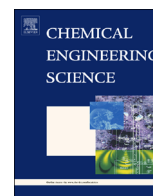




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## Propylene epoxidation with hydrogen peroxide in acidic conditions

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### H I G H L I G H T S

- Epoxidation of propylene with hydrogen peroxide.
- Positive effect of acids on hydrogen peroxide stabilization.
- Slower effect of H<sub>3</sub>PO<sub>4</sub> acid on the propylene oxide ring opening reaction.
- No effect of NaBr on the propylene oxide selectivity.
- H<sub>3</sub>PO<sub>4</sub> and NaBr can be used in the future direct synthesis of PO.

### A R T I C L E I N F O

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### A B S T R A C T

In the present work, the epoxidation of propylene with hydrogen peroxide in the presence of acids and halides is studied. The presence of acids and halides is indispensable for increasing the selectivity of the direct synthesis of hydrogen peroxide, the first step of the direct propylene oxide production from hydrogen, oxygen and propylene. Therefore, we focus on the systematic study of the effect of these compounds on the epoxidation of propylene with hydrogen peroxide in prospective of its future integration with hydrogen peroxide in-situ formed. Indeed, the epoxidation of propylene with hydrogen peroxide is the second step of the direct PO synthesis from hydrogen, oxygen and propylene. The acid concentration and type were shown to have an effect on the PO selectivity. Sulphuric and hydrochloric acids, typical compounds used to stabilize the hydrogen peroxide, are not suitable for the direct propylene oxide due to their fast dissociation in the solution. This leads to a fast ring opening reaction of the epoxide. Phosphoric acid was shown to have a much milder effect on the propylene oxide selectivity, therefore being an option for the direct propylene oxide synthesis. Also, the amount of halides (NaBr) needed to stabilize the hydrogen peroxide, does not have an effect on the epoxidation step. Therefore phosphoric acid and NaBr can be implemented in the direct propylene oxide synthesis from hydrogen, oxygen and propylene.

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### 1. Introduction

Oxidations are an extremely important class of reactions largely utilized in the chemical industry (Clerici and Ingallina, 1998; Puertolas et al., 2015). The challenge raised to the scientific community has always been to improve the current technological state of the art towards more sustainable, green, economically advantageous and efficient processes (Cavani and Teles, 2009). This explains the increased interest in a small and rather simple molecule such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (Clerici and Ingallina, 1998; Puertolas et al., 2015; Ishihara et al., 2015). H<sub>2</sub>O<sub>2</sub> is known to be a very strong and versatile oxidizing agent and green

compound due to only water formed as a by-product (Campos-Martin et al., 2006; Landon et al., 2003; Garcia-Serna et al., 2014; Samanta, 2008). A positive example where H<sub>2</sub>O<sub>2</sub> has been successfully implemented as a green oxidizer is the HPPO process where H<sub>2</sub>O<sub>2</sub> (HP) is used together with the epoxidation reaction of propylene to form propylene oxide (PO) obtaining mainly water as by-product (Bassler, 2010; The Dow Chemical Company, 2014). PO is an important compound used as a chemical intermediate in the manufacturing of several daily-life compounds such as polyurethanes, polyesters and glycol ethers (Nijhuis et al., 2006). The high demand of PO has increased even more the need of improving and substituting the traditional existing processes for its production with more efficient and economically advantageous ones (Russo et al., 2013; Blanco-Brieva et al., 2008). The first answer to these requirements is given by the direct synthesis of PO from hydrogen, oxygen and propylene (Monnier, 2001; Chen and

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### Nomenclature

$k$	initial reaction rate constant [1/min]
$r_{obs}$	observed reaction rate [mol/s m <sup>3</sup> ]
$r_{theor}$	theoretical reaction rate [mol/s m <sup>3</sup> ]
$\theta$	effectiveness factor [dimensionless]
$\Phi$	Thiele modulus [dimensionless]

$d_p$	particle size diameter [m]
$C_{AS}$	H <sub>2</sub> O <sub>2</sub> bulk concentration [mol/m <sup>3</sup> ]
$D_{eff}$	effective diffusion coefficient [m <sup>2</sup> /s]
1M2P	1-Methoxy 2-propanol
2M1P	2-Methoxy 1-propanol
1Cl2P	1-Chloro 2-propanol
2Cl1P	2-Chloro 1-propanol

