



## Studies on styrene selective oxidation to benzaldehyde catalyzed by Cr-ZSM-5: Reaction parameters effects and kinetics

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### ABSTRACT

The selective styrene oxidation to benzaldehyde was studied over Cr-ZSM-5 zeolite which was selected after probed a series of transition metal cations (chromium, cobalt, iron, zinc, manganese and copper) using hydrogen peroxide as oxidant agent. The effects of various reaction parameters such as reaction time, catalyst mass, styrene/hydrogen peroxide molar ratio, solvent nature and reaction temperature effect were evaluated over it. Using the initial rate method, a first order with respect to styrene and oxidant concentrations was determined. An apparent activation energy of 14.54 kJ/mol was obtained.

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### 1. Introduction

Oxidation catalysis constitutes an important research area because it represents the core of a variety of chemical processes for producing bulk and fine chemicals. Therefore, the design of active, selective and recyclable heterogeneous catalysts is a challenging goal in the field of oxidation catalysis [1].

The oxidation of styrene at side chains is of considerable interest for academic research and utilization in the industry. Consequently, there is a growing concern in the synthesis of fine chemicals via this versatile reaction, such as the oxidative conversion of styrene to benzaldehyde [2]. Benzaldehyde is a very valuable chemical which has widespread applications as an important intermediate for the production of perfumes, pharmaceuticals, dyestuffs and agrochemicals. It is commercially produced as a by-product of the catalytic oxidation of toluene to benzoic acid [3]. This process is usually carried out in organic solvents which are environmentally undesirable [4,5]. It can also be produced by the hydrolysis of benzal chloride. However, the latter process provides benzaldehyde with trace contamination from chlorine which is not acceptable in perfumes and pharmaceuticals and copious waste is generated in this

process [6]. With regard to chlorine-free benzaldehyde production, the selective styrene oxidation becomes an interesting alternative.

The increasing demand for environment-conscious chemical processes has impelled many researchers to investigate truly “green” technologies. In this context, and due to the ease in separation, recovery and recycling for continuous processing, heterogeneous catalytic oxidation is a more acceptable pathway compared to homogeneous counterparts. The supported transition metals showed high catalytic activity and selectivity comparable to that of unsupported ones used as homogeneous catalysts in various reactions. Their use as heterogeneous catalysts has become very important for ecofriendly industrial processes. These materials have been developed with the objective to perform reactions under milder conditions and without hazardous wastes. These new catalysts can easily be separated from the reaction media and reused, as they are quite stable when compared with the corresponding homogeneous ones. Among a variety of supports, zeolites have been often used [7–10]. In particular, ZSM-5 matrix showed good performance as we have demonstrated on our previous paper for cobalt modified one [11]. However, the research in this area is still not enough and it is necessary to develop a better solid catalyst to improve the catalytic activity. In this way, transition metal modified zeolites are interesting materials to be probe as catalyst in oxidation reactions, particularly for styrene partial oxidation.

Among the increasing interest in the development of heterogeneous catalysts for this reaction in the liquid phase, eco-friendly oxidants, such as molecular oxygen, aqueous hydrogen peroxide or organic peroxides, have been studied as well. Aqueous hydro-

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gen peroxide is a highly attractive oxidant because it is a cheap, mild and environmentally benign reagent with a high content of 'active' oxygen, and water is the only by-product [5].

In the current work, we prepared ZSM-5 zeolites which were modified with a series of transition metals. These materials were employed as catalysts on the styrene selective oxidation using hydrogen peroxide as oxidant under mild reaction conditions, obtaining benzaldehyde as the main product. Key reaction parameters such as substrate/oxidant molar relationship, nature of the solvent, mass of catalyst, reaction temperature, were evaluated and kinetic parameters were obtained.

