



CATALYTIC TREATMENT OF CHLOROBENZENE AND CHLOROBENZENE DERIVATIVES

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Abstract

Halogenated hydrocarbons such as chlorobenzenes and chlorophenoles are useful materials for everyday applications. These are used on a large scale in the chemical and petrochemical industries, as well as in the agriculture as pesticides or in medical practice as disinfectants. An efficient procedure for their non-oxidative treatment is the hydrodechlorination that can be performed upon reaction the chlorinated compounds with hydrogen at atmospheric or higher pressures in the presence of transition metal catalysts. From economical consideration it would be very important to find and to apply not expensive materials having catalytic activity in oxidation reactions. As such type potential catalyst, the modified Al-Mg mixed oxides originated from Al-Mg layered double hydroxides (hydrotalcite) have been studied. To improve the efficiency of the catalyst some transition metal modifier, such as Fe, Cu, Co, etc. have been tested.

Keywords

chlorobenzenes, chlorophenoles, halogenated hydrocarbons
catalytic treatment, not expensive materials

1. INTRODUCTION

Halogenated hydrocarbons such as chlorobenzenes and chlorophenoles are useful materials for everyday applications. These are used on a large scale in the chemical and petrochemical industries, as well as in the agriculture as pesticides or in medical practice as disinfectants.

However, most of them are environmental pollutants and the disposal of organic wastes containing halogen has become a major environmental and social problem, because most of them are toxic but stable, accumulating in the surroundings for long time periods [1].

Thus they are the subjects to stringent regulations. Therefore, a lot of effort is devoted in finding proper solutions to detoxifying or to decompose these chemicals in environmentally friendly ways.

Thermal combustion, requiring relatively high temperatures, is one of the current technologies for eliminating halogenated organic waste. The incineration technologies use about 1200°C because of the formation of very toxic byproducts - dioxins, polychlorinated biphenyls and benzofurane derivatives - at lower temperature [2].

Beside the demand of additional fuel, increasing formation of nitrogen oxides is also observed at these high temperatures. Therefore, the development of catalytic processes operating under mild conditions is of considerable interest [3].

An efficient procedure for their non-oxidative treatment is the hydrodechlorination that can be performed upon reaction the chlorinated compounds with hydrogen at atmospheric or higher pressures in the presence of transition metal catalysts [4,5].

Supported noble metals, transition metal oxides or modified zeolites can be use as catalyst in the practice [6], however, formation of toxic polychlorinated by-products and loss of catalytic materials as volatile oxychlorides due to the production of HCl or Cl₂ are often encountered as drawbacks.

Catalysts contained two metallic components, i.e. the bimetallic catalysts might have more resistant against the HCl formed, hence we have studied the behavior of Pt, Co-ZSM5 zeolite in comparison to the monometallic (Pt or Co) samples.

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2. EXPERIMENTAL

The Al/Mg-hydrotalcite ($M^{2+}/M^{3+} = 2$) and its derivatives (10 atom% Cr, Fe, Co or Cu) were prepared by coprecipitation at a constant pH = 10 ± 0.2 using aqueous solution of $Mg(NO_3)_2$, $Al(NO_3)_3$ and the nitrates of transition metals with a solution of NaOH and Na_2CO_3 .

For the preparation of zeolite catalyst a Na-ZSM5 (Si/Al = 40) sample was synthesized. Co-ZSM5 sample was obtained after ion-exchange of Na-form in $Co(NO_3)_2$, and this zeolite was impregnated with $[Pt(NH_3)_4]Cl_2$ solution. After drying the Pt content of this sample was 1.2 %. The Pt-ZSM5 was also prepared by ion-exchange in $[Pt(NH_3)_4]Cl_2$ solution followed by filtering, washing and drying.

The structure of catalysts has been checked by XRD and IR spectroscopy, the metal and chlorine contents of the used catalyst samples were determined by XR-fluorescence and spectrophotometric analysis. The oxidation reactions (chlorobenzene or 1,2-dichlorobenzene) have been carried out in a fixed bed flow reactor with GC analysis in the temperature range of 300 - 500°C using air as oxidation agent, while the hydrogenation of chlorobenzenes and 2-chlorophenole have been studied in the range of 200...400°C. The effluent gas was analyzed by gaschromatography, sampling directly from the endpoint of the reactor. GC analyzed the condensed product as well, and the mineralized chlorine was determined by argentometry.

3. RESULTS AND DISCUSSIONS

The efficiency of the oxidative destruction of mono- and dichlorobenzenes over the hydrotalcite-originated catalysts is comparable to the results obtained in the presence of other commercial catalysts. The best oxidation activity has been observed in the presence of the Fe-containing catalyst sample. A decrease of aluminum and iron content of the catalyst samples could be detected during the reactions with increasing formation of aluminum and iron chlorides. In these oxidation reactions the catalysts used are really reactants, and these processes can be considered as gas-solid reactions.

Moreover, in the presence of copper containing catalysts the formation of polychlorinated benzene derivatives were observed due to the enhanced activity for the Deacon process. The chlorine formed in this reaction can take part in radical chlorination reactions result in the formation polychlorinated compounds.

In the reaction over Pt containing catalyst high initial conversion can be established, the transformation takes place into cyclohexan, but the activity of catalyst decreases significantly. In the presence of Co-ZSM-5, the main reaction is the simple hydrodechlorination resulting in phenol as main product, however, this catalyst is stable, and the activity does not changed. The bimetallic catalyst combines the advantages of the monometallic samples. The hydroconversion of 2-chlorophenole over this catalyst has resulted benzene with relatively high selectivity and high catalyst lifetime.

The elemental chlorine formed in this reaction can take part in radical chlorination reactions result in the formation polychlorinated compounds.

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