_3 (Air Liquide 99.9%).

2.2. Catalysts preparation

The support used in this work was commercial silica (Cab-o-sil M-5, Riedel-de Haen, Sigma–Aldrich). The catalysts were prepared following the incipient wetness impregnation method. The cobalt based catalyst (5 wt.% Co) were prepared employing an aqueous solution of cobalt(II) nitrate. The impregnated support was air dried at 40 °C for 24 h and calcined at 500 °C during 4 h. The catalyst precursor was reduced under a hydrogen flow of 60 mL min^{-1} (10 °C min^{-1}) by heating from r.t. until 500 °C (2 h). On the other hand, cobalt phosphide catalysts were prepared keeping constant the cobalt content (5 wt.% Co) and varying the initial P/Co atomic ratios from 0 to 2.5 to obtain cobalt phosphides with different stoichiometries. Thus, the sample with an initial P/Co atomic ratio = 2 was prepared by adding to the incipient volume stoichiometric amounts of $Co(OH)_2$ and H_2PO_3H to form $Co(HPO_3H)_2$ (5 wt.% of Co). The samples containing an initial P/Co atomic ratio <2 were prepared by mixing $Co(HPO_3H)_2 + Co(OH)_2$ (5 wt.% Co and P/Co atomic ratios = 0.5, 1 and 1.5); while the sample with an initial P/Co atomic ratio >2 was prepared by mixing $Co(HPO_3H)_2 + H_2PO_3H$ (5 wt.% Co and P/Co atomic ratio = 2.5). The precursors were air dried at 40 °C for 24 h and reduced under a hydrogen flow of 100 mL min^{-1} (3 °C min^{-1}) from r.t. to 720 °C (2 h) for cobalt phosphide based catalysts. These reduction conditions have been chosen according to TPR experiments (see below). The prepared catalysts will be denoted as CoP-x, x being the initial P/Co atomic ratio present on each sample.

2.3. Catalyst characterization

Elemental bulk composition of the catalysts was determined by X-ray fluorescence spectrometry (XRFS) using a Horiba XGT-500 spectrometer with a probe diameter of 1.2 mm. The X-ray tube was set at 50 kV with an acquisition time of 500 s and a current intensity between 0.26 and 0.32 mA.

The temperature programmed reduction with hydrogen (H_2-TPR) of phosphite precursor to form cobalt phosphide was carried out by placing 80 mg of precursor in a tubular reactor, with heating at a linear temperature ramp (3 °C min^{-1}) in flowing hydrogen (100 mL min^{-1}) from 100 to 800 °C as described elsewhere [29]. The H_2-TPR of cobalt catalyst was carried out between 40 and 800 °C (heating rate of 10 °C min^{-1}), using H_2/Ar (10/90%) flow of 40 mL min^{-1}. The evolved H_2 was analyzed by an on-line chromatograph (Shimadzu GC-14A) provided with a TCD. A cold finger (−80 °C) was employed as water tramp.

Powder diffraction patterns were collected on an X'Pert Pro MPD automated diffractometer equipped with a Ge(1 1 1) primary monochromator (strictly monochromatic Cu-Kα radiation) and an X'Celerator detector.

The textural parameters (S_{BET}, V_P and d_P) were evaluated from the N_2 adsorption–desorption isotherms at −196 °C as determined by an automatic ASAP 2020 system from Micromeritics. Prior to the measurements, samples were outgassed at 200 °C and 10^{-4} mbar overnight.

Hydrogen temperature-programmed desorption (H_2-TPD) was carried out by placing 0.300 g of catalyst precursor in a U tube reactor where it was firstly reduced in situ. After the H_2 chemisorption (50 °C) the H_2-TPD was carried out from r.t. to 800 °C (10 °C min^{-1}) [42].

The total surface acidity of the catalysts was evaluated by temperature-programmed desorption of ammonia (NH_3-TPD). To this end, a quantity of 80 mg was placed in a tubular reactor, where it was firstly reduced in situ. After cleaning with He (35 mL min^{-1})