



Short Communication

Optimized benzaldehyde production over a new Co-ZSM-11 catalyst: Reaction parameters effects and kinetics



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ABSTRACT

An efficient Co-ZSM-11 catalyst has been synthesized for benzaldehyde production by the selective styrene oxidation. Reaction parameters such as catalyst mass, reaction temperature, molar ratio styrene/hydrogen peroxide and stirring speed were optimized, by performing the styrene oxidation reaction in a stirred batch system with fine particles of Co-ZSM-11 in suspension under microwave heating. A kinetic study was done by using the initial rate method and the Arrhenius parameters were estimated. This catalyst presents a higher reaction rate about 30% with respect of those found in literature and a higher selectivity towards benzaldehyde about 80% at optimal conditions.

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1. Introduction

The catalytic partial oxidation is an important source of research at different levels, from the industrial production of commodities to the small amount synthesis of pharmaceuticals and fine chemicals. The continuing development of new catalysts is a key point for the catalytic oxidation processes in order to reduce or eliminate the separation stages and to reduce the generation of pollutants by developing processes compatible with the environment.

Styrene catalytic oxidation for benzaldehyde production is of great interest for academic research as well as for industrial use [1]. Benzaldehyde is a very important fine chemical that is used in many fields such as medicine, dyes, flavors and resin additive. It is also an important intermediate in the synthesis of perfumes, pharmaceuticals and agrochemicals. Commercially, it can be obtained by catalytic oxidation of toluene to benzoic acid with oxygen in the liquid phase and in the presence of bromine-promoted cobalt and manganese catalysts [2]. Benzaldehyde can also be produced by the hydrolysis of benzal chloride. This process employs environmentally undesirable organic solvents as toluene and the benzaldehyde produced contains traces of chlorine and in the latter process, the selectivity for benzaldehyde is very poor [3,4]. Another way of benzaldehyde production is the styrene selective oxidation using hydrogen peroxide as oxidant agent. It offers the advantages of a production without chlorine traces that make this process greener

than those presented above. Despite this fact, most of the catalysts used in this process are homogeneous noble metal-organic compounds like ruthenium (II) perchlorate complexes [5,6]. The product separation from the catalyst is a common problem. Thus, it is important to develop novel and active heterogeneous catalysts for benzaldehyde production.

In a previous study, Azzolina Jury et al. [7] have developed ZSM-11 zeolites doped with transition metals like Co, Fe, Cr, Ni, Mn and Zn showing a significant catalytic activity improvement on the styrene partial oxidation reaction at mild conditions under microwave irradiation. Microwave heating has shown no influence on the catalytic efficiency compared to classical heating [7], but it is an ideal mean of controlling accurately the reaction parameters like temperature [8]. Thus, this heating mode was adopted in the present study.

Benzaldehyde can be synthesized through two pathways [9–11] as shown in Fig. 1.

One possible way is the oxidation of the side chain by a radical mechanism by causing the cleavage of the C=C bond to form benzaldehyde (1'). It could also be obtained by an epoxidation reaction to form styrene oxide (1) which would then be nucleophilically attacked to form benzaldehyde (2). The first pathway (1') is favored at low temperatures and it allows the synthesis of benzaldehyde with a high selectivity towards this product. Otherwise, through the second pathway, benzaldehyde could be obtained but with significant amounts of epoxide reaction products like styrene oxide and phenylacetaldehyde.

In this study, the Co-ZSM-11 zeolite was employed in the styrene partial oxidation using hydrogen peroxide as oxidizing agent. This zeolite showed the highest activity in the catalytic partial oxidation of styrene in an earlier study [8] compared to other doped zeolites where