## 2. Experimental

### 2.1. Catalysts preparation

ZSM-5 zeolite (Si/Al=17) was obtained by hydrothermal crystallization in the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system, using TPAOH (Tetrapropylammonium Hydroxide, Fluka) as a structure directing agent by known methods [12]. The obtained gel reached a pH > 9 and was maintained at 120–160 °C for 10–12 days under self-generated pressure on autoclave. Afterwards, the reaction product was extracted, washed and dried at 110 °C for 12 h. The structure directing agent (TPA) was desorbed in  $\text{N}_2$  atmosphere (20 ml/min) at programmed temperature (10 °C/min) from room temperature to 500 °C and then it was calcined in air at 500 °C for 12 h to obtain Na-ZSM-5.

The ammonium form of the catalyst (NH<sub>4</sub>-ZSM-5) was prepared by ion-exchange of Na-zeolite with NH<sub>4</sub>Cl (Fluka, 1 M) for 40 h at 80 °C. In order to obtain M-ZSM-5 (M=chromium, copper, zinc, cobalt, manganese, iron cations) the ammonium form was suspended in a solution of the metal salt with known concentration in the least amount of distilled water.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Fluka),  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Fluka),  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (Mallinckrodt),  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$  (Mallinckrodt),  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (Fluka) and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich) were used as metal salts to modify the ammonium form of the zeolite matrix. The water was evaporated using a rotator–evaporator at 80 °C under vacuum until complete dryness. A ~3 wt% was incorporated in every case.

Afterwards, samples were dried at 110 °C and treated under  $\text{N}_2$  flow at 500 °C for 12 h, followed by calcination in air at 500 °C for 8 h to obtain M-ZSM-5 samples.

### 2.2. Catalysts characterization

The metal effective percentage of all the samples under study was determined by Atomic Absorption in a Perkin Elmer AAnalyst 800 spectrometer after the digestion of the samples by microwave in a Milestone ETHOS 900 digester. BET surface area determinations were carried out with an ASAP 2000 equipment. Crystal structure determinations were performed by means of X-ray diffraction patterns collected in air at room temperature in a Philips diffractometer using  $\text{CuK}\alpha$  radiation. Diffraction data were recorded between  $2\theta = 5^\circ$  and  $60^\circ$  at an interval of  $0.05^\circ$ . A scanning speed of  $2^\circ/\text{min}$  was used. Infrared measurements in the lattice vibration region ( $400-1800 \text{ cm}^{-1}$ ) were performed on a JASCO 5300 FTIR spectrometer using KBr 0.05% wafer technique.

### 2.3. Catalytic activity

Catalytic partial oxidation of styrene (99.5%, Fluka) with  $\text{H}_2\text{O}_2$  (aqueous solution 30 wt%, Cicarelli) as oxidant agent was carried out in a glass flask reactor (25  $\text{cm}^3$ ) with magnetic stirring immersed in a thermostated bath, equipped with a reflux condenser. The catalytic tests were performed varying the following parameters: styrene/hydrogen peroxide molar ratios (R) from 0.45

**Table 1**

Comparison of catalysts for the oxidation of styrene with hydrogen peroxide.

Catalyst	Metal loading (wt%)	Styrene conversion (mol%)	Benzaldehyde selectivity <sup>a</sup> (mol%)
Zn-ZSM-5	2.5	11.29	70.6
Fe-ZSM-5	2.9	12.80	88.9
Co-ZSM-5	2.8	11.65	71.6
Cr-ZSM-5	2.7	17.35	78.0
Mn-ZSM-5	2.8	7.89	98.1
Cu-ZSM-5	3.0	3.58	67.3
–	–	1.28	96.3

Reaction conditions: catalyst, 0.2 g; T = 60 °C; styrene, 0.08 mol;  $\text{H}_2\text{O}_2$ , 0.05 mol; solvent: acetonitrile; reaction time, 7 h.

<sup>a</sup> Selectivity to benzaldehyde.

to 3.2; reaction temperatures between 40 and 80 °C and catalyst mass from 0.05 to 0.2 g. Several solvents with different dielectric constants were tested for the reaction: acetonitrile (99.5%, Cicarelli), acetone (99.5%, Aldrich), ethanol (99.5%, Cicarelli), 2-propanol (99.5%, Aldrich) and 2-butanol (99.5%, Merck).