Beckman, 2008). This is a two step reaction where H<sub>2</sub>O<sub>2</sub> is in-situ formed from hydrogen and oxygen and further utilized in the epoxidation of propylene. However, the applicability of this reaction on a large industrial scale is hindered by the instability of H<sub>2</sub>O<sub>2</sub> (Landon et al., 2003; Samanta, 2008). The synthesis of H<sub>2</sub>O<sub>2</sub> has been appointed as the rate limiting step for the integration of these reactions in a single unit (Monnier, 2001). The low H<sub>2</sub>O<sub>2</sub> selectivity limits the hydrogen efficiency to values that are too poor for any possible large scale implementation of the direct PO synthesis (Edwards et al., 2015; Puertolas et al., 2015). Therefore, an improvement of the direct PO synthesis can be achieved by optimizing the synthesis of H<sub>2</sub>O<sub>2</sub>. This is complicated by the capacity of the catalyst, responsible for the H<sub>2</sub>O<sub>2</sub> production, to catalyze also undesired consecutive-parallel reactions making the selectivity the main limiting factor (Samanta, 2008). The major achievement on improving the H<sub>2</sub>O<sub>2</sub> selectivity was the discovery of the beneficial effect of promoters on this reaction (Burch and Ellis, 2003; Edwards et al., 2015). These compounds consist of acids and halides which have the function to poison the active sites of the catalyst responsible for the H<sub>2</sub>O<sub>2</sub> decomposition, reduction to water and direct water formation from hydrogen and oxygen (Ntainjua et al., 2009; Edwards et al., 2015; Liu et al., 2008). Several tests on the H<sub>2</sub>O<sub>2</sub> direct synthesis without the presence of acids and halides have been conducted. No H<sub>2</sub>O<sub>2</sub> production was observed underlining the importance of these compounds in the reaction medium (Liu and Lunsford, 2006; Choudhary and Samanta, 2006). For the improvement of the direct PO synthesis through the optimization of the rate limiting step, the presence of halides and acids is required. However, the contact of an acid and an epoxide leads to a selectivity problem (Parker and Isaacs, 1959). The epoxide gets protonated from the acid opening the ring and forming undesired by-products. Also the presence of halides, mostly added to the H<sub>2</sub>O<sub>2</sub> direct synthesis in the form of metal earth salts, may cause the blocking of the active sites for the epoxidation step (Li et al., 2001). Some interesting results on the effect of additives on the direct PO synthesis reaction have been presented in literature. The main discovery was the beneficial effect of buffer compounds on the PO reaction (Grey and Jones, 2002; Grey, 2002). These compounds are oxyacids salts (Grey and Jones, 2002; Grey, 2002) which increase the PO selectivity lowering the ring opening reaction to glycols and glycol ethers and increasing the catalyst activity. The most preferred buffers to utilize in the one-pot PO synthesis were alkali metal phosphate materials (Grey and Jones, 2002). Further improvement of the PO productivity was achieved pre-treating the catalyst with a bromide compound (Grey, 2002). Other investigated materials such as phosphorus, sulfur, selenium or arsenic additives (Dessau et al., 1999) and nonbasic salts (Crocco and Zajacek, 1997) were found to be beneficial for the epoxidation reaction. The nonbasic salts had the double advantage of increasing the PO selectivity and stabilizing the hydrogen peroxide. The positive effect of the nonbasic salts was particularly surprising since opposite results were already reported in literature (Clerici and Ingallina, 1993). Moreover, the acidic content of the catalyst is well known to lower the PO selectivity due to ring opening consecutive reactions and

neutral treatments are required (Crocco and Zajacek, 1997; Chang et al., 1997). Also Clerici investigated the effect of many additives on the epoxidations of different olefines. Acids such as HCl and HF were found to have opposite effects on the epoxidation of allyl chloride (Clerici and Ingallina, 1993). A positive effect of HCl and an inhibiting effect of HF was observed on the epoxidation rate. It was shown that some acids have a positive effect on intermediate species of the epoxidation reaction therefore on the final PO productivity (Clerici and Ingallina, 1993). It is clear that in literature many efforts have been made to perform the direct PO synthesis in a single step reaction maximizing the selectivity and productivity. The presence of buffers seems to be beneficial for the PO selectivity and contradictory results have been reported on the effect of the nonbasic compounds.

The focus of the present work is to systematically study the influence of acids and halides on the PO formation from H<sub>2</sub>O<sub>2</sub> and propylene. The acids and the halides chosen for this purpose are the main compounds used for the H<sub>2</sub>O<sub>2</sub> stabilization: sulphuric, hydrochloric and phosphoric acid (Samanta, 2008). The halide ions mostly utilized in literature are Cl<sup>-</sup> and Br<sup>-</sup> (Choudhary et al., 2007; Samanta, 2008). The comparison of the different behaviour of these compounds on PO formation leads to establish the best option to utilize for the integration of in-situ hydrogen peroxide synthesis with the H<sub>2</sub>O<sub>2</sub>.

## 2. Experimental method

### 2.1. Experimental setup-procedure

PO synthesis and H<sub>2</sub>O<sub>2</sub> decomposition tests were carried out in a glass reactor of 100 ml volume. The reaction was performed at a total pressure of 4.5–6 bar and the temperature was kept constant at 40 °C using an external heating bath. The temperature and pressure were measured with a pressure sensor and thermocouple placed in the autoclave. The solution was mechanically stirred using a gas inducing stirrer at 700 rpm. A schematic representation of the setup is shown in Fig. 1.

The experiments were conducted in the autoclave by charging

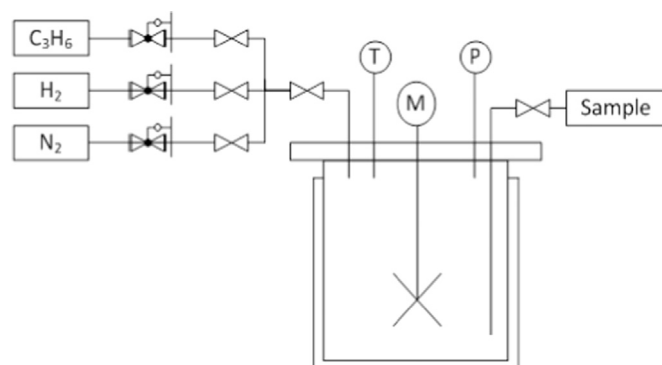


Fig. 1. Schematic representation of the experimental setup. M=Motorized stirrer. P=Pressure sensor. T=Thermocouple.

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