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Effect of solvents on propylene epoxidation over TS-1 catalyst

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Abstract Solvents have an important effect on the epoxidation of propylene catalyzed by TS-1. The experimental results show that, in different solvents, the catalytic activity of epoxidation is in the following order: methanol > 2-propanol > 2-butanol > acetonitrile > acetone > tetrahydrofuran. Based on the reaction mechanism, the effects of solvents on the epoxidation were studied from eight aspects, which included the electronic effect, the steric effect, the polarity of solvent, the effect of solvent on sorption and diffusion of reactant, the oxidation of alcohol, the etherification of PO, the deactivation of TS-1 and the solubility of propylene in the solvents. The electronic effect, steric effect and the polarity of solvent were considered to be the main aspects. This work may provide theoretical guidance for choosing solvents for these kinds of reactions and also may serve as basis for further industrialization.

Keywords titanium silicalite-1 (TS-1), propylene, epoxidation, solvent effects

1 Introduction

Propylene oxide (PO) is an important chemical product with very broad applications in the industry. Nowadays, PO is produced in industry using traditional technologies including a combined chlorine-alcohol process and a co-oxidation process. The former produces a lot of pollution and the latter produces a large amount of side products. The epoxidation of propylene catalyzed by titanium

silicalite-1 (TS-1) using H_2O_2 as the oxidant offers a clean and economically viable alternative to existing processes. Considering that H_2O_2 is still relatively expensive, in order to reduce the cost, it is better to integrate the production of H_2O_2 and PO [1]. In practical epoxidation processes, methanol, 2-propanol and 2-butanol are often used as solvents.

The effect of solvents on chemical reactivity has been known for over a hundred years. Most of the reports published about solvent effects focus on homogenous reaction and only a few works involve heterogeneous catalytic reactions. Solvents exert a more considerable influence on the epoxidation of propylene catalyzed by TS-1 [2–5] because alcohol solvents generally used can coordinate with the active site of a catalyst to form an intermediate. However, most research on solvent effects involves only a few factors. There is a clear lack of comprehensive understanding about the solvent effects considering the most effective factor.

This work aims to discuss the solvent effect of TS-1 catalyzed epoxidation of propylene reaction in a comprehensive manner. The considered factors include the electronic factor, steric affect, physisorption, polarity of solvent, side reaction (including oxidation of solvent and ring-opening of PO), and solubility of propylene in solvents. All these results lay the groundwork to further the industrialization of green PO production.

2 Experimental

2.1 Materials

TS-1 zeolite was synthesized according to the procedure described in Ref [6]. H_2O_2 (30 wt%), methanol, 2-propanol and 2-butanol were all analytical grade.

2.2 Epoxidation of propylene

The epoxidation of propylene was carried out in a stirred tank reactor consisting of a 120 mL stainless steel tank, an electromagnetic stirrer and a heating jacket, as shown in Fig. 1. Before the reaction, alcohol solvent, 30 wt%

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H_2O_2 and TS-1 were fed into the reactor. When the temperature rose to the required point, propylene from a steel cylinder was charged into the reactor at a certain pressure. The reaction was carried out at $T = 303.15\text{--}323.15\text{ K}$, $P = 0.1\text{--}0.6\text{ MPa}$. The variation of the temperature of the reaction system should be controlled to within 0.5 K . In order to eliminate the reactor metal's effect on propylene epoxidation and the decomposition of H_2O_2 , the reactor was passivated.

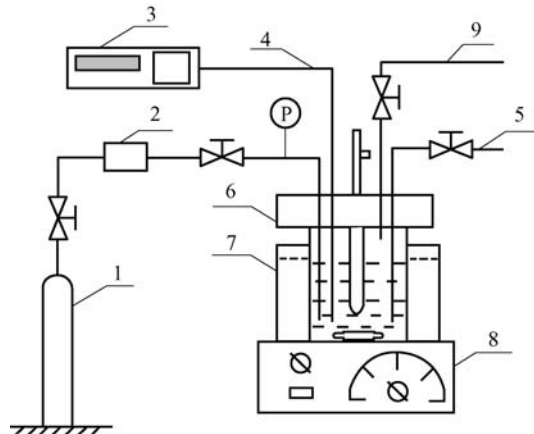


Fig. 1 Experimental apparatus and flow sheet
1. propylene cylinder; 2. pressure gauge; 3. thermometer; 4. thermocouple; 5. samples exit; 6. stainless steel reaction vessel; 7. hot water bath; 8. magnetic stirrer; 9. off gas exit