The reaction was monitored by taking aliquots of the reaction mixture at different reaction times. Prior to analysis, the catalyst was separated by filtration. Products were analyzed quantitatively by gas chromatography (Hewlett Packard HP-5890) with a Methyl Silicone capillary column (30 m × 0.32 mm i.d) and a flame ionization detector (FID), and qualitatively, by mass spectrometry GC-Mass (Shimadzu QP 5050 GC-17 A), using a HP-S (25 m × 0.2 mm i.d) capillary column. The substrate conversions are reported as mol%.

## 3. Results and discussion

### 3.1. Influence of the metal cation incorporated

Table 1 reports the catalytic activity of the Metal-ZSM-5 synthesized in the styrene selective oxidation and metal loading of the samples which were determined by Atomic Absorption.

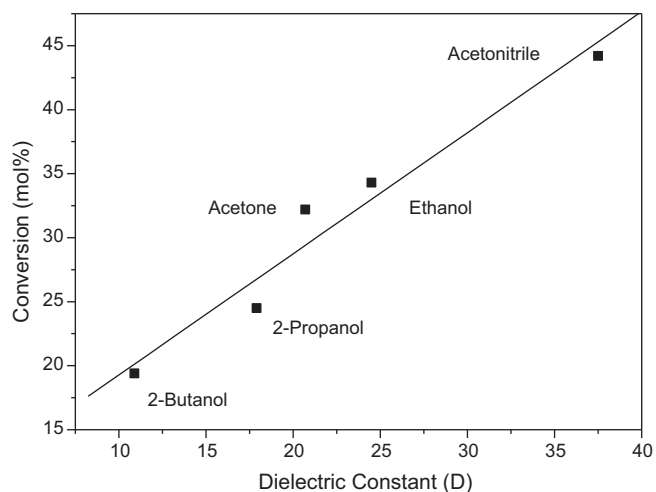
No alterations on crystallinity, neither structure were confirmed according to characterization results obtained from XRD and FTIR techniques. Zeolite matrix was not affected by the incorporation of transition metal cations using the wet impregnation method, neither with thermal treatments applied to the samples. Crystallinity was always superior to 98%. Surface areas varied between 384 and 392  $\text{m}^2/\text{g}$  for all the samples.

The catalysts were active for the reaction with benzaldehyde as the main product, even though others could still be found, such as styrene oxide, phenylacetaldehyde, 1-phenyl, 1,2-ethanediol and benzoic acid. The selectivity for benzaldehyde was high for all the catalysts. A blank experiment was performed in identical conditions, but in absence of catalyst. In this situation, the oxidation reaction occurs at a very low rate, obtaining a final conversion in the order of 1 mol% after 7 h of reaction.

From the values reported in Table 1, Cr-ZSM-5 results in the most active one considering its highest conversion values and the good performance in terms of selectivity towards benzaldehyde (78 mol%). Thus, chromium catalyst was chosen to study reaction parameters effects and kinetic.

### 3.2. Solvent effect

It is well-known that the solvent plays an important and sometimes decisive role in the catalytic behavior of a catalyst [13]. Therefore, the effect of solvents on reactivity was studied in the current catalytic system. Fig. 1 shows the conversion results obtained using 0.2 g of Cr-ZSM-5, after 7 h of reaction at 60 °C and a sub-



**Fig. 1.** Solvent effect on styrene conversion after 7 h of reaction using Cr-ZSM-5 as catalyst.

strate/oxidant molar ratio of 0.9. From the figure, it is evident the importance of the correct solvent selection. As solvent polarity increase, an important activity enhancement is observed. Thus, the best behavior was obtained using acetonitrile as solvent (high polar aprotic solvent with the highest dielectric constant of all the solvents tested). This behavior may be explained by the increase of substrate concentration over Cr-ZSM-5 surface, as the polarity of the solvent increases. Indeed, the higher the solvent polarity, the higher the concentration of the substrate in the vicinity of the active sites and the higher the styrene conversion will be, as indicated by the experimental results [11].