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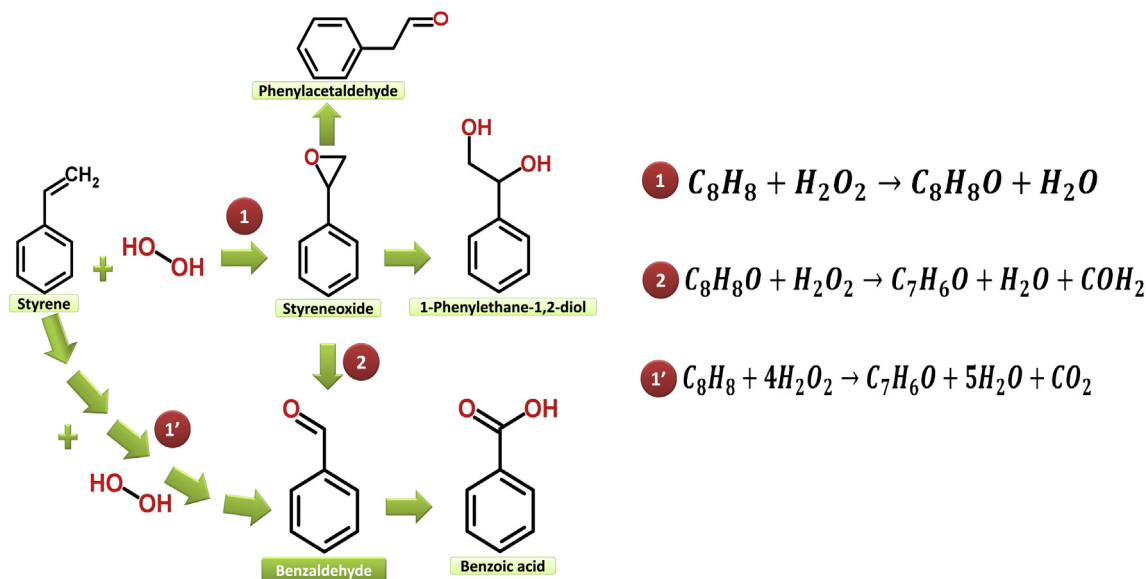


Fig. 1. Reaction scheme for styrene oxidation.

Table 1
Characterization of Co-ZSM-11 zeolite.

Zeolite	Surface area [m ² ·g ⁻¹]	Transition metal content [wt.%]	Exchange level [%]	Lewis acid sites [μmol pyridine·mg·cat. ⁻¹]	Brønsted acid sites [μmol pyridine·mg·cat. ⁻¹]	L/B
Co-ZSM-11	318	1.87	36	0.15	0.05	3.0

benzaldehyde was obtained as main product. The goal of this work is first to optimize the reaction conditions for benzaldehyde production by evaluating several reaction parameters such as reaction temperature, stirring speed, molar ratio substrate/hydrogen peroxide and catalyst mass. The second aim is to propose an accurate kinetics of the reaction under optimized conditions.

2. Experimental

2.1. Catalysts preparation

The ZSM-11 zeolite was obtained by hydrothermal synthesis and doped by ionic exchange as detailed in an earlier study [7].

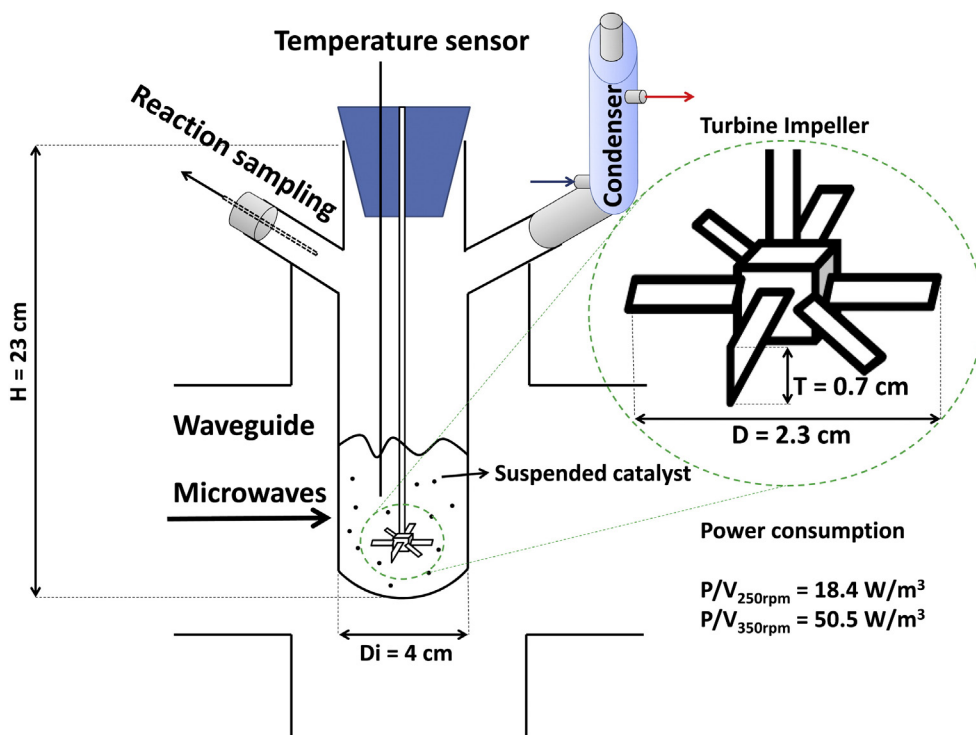


Fig. 2. System for styrene partial oxidation.