2.3 Analytical method

With MTBE as the internal standard, the products of the reaction were analyzed by a HP-4890 gas chromatograph with a column ($4\text{ m} \times 3\text{ mm}$) containing GDX-103 as the stationary phase and H_2 as carrier, at the rate of 30 mL/min . The working conditions were as follows: the temperature of the feed space was 493.15 K . The oven temperature was programmed from 428.15 K to 473.15 K , the temperature of the thermal conductivity detector and the detector space was 493.15 K . The residual H_2O_2 was measured by iodimetric titration.

3 Results and discussion

3.1 Experimental results

For the purpose of investigating the effect of solvent on the epoxidation reaction, we have selected six solvents with different properties including methanol (MeOH), 2-propanol (2-PrOH), 2-butanol (2-BuOH), acetone (MeCOMe), acetonitrile (MeCN) and tetrahydrofuran

(THF). The epoxidation reaction conditions are the same: temperature 40°C , pressure of propylene 0.45 MPa , contents of TS-1 1.1 wt\% , concentration of H_2O_2 3 wt\% . The relation between the conversion of H_2O_2 and reaction time to propylene epoxidation in different solvents is shown in Fig. 2.

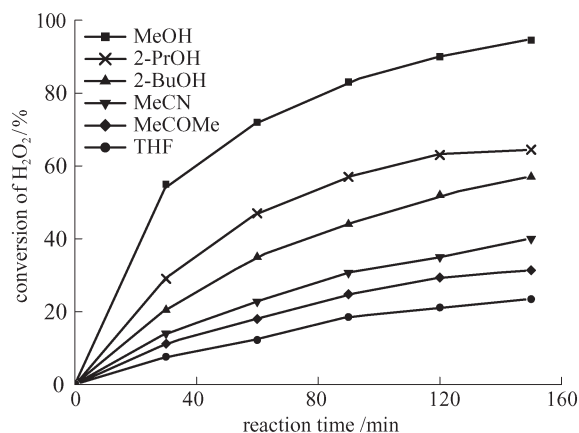


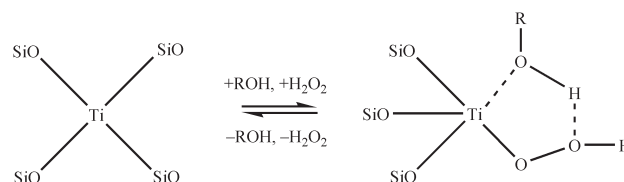
Fig. 2 Kinetics of propylene epoxidation with H_2O_2 over TS-1

Figure 2 indicates that under the same experiment condition, the order of propylene epoxidation rate is: $\text{MeOH} > 2\text{-PrOH} > 2\text{-BuOH} > \text{MeCN} > \text{MeCOMe} > \text{THF}$.

3.2 Discussion on solvent effect

3.2.1 Electronic factor in solvent effect

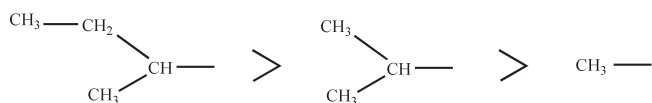
The hypothesis about mechanism of epoxidation of propylene on TS-1 proposed by Clerici is generally accepted [6]. In this hypothesis, an intermediate, Ti (OOH), is formed by reaction of H_2O_2 with the Ti site. This intermediate can be responsible for epoxidation reaction. With protic alcohol as solvent, a special five-membered ring intermediate is formed via coordination of alcohol ROH on Ti site, as shown below. The coordinated alcohol ligand enhances the stability of Ti (OOH) and also increases the electrophilicity of the distal peroxide oxygen via formation of a hydrogen bond.



Due to inductive effect, the electron cloud of oxygen atom in alcohol molecule can transfer to vacant electron site of Ti, and thus enhance electrophilicity of this oxygen. The electrophilic attack on π electron cloud of

double bond in propylene by intermediates gives rise to epoxidation of propylene. Thus, increase of electrophilicity can favor epoxidation [7,8]. Due to the lack of the proton donating group, the non-protic solvents, such as MeCN, MeCOMe and THF, can't increase stability of intermediate by formation of hydrogen bond with Ti (OOH), and hence they have lower reaction activity.