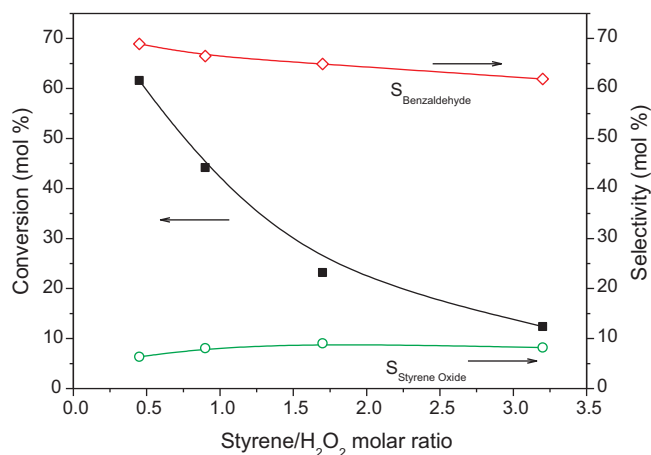
It is to be noted here that no leaching of chromium from Cr-ZSM-5 samples occurs during the reaction. The chromium content in the sample after several reaction cycles did not change, and chromium could not be detected in the filtrate after the reaction. No significant conversion of styrene was observed when the liquid filtrate was used instead of the solid catalyst for further reaction. Furthermore, the repeated use of the catalysts did not show any decrease in the catalytic activity. These observations strongly suggest that the reaction proceeds heterogeneously over the catalyst.

### 3.3. Influence of styrene/oxidant molar ratio

The effect of  $H_2O_2$  concentration on oxidation of styrene was studied by varying the molar ratio of substrate to hydrogen peroxide ( $R$ ) from 0.45 to 3.2. On increasing  $R$ , the conversion of styrene decreased (Fig. 2). This behavior could be attributed to the reduction of oxidant concentration in the reaction medium.

From Fig. 2 is also possible to observe an increment on selectivity to benzaldehyde at lower  $R$  values. Even more, the selectivities to benzaldehyde and styrene oxide remained almost unchanged with reaction time indicating that the epoxidation proceeds in parallel with the formation of benzaldehyde. So the formation of benzaldehyde from styrene can occur by two different routes. One possible pathway is the oxidation of the side chain by a radical mechanism, which causes the cleavage of the  $C=C$  bond to form benzaldehyde. It also could be obtained by an epoxidation reaction to form styrene oxide which is further nucleophilically attacked forming benzaldehyde [14,15].

To gain insight into the reaction mechanism and confirm the coexistence of these two pathways and their relevance on the oxidation, a radical scavenger, isopropyl alcohol, was added after the first hour of reaction (Fig. 3). When the radical scavenger was added, styrene conversion suffers an important reduction of  $\sim 13$  mol%



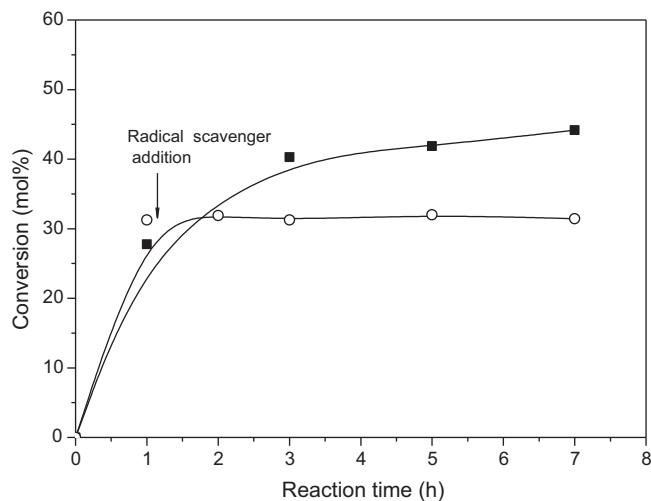
**Fig. 2.** Effect of styrene/ $H_2O_2$  molar ratio on conversion (■) and selectivity to benzaldehyde (◇) and styrene oxide (○). Reaction conditions: 0.2 g of Cr-ZSM-5; acetonitrile as solvent; 60 °C.

confirming the presence of these two competitive reaction mechanisms.