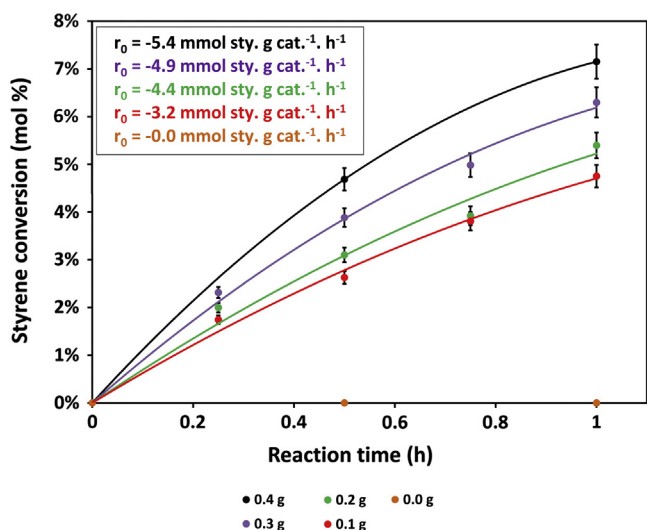


Fig. 3. Catalyst mass effect on styrene conversion. Reaction conditions: $T = 60\text{ }^{\circ}\text{C}$; $n_0\text{ CH}_3\text{CN}: 0.465\text{ mol}$; $n_0\text{ C}_8\text{H}_8: 0.016\text{ mol}$; $n_0\text{ H}_2\text{O}_2: 0.019\text{ mol}$; 350 rpm.

2.2. Catalyst characterization

A complete characterization study of Co-ZSM-11 zeolite was performed in an earlier study [7]. Table 1 resumes the characterization data of this zeolite.

2.3. Catalytic activity measurements

The styrene partial oxidation was carried out by using hydrogen peroxide as oxidizing agent and acetonitrile as solvent. The reactions were performed under microwave irradiation inside a WR-340 waveguide with a temperature control of $\pm 0.3\text{ }^{\circ}\text{C}$.

Co-ZSM-11 zeolite was under the form of fine particles ($0.5\text{ }\mu\text{m}$ in diameter) suspended in the reaction medium under agitation of 350 rpm (Fig. 2).

The organic products were analyzed and quantified by gas chromatography. A sample of the reaction solution was analyzed by ICP, after completion of the reaction, in order to determine the concentration of cobalt ions Co^{2+} in the reaction medium. It was found to be null (0.00 ppm) for each experiment presented in this study, confirming the leaching absence of Co^{2+} ions from the zeolite.

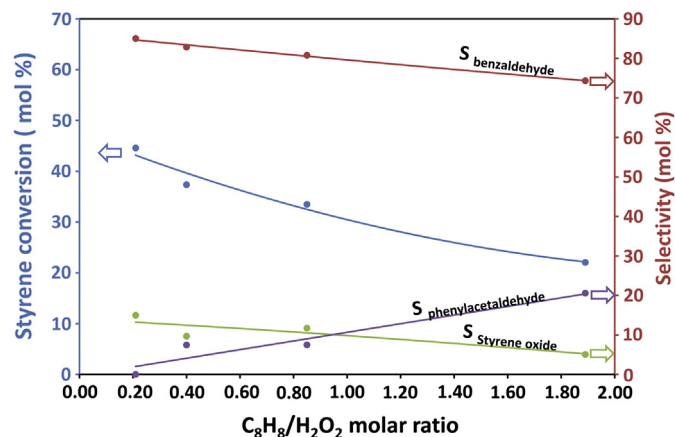


Fig. 4. Effect of $\text{C}_8\text{H}_8/\text{H}_2\text{O}_2$ molar ratio on styrene conversion and selectivity to benzaldehyde, styrene oxide and phenylacetaldehyde. Reaction conditions: 0.4 g of Co-ZSM-11; $T = 60\text{ }^{\circ}\text{C}$; 350 rpm.