Such a mechanism would allow the prediction of the relative reactivity of epoxidation in alcohol solvents from an electronic factor. Adjacent alkyls to OH group in following three alcohols have different electron donating abilities [9] with the following order:



The higher electron donating ability of alkyls in alcohols gives rise to a higher electron density of oxygen in OH group due to the inductive effect. When coordinating with a Ti site, this oxygen atom would be expected to donate more electron density to Ti which reduces the electrophilicity of the intermediate. Consequently, the epoxidation reactivity decreases. Therefore, from the point of view of the electronic effect, the electron donating ability of alkyl in these three alcohols has a significant influence on the electrophilicity of the intermediate and hence affects the reactivity of epoxidation.

3.2.2 Steric factor in solvent effect

The pore sizes of TS-1 are 0.53 nm × 0.56 nm for the straight channel and 0.51 nm × 0.55 nm for the sinusoidal channel. The effect of the steric factor on selectivity can't be ignored. From literature [10], reactants of propylene epoxidation have no obvious diffusional limitations. The steric effect is mainly caused by the geometrical constraints of the five-membered ring intermediate inside the pores of TS-1. The larger molecular size of alcohol leads to the higher steric constraint for the formation of intermediate, hindering the propylene molecule from getting into pores and reaching the active site and eventually leads to a lower reactivity. Therefore, from the point of view of steric factors, the reaction activity increases with a decreasing size of the solvent molecule. Thus, the order of reactivity in three alcohol solvents is: methanol > 2-propanol > 2-butanol. This is consistent with experimental results.

3.2.3 Effect of solvent polarity on epoxidation

Polarity is one of the most important properties of organic solvents traditionally expressed by some physical

parameters such as dielectric constant (ϵ) and permanent dipole moment (μ). In fact, it is not a precise definition, because the interactions between the solute and solvent molecules are much more extensive and complicated: in addition to the non-specific Coulombic, directional, inductive, and dispersion interactions. There is also a specific hydrogen bond, electron pair donor (EPD)/electron pair acceptor (EPA), and solvophobic interactions. The solvent polarity as thus defined generally cannot be described quantitatively by a single physical parameter (ϵ, μ , etc.), whereas empirical parameters of solvent polarity E_T (mole transition energy) generally provide a more comprehensive understanding of the over-all solvation ability of the solvent in the microscopic region than individual physical data. So E_T is an overall manifestation of the interactions between the solvent and the solute [11]. E_T can be obtained by experimental method such as equilibrium of chemical reaction, dynamics method and spectroscopic measurement [12].

Organic solvents can be divided into two classes: protic solvents and aprotic solvents. Aprotic solvents can further be divided into polar aprotic solvents and non-polar aprotic solvents. Protic solvents are hydrogen bond donors with strong polarities, having a dielectric constant greater than 15 and E_T ranging from 47 to 63. Water, methanol, 2-propanol and 2-butanol are all protic solvents. MeCOMe and MeCN are polar aprotic solvents with a dielectric constant greater than 15 and E_T range of 40–47. This kind of solvent can't be used as a hydrogen bond donor, but can be a good electron donor. THF is non-polar aprotic solvent with a dielectric constant less than 15 and E_T from 30 to 40, which cannot be hydrogen bond donor, and only has very weak interaction with solute. The property parameters are listed in table 1.

Table 1 Some properties of organic solvents [13]

solvents	ϵ	$\mu/10^{30}\cdot\text{C}\cdot\text{m}$	n_D^{20}	pK_{auto}	$E_T/\text{kJ}\cdot\text{mol}^{-1}$
MeOH	32.66	5.67	1.3284		232.68
2-PrOH	19.92	5.54	1.3772	17.2	204.12
2-BuOH	16.56	5.54	1.3972	20.80	197.82
MeCN	35.94	11.48	1.3441		191.52
MeCOMe	20.56	9.54	1.3587	33.3	178.08
THF	7.58	5.84	1.4072	32.5	157.08

ϵ : dielectric constant at 25°C; μ : dipole moment; n_D : refractive index; pK_{auto} : autoprotolysis constant at 25°C; E_T : mole transition energy from spectroscopic