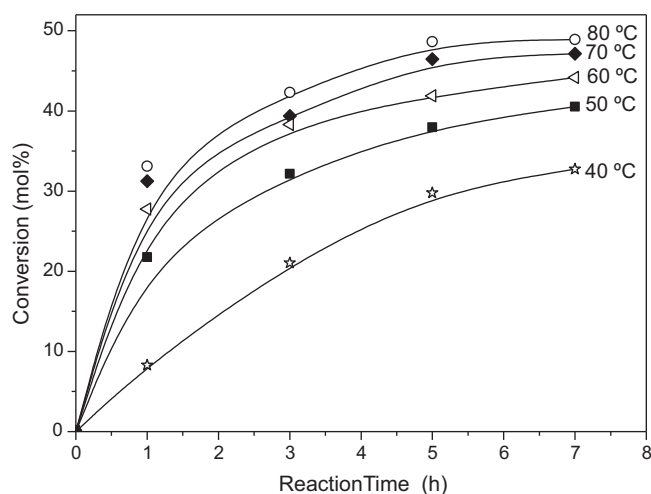
### 3.4. Effect of reaction temperature

The effect of reaction temperature on the catalytic performance of Cr-ZSM-5 is shown in Fig. 4. As expected, by increasing reaction temperature from 40 to 80 °C, styrene conversion increased from 32 to 49 mol%. At temperatures lower than 60 °C, styrene conversion increased remarkably with the reaction temperature. Such increases were decelerated at higher temperatures. This behavior may be due to a competitive thermal decomposition of  $H_2O_2$  to  $H_2O$  and  $O_2$  with reaction temperature enhancement.

In Table 2 the effect of temperature on products selectivity is shown. Benzaldehyde selectivity decreases with temperature enhancement while other epoxidation products (styrene oxide, phenylacetaldehyde, 1-phenyl-1,2-ethanediol) selectivity is improved. This confirms that the cleavage of  $C=C$  is higher at lower temperatures and the epoxidation competes more favorably against  $C=C$  cleavage at higher temperatures [16–18].



**Fig. 3.** Effect of the introduction of a radical scavenger on styrene conversion: (■) without radical scavenger reaction; (○) adding isopropyl alcohol after 1 h. Reaction conditions: 0.2 g of Cr-ZSM-5; acetonitrile as solvent;  $R = 0.9$ ; temperature: 60 °C.



**Fig. 4.** Reaction temperature effect on styrene conversion. Reaction conditions:  $R=0.9$ ; catalyst: 0.2 g Cr-ZSM-5; solvent: acetonitrile.

### 3.5. Kinetic measurements

In order to determine the kinetic parameters, the initial rate kinetic method was applied in absence of external or internal diffusional effects. The functionality between reaction rate and the reactant concentrations was found through an empirical power law considering that the kinetic constant and the reaction orders were apparent [19].

The rates of styrene oxidation, in all the experiments, were evaluated graphically from the amount of styrene converted as function of time. The initial rates were determined from the slopes of the tangents of the plots at  $t=0$  [20–23].

To obtain the kinetic order with respect to hydrogen peroxide concentration, the reaction was carried out keeping constant styrene and acetonitrile concentrations, catalyst mass and reaction temperature. Afterwards the initial concentration of oxidant was varied. Fig. 5 shows that the initial reaction rates increased almost linearly with hydrogen peroxide concentrations suggesting a first order dependence.

The styrene reaction order was determined maintaining constant  $H_2O_2$  and acetonitrile concentrations, catalyst mass and reaction temperature. Styrene conversion versus reaction time for a styrene concentration range from 0 to 0.57 mol/l was plotted and the initial reaction rates were measured. These initial rates are fitted against styrene concentrations in Fig. 6 and a first order dependence is obtained.