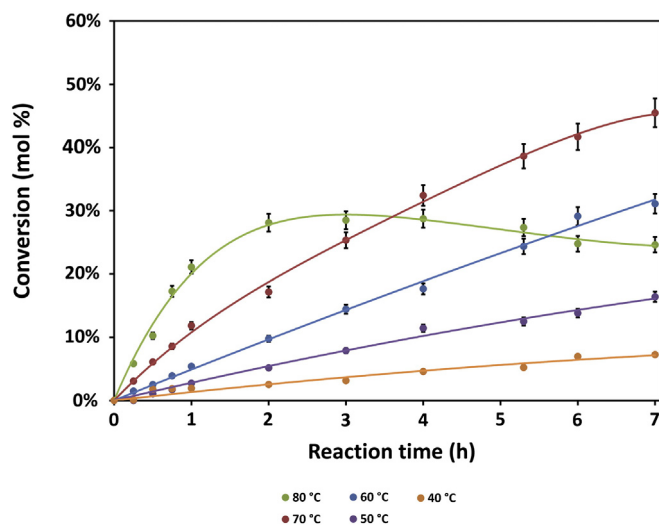


Fig. 5. Reaction temperature influence on styrene conversion. Reaction conditions: $R = 0.9$; 0.2 g of Co-ZSM-11; 350 rpm.

3. Results and discussion

3.1. Optimization of the reaction parameters

The styrene partial oxidation reaction was evaluated at two different stirring speeds of 250 and 350 rpm.

No influence of the stirring rate on the styrene partial oxidation reaction was observed. This experiment verifies that the stirring speed of 350 rpm is adequate to ensure the absence of external diffusion resistances within the liquid system and the correct suspension of the fine catalyst particles in the reaction system [12]. This value (350 rpm) will be used in all this study.

3.1.1. Influence of catalyst mass

In order to evaluate the influence of the Co-ZSM-11 mass, the styrene oxidation reaction was carried out with different catalyst masses under identical conditions.

The styrene conversion and the reaction rates are increased by the catalyst mass. But, the initial reaction rate is not proportional to the catalyst mass (Fig. 3). This fact is probably caused by the decomposition of hydrogen peroxide which is favored by the increase of the catalyst concentration [4]. This fact will be considered in the kinetic study through the determination of the apparent order with respect to the catalyst concentration.

3.1.2. Influence of $\text{C}_8\text{H}_8/\text{H}_2\text{O}_2$ molar ratio (R)

The styrene partial oxidation was carried out at different R values by varying H_2O_2 amount: 0.21, 0.40, 0.85 and 1.89. As the ratio R increases, the styrene conversion after 7 h of reaction decreases (Fig. 4). This is due to the concentration diminution of the oxidant in the reaction

Table 2
Temperature influence on reaction products selectivity.

Reaction temperature [$^{\circ}\text{C}$]	Styrene conversion [mol%]	Selectivity benzaldehyde [mol%]	Selectivity styrene oxide [mol%]	Selectivity phenylacetaldehyde [mol%]
40	7	100	0	0
50	16	80	20	0
60	31	81	15	4
70	45	67	21	12
80	25	81	9	10

Table 3
Co-ZSM-11 efficiency on styrene oxidation with respect to other catalysts found in literature.

Reference	Catalyst	Temperature [°C]	Selectivity towards benzaldehyde (mol%)	Efficiency [g·sty·g·cat. ⁻¹ ·h ⁻¹]	Efficiency [g·sty·g·metal ⁻¹ ·h ⁻¹]
[15]	TS-1	60	29	0.11	1.7
[13]	Fe-ZSM-5 (0.6 wt.%)	173	63	1.13	18.9
[13]	Co-VSB-5 (3.98 wt.%)	70	65	0.21	5.4
[13]	Co-VSB-5 (8.78 wt.%)	70	55	0.27	3.1
[16]	LaCo-MCM-41	50	0	0.35	–
[17]	Sr-Fe ₂ O ₄	70	64	0.29	–
[18]	Ni-Fe ₂ O ₄	60	55	0.27	–
[18]	Zn-Fe ₂ O ₄	60	50	0.22	–
[18]	Fe ₃ O ₄	60	68	0.26	–
[19]	MnX	60	55	–	20.8
[19]	MnY	60	53	–	18.9
[20]	Co-ZSM-5	60	80	0.23	8.5
[14]	Co-ZSM-5 (2.80 wt.%)	60	72	0.43	15.5
[14]	Zn-ZSM-5 (2.50 wt.%)	60	71	0.42	16.8
[14]	Cu-ZSM-5 (3.00 wt.%)	60	67	0.13	4.4
[14]	Fe-ZSM-5 (2.90 wt.%)	60	89	0.47	16.4
[7]	Co-Y (5.13 wt.%)	60	90	0.06	1.2
[7]	Co-ZSM-11 (0.86 wt.%)	60	90	0.22	25.6
This article	Co-ZSM-11 (1.87 wt.%)	60	81	0.37	19.8
This article	Co-ZSM-11 (1.87 wt.%)	70	67	0.54	28.9

