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Carbon-supported iridium catalyst for reduction of chlorate ions with hydrogen in concentrated solutions of sodium chloride

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ABSTRACT

In production of chlorine by electrolysis of NaCl, chlorate is formed as by-product and must be removed. The back conversion of ClO_3^- to Cl^- via catalytic reduction with H_2 on Ir catalyst in NaCl brine has been studied. The catalysts contained 0.5–5 wt.% of Ir and were prepared via impregnation of mesoporous carbon support (Sibunit™) with solutions of $IrCl_3 \cdot xHCl \cdot yH_2O$ or H_2IrCl_6 and reduction in flowing H_2 at 400 or 500 °C. The Ir/C samples have been characterized with CO adsorption, XPS and HRTEM. The rate of ClO_3^- reduction in concentrated solutions of NaCl was found dependent on pH (in the range 2–6), content of Ir in the catalyst, dispersion and distribution of Ir on the support. The best properties have been shown by 5%Ir/C catalyst which was prepared with H_2IrCl_6 as the metal precursor and contained small Ir particles (~1.5 nm in diameter) located inside the cavities of carbon globules. Stable catalytic performance in multiple successive runs has been achieved.

1. Introduction

In contrast to platinum and palladium, iridium is rarely employed in applied catalysis, although scientific studies with Ir-containing catalysts are currently made. Compositions of Ir with metal oxides and/or other noble metals show high selectivity in purification of gas mixtures [1–4] and can be used as stable anode catalysts [5–7]. Ir complexes are known as selective catalysts for conversion of organic compounds [8,9]. Supported Ir catalysts have been studied in liquid phase oxidations of butyric acid [10,11] and α-pinene [12] with oxygen, in hydrogenation of cyclohexene [13], dinitrotoluene [14], cinnamaldehyde [15] and methyl oleate [16].

The present work was aimed at evaluating potentialities of Ir catalysts for reductive elimination of chlorate ions from aqueous solution of NaCl. The problem manifests itself as challenging one in an industrial production of chlorine by electrolysis of NaCl brine, where presence of significant amount of ClO_3^- has negative effect on the anodic reaction of chlorine evolution. Catalytic reduction of chlorate with H_2 is very attractive because H_2 is by-product of the chloralkali process. Typical reduction catalysts, such as Raney Ni [17] and certain platinum group metals [18–21], are capable of reducing ClO_3^- with H_2. However, the reduction of ClO_3^- in solutions with a high concentration of chloride ions is a specific process, because adsorption of Cl^- on the catalyst surface may lower the rate of ClO_3^- reduction [21]. Another problem is the loss of catalytic activity with time, due to oxidation and leaching of the active metal under simultaneous action of the strongly oxidizing (ClO_3^-) and complexing (Cl^-) anions. Ru, Rh, Pd, Pt compounds [19,20] and carbon-supported metallic Ru [20] and Rh [21] have been offered for removing chlorate from aqueous solutions with large amounts of NaCl. Rh/C catalyst was claimed to be suitable for the given purpose [21]. There are no data for Ir catalysts in the process.

The composite carbon material Sibunit™ [22,23] was used as the catalyst support. It is distinguished by a high purity, stability, and has a mesoporous structure with a negligible volume of micropores. Using chlorides of Ir(III) or Ir(IV) as metal precursor, we prepared a number of Ir/C samples with different dispersion of Ir and character of the metal distribution on the support. Influence of preparation variables and conditions of catalytic testing in the reduction of chlorate ions with H_2 has been investigated, and a highly active and resistant in concentrated NaCl brine catalyst has been obtained.

2. Experimental

2.1. Catalyst preparation

Ir/C samples were prepared by an impregnation–adsorption procedure. Freshly prepared aqueous solutions of iridium(III)

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