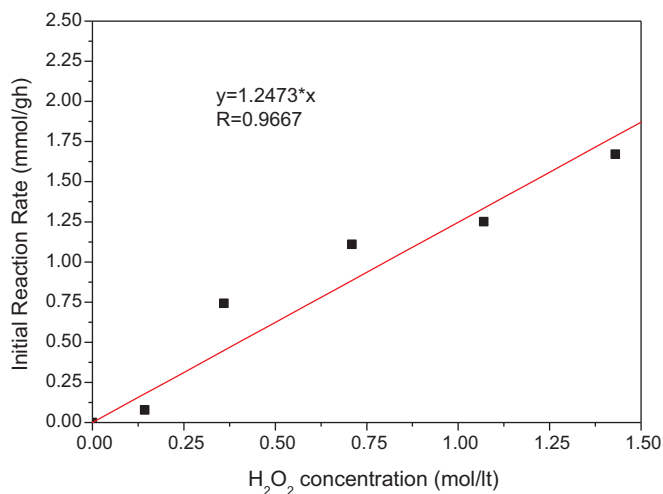
The effect of catalyst mass on the progress of styrene oxidation was studied at fixed initial concentrations of both the reactants. From the data presented in Fig. 7, fractional order with respect to catalyst mass is suggested.

As shown in Fig. 4, the reaction temperature was varied between 40 and 80 °C and styrene conversion increases with temperature. The apparent first order kinetic constant was calculated and the

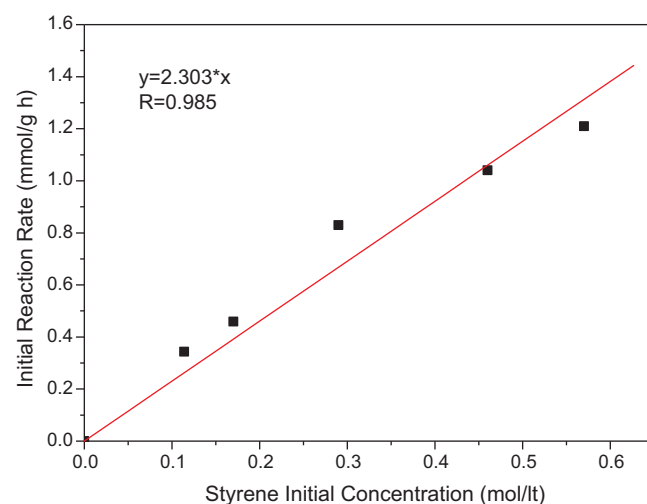
**Table 2**  
Reaction temperature effect on oxidation products selectivity.

Temp. (°C)	Conv. (mol%)	$S_{Benz}$ (mol%)	$S_{Epox}$ (mol%)	$S_{Otros}$ (mol%)
40	32.7	80.6	6.5	13.0
50	40.5	73.5	7.2	19.3
60	44.2	66.5	8.1	25.4
70	47.2	63.0	9.1	27.9
80	48.9	60.9	10.6	28.5

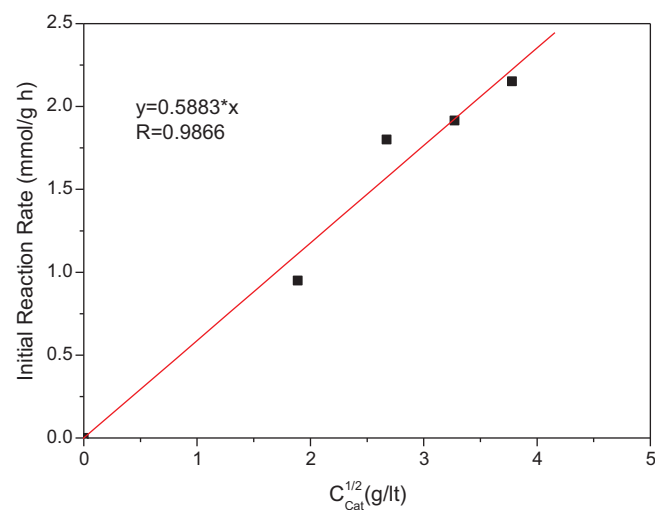
Reaction conditions: reaction time: 7 h;  $R=0.9$ ; catalyst: 0.2 g Cr-ZSM-5; solvent: acetonitrile.