medium. Also, an increase in selectivity towards benzaldehyde is observed when decreasing R. The selectivity values towards styrene oxide do not present any significant variation with R. Nevertheless, the selectivity values to phenylacetaldehyde, as a consequence of the epoxidation reaction, increase with R. Thus, the optimum value of R is 0.2. Below this value, at higher hydrogen peroxide concentration, a cobalt active species leaching causing catalyst activity loss was observed.

Another disadvantage of the high hydrogen peroxide concentration is that it can also oxidize the stationary phase of the chromatographic column and produce permanent damage. For that reason, we decided to perform the rest of the study with R = 0.9 despite the fact that R = 0.2 is the optimum value.

3.1.3. Effect of the reaction temperature

The styrene conversion increases with temperature from 40 °C to 70 °C (Fig. 5). At 80 °C, the styrene oxidation reaction stops after 2 h which is not observed for the other temperatures.

This phenomenon is mainly attributed to the hydrogen peroxide decomposition reaction after 2 h of reaction, at 80 °C. Gao et al. [13] have also found that the styrene conversion and selectivity towards benzaldehyde was diminished beyond 80 °C due to the hydrogen peroxide decomposition over Co-VSB-1 catalyst.

The data at 80 °C will not be used for activation energy determination. Thus, the kinetic model developed in this work will only be valid for reaction conditions up to 70 °C.

The temperature increase produces a decrease in the selectivity towards benzaldehyde. But the selectivity towards the epoxidation products (like styrene oxide and phenylacetaldehyde) becomes more significant (Table 2). The breaking of the C=C bond is more favorable at low temperatures, while at higher temperatures the epoxidation reaction competes more favorably with the cleavage of the C=C [14].

From 60 °C, the selectivity towards benzaldehyde is greatly decreased. Thus, the optimum working temperature for this reaction is 60 °C.

The styrene conversion and selectivity towards benzaldehyde values, for different catalysts found in literature, are shown in Table 3.

Table 4
Kinetic constant values from 40 to 70 °C.

T [°C]	k [L·g ^{-0.5} ·mol ^{-0.5} ·h ⁻¹]	ln(k)
40	0.0052	-2.28
50	0.0142	-1.84
60	0.0248	-1.60
70	0.0580	-1.24

Co-ZSM-11 (0.86 wt.%) zeolite, prepared and synthesized in an earlier study [7], and Co-ZSM-11 (1.87 wt.%) present the highest catalytic efficiency, expressed in grams of styrene transformed per transition metal mass (25.61 and 19.79 g·sty·g·metal⁻¹·h⁻¹ respectively). However, the low metal content of Co-ZSM-11 (0.86 wt.%) leads to the need of using higher mass of catalyst in order to reach the same efficiency than Co-ZSM-11 (1.87 wt.%) zeolite. Thus, Co-ZSM-11 (1.87 wt.%) presents a higher efficiency value per catalyst mass than Co-ZSM-11 (0.86 wt.%) zeolite (0.37 vs. 0.22). Compared to the catalysts found in literature, Co-ZSM-11 (1.87 wt.%) zeolite used in this work, presents the highest catalytic activity for the styrene partial oxidation at mild conditions (60 °C) and selectivity towards benzaldehyde.

3.2. Kinetic study

To determine the kinetic parameters of the styrene oxidation reaction under microwave irradiation, the initial rate kinetic method was applied in the absence of external and internal diffusional resistances [8,14,21]. In this study, the initial reaction rates were evaluated from the consumed amount of styrene as a function of time. Initial reaction rates were calculated from the tangent slopes of the styrene concentration curves at time zero [14]. Thus, a kinetic model was proposed in order to predict the styrene concentration as a function of reaction time.

In order to obtain the kinetic order with respect to the hydrogen peroxide concentration, the reaction was carried out by varying the concentrations of the oxidizer while maintaining constant the concentrations of

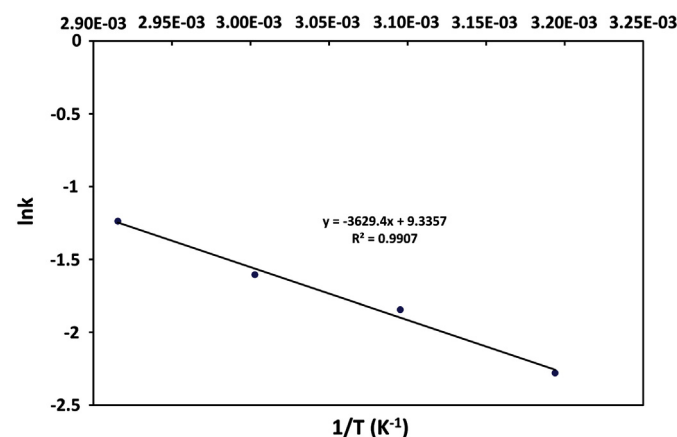


Fig. 6. Arrhenius plot of the pseudo first order rate kinetic constants of styrene oxidation over Co-ZSM-11.

acetonitrile and styrene, the mass of catalyst, temperature and stirring speed. A linear increase of the initial reaction rate with respect to the square root of the hydrogen peroxide concentration was found. This fact may be explained by the increase of the initial reaction rate of the non-desirable hydrogen peroxide decomposition.

To determine the kinetic order with respect to the styrene concentration, the reaction was carried out by varying the concentrations of this reagent while maintaining constant the concentrations of acetonitrile and hydrogen peroxide, the mass of catalyst, temperature and stirring speed. A linear increase of the initial reaction rate with respect to the styrene concentration was found.

The effect of the catalyst concentration on the reaction rate was studied at fixed initial styrene and hydrogen peroxide concentrations. An apparent fractional order of 0.5 with respect to the catalyst concentration was found.

As discussed in Section 3.1.1, this fact could be caused by the increase of the initial reaction rate of the hydrogen peroxide decomposition with the catalyst mass [4].

The law for the reaction rate is:

$$r = [C_{\text{cat}}]^{1/2} k [C_8H_8][H_2O_2]^{1/2}.$$

The kinetic constant was calculated from the initial reaction rates values, reagent concentrations and catalyst mass for each temperature between 40 and 70 °C (Table 4).

The apparent activation energy obtained from the slope of the line is 30.2 kJ·mol⁻¹ and the frequency factor is 11,335 l·g^{-0.5}·mol^{-0.5}·h⁻¹ (Fig. 6). The order of magnitude of the apparent activation energy is correct, compared to the value found by Saux and Pierella [14] on a Co-ZSM-5 zeolite. On the other hand, the frequency factor is higher but this value can be explained by the different zeolite structures employed for the styrene oxidation kinetic study. In addition, the transition metal content and the ion distributions in the zeolite framework are not certainly the same for the Co-ZSM-11 zeolite used in this study and for those employed in literature [14].

4. Conclusions

An efficient catalyst Co-ZSM-11 was synthesized and the optimal reaction conditions for benzaldehyde production from partial styrene oxidation were found. This catalyst has the highest efficiency with respect to the mass of the transition metal.

The optimal molar ratio substrate/oxidant is 0.2. The optimal temperature found for this reaction is 60 °C. The styrene conversion increases with temperature, however from 60 °C the generation of styrene epoxidation products becomes significant. The styrene conversion increased

with the catalyst mass, but a nonlinear function between the initial reaction rate and the catalyst concentration was found. This fact is caused by the increase of the non-desirable hydrogen peroxide decomposition reaction rate with the catalyst mass and with temperature.

Kinetics of the reaction was determined from 40 to 70 °C. The reaction rate is of first order with respect to the styrene concentration and a fractional order with respect to the oxidant concentration is suggested. The apparent activation energy obtained is 30.2 kJ·mol⁻¹ with a high pre-exponential factor of the Arrhenius expression. This kinetics will be used for further reactor calculations for benzaldehyde production in continuous mode under microwave.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2013.11.020>.

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