

ARTICLES

CATALYST SYSTEMS FOR THE OXIDATION OF PHENOL IN WATER

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Abstract– The oxidation of phenol solutions (5 g/L) has been studied in a semibatch autoclave reactor. Activity screening experiments were performed over two commercial catalysts: CuO+ZnO (Topsoe) and CuO+NiO (Engelhard), and CuO/Al₂O₃ prepared in our laboratory. Isothermal runs between 393 and 423 K were carried out under an oxygen pressure of 7 bar. Phenol conversion as well as pH and Chemical Oxygen Demand (COD) measurements were recorded. Almost complete phenol conversion was obtained for all catalysts. However, conversion to CO₂ was only partial. Laboratory prepared catalysts gave the best performance in terms of activity and selectivity with the lowest induction period. Stability tests showed that catalysts remained moderately active after 60 h of operation. A simple kinetic model fits experimental results.

Keywords– Catalytic oxidation of phenol, pollution control, copper catalysts.

I. INTRODUCTION

There is an increasing need for decontamination of refractory compounds, such as phenolic contaminants, that cannot be degraded by conventional means. The phenol and derivatives are generally toxic even at very low concentrations. The Environmental Protection Agency of the USA has recommended discharge limits of 0.1 mg/L in wastewaters. These chemicals are present in the effluents of different industries, (e.g. petroleum refineries, petrochemical facilities, resin manufacturers, wood-preserving sites). Several methods have been proposed for treatment: recovery, incineration, adsorption, biological treatment and chemical oxidation (ozone, wet-air and catalytic, for example).

The oxidation of organic compounds over a solid catalyst has been recently proposed. The organic matter can be mainly converted to carbon dioxide and water, at temperatures and pressures much more moderate than those required for a non-catalyzed process. Nevertheless, the development of a satisfactory catalyst for this process has not been reported yet. Such catalyst should be able to oxidize low concentrations in aqueous media and possess resistance

to inactivation by leaching. Relatively few studies exist on the catalytic oxidation of organic matter in aqueous solutions, and there is a large discrepancy in the results. Sadana and Katzer (1974a) determined that copper oxide supported over γ -alumina was effective for phenol oxidation in the temperature range of 96°C to 246°C. A transition to a state of higher catalytic activity was observed after an induction period. The authors postulated that the heterogeneously catalyzed aqueous-phase phenol oxidation occurs by a free radical mechanism, involving initiation on the catalytic surface, followed by homogeneous propagation. The kinetics seemed to be first order with respect to the phenol concentration in both cases, but the oxygen dependence changes from order 1 to 0.5. Ohta *et al.* (1980) found reaction orders of 0.44 and 0.55 for phenol and oxygen respectively, working with the same catalyst. More recent works (Pintar and Levec, 1992; Levec and Pintar, 1995; Fortuny *et al.*, 1995) used commercial catalysts with CuO, ZnO and alumina developed for different processes. Pintar and Levec (1995) studied the catalytic oxidation of p-chlorophenol and p-nitrophenol using a commercial catalyst (Süd-Chemie AG, Munich) with copper oxide, cobalt and zinc, modified with porous cement. The experiments were carried out in a fixed bed reactor filled with liquid at 30 bar and 150-190°C. These authors recommended working with low liquid/catalyst ratios so as not to favor undesired reactions (polymerization). Akyurtlu *et al.* (1998) studied the performance of six commercial catalysts in a batch autoclave. Depending on the operating conditions, complete phenol conversion was obtained within 90 min. In some cases, the reaction underwent an induction period after which there was a transition to a much higher activity regime. But when the reaction was started after preheating the aqueous solution saturated with oxygen, no induction period was observed. Vogel *et al.* (1999) studied the promoted oxidation of phenol in aqueous solution. Phenol was degraded at temperatures as low as 100°C without observing induction time. The remaining solution mainly contained