**Fig. 5.** Styrene oxidation initial reaction rates over Cr-ZSM-5 as function of hydrogen peroxide initial concentrations. Reaction conditions:  $T=60\text{ }^\circ\text{C}$ ; catalyst: 0.2 g Cr-ZSM-5;  $n_{acetonitrile}^0: 0.223\text{ mol}$ ;  $n_{styrene}^0: 0.008\text{ mol}$ .



**Fig. 6.** Styrene oxidation initial reaction rates over Cr-ZSM-5 as function of substrate initial concentrations. Reaction conditions:  $T=60\text{ }^\circ\text{C}$ ; catalyst: 0.2 g Cr-ZSM-5;  $n_{acetonitrile}^0: 0.223\text{ mol}$ ;  $n_{H_2O_2}^0: 0.010\text{ mol}$ .



**Fig. 7.** Styrene oxidation initial reaction rates over Cr-ZSM-5 as function of catalyst concentrations. Reaction conditions:  $T=60\text{ }^\circ\text{C}$ ;  $n_{acetonitrile}^0: 0.223\text{ mol}$ ;  $n_{styrene}^0: 0.008\text{ mol}$ ;  $n_{H_2O_2}^0: 0.010\text{ mol}$ .

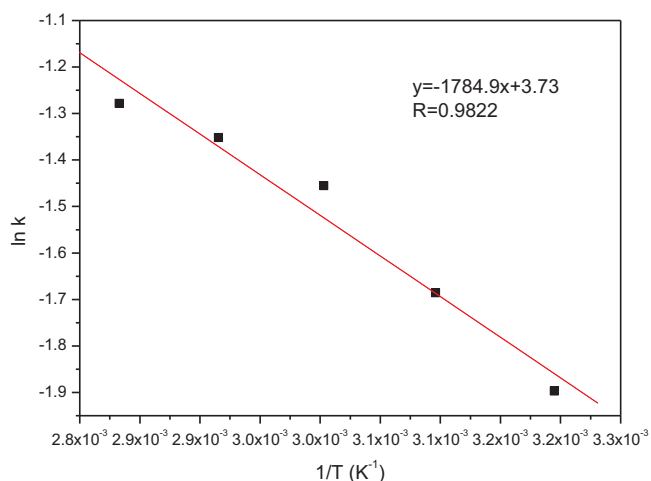


Fig. 8. Arrhenius plot of the pseudo first order rate kinetic constants of styrene oxidation over Cr-ZSM-5.

results have been fitted to the Arrhenius equation as shown in Fig. 8. The apparent activation energy obtained from the slope of the plot is 14.54 kJ/mol and the frequency factor is 41.6.

#### 4. Conclusions

The results reported in this paper allow us to select chromium zeolite as the most active of all the metal-ZSM-5 evaluated (cobalt, chromium, iron, zinc, manganese and copper) for styrene selective oxidation to benzaldehyde using hydrogen peroxide as oxidant. Other products as styrene oxide, phenylacetaldehyde, 1-phenyl, 1,2-ethanediol and benzoic acid were also obtained but with lower selectivities.

Best results under evaluated conditions were obtained using a 0.45 substrate/oxidant molar ratio and acetonitrile as solvent, because of its aprotic and highest polar character of all the evaluated solvents. The reaction temperature enhancement produced an

increase on styrene conversion, showing a deceleration over 60 °C because of the competitive H<sub>2</sub>O<sub>2</sub> thermal decomposition.

The reaction rate is first order with respect to styrene and oxidant concentration. The apparent activation energy obtained is 14.54 kJ/mol.

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