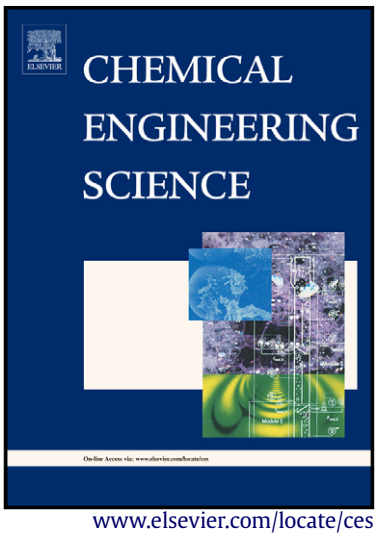

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Modeling of CO_2-assisted liquid phase oxidation of para-xylene catalyzed by transition metals/bromide

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Abstract: The promoting effect of CO_2 on liquid phase oxidation of para-xylene (PX) catalyzed by transition metals/bromide was investigated in batch experiments under conditions of industrial interests such as temperature, pressure, and catalyst. On the basis of free radical chain reaction mechanism of alkyl aromatics oxidation, the kinetic model of CO_2-assisted PX oxidation involving six parameters was developed. The model fits the PX oxidation kinetics well with narrow confidence intervals of rate constants under conditions of various CO_2 addition, temperatures, and catalysts. It was found that the presence of CO_2 could obviously promote the chain initiation reactions that are the rate-limiting steps, while it has no impact on the propagation reaction kinetics. Only the rate constant concerning chain initiation was dependent of different experimental conditions while other model parameters kept constant. The promoting function of CO_2 can be ascribed to the formation of active peroxocarbonate that results from a synergistic interaction of CO_2 and O_2. This postulated specie may participate in the generation of free radicals by oxidizing Co^{II} to Co^{III}. Hopefully, the kinetic model proposed in this work can be used to optimize the CO_2 assisted PX oxidation process and bring insights into PX oxidation mechanism with the presence of CO_2.

Keywords: Liquid phase oxidation; Alkyl aromatics; Kinetic model; Carbon dioxide; para-Xylene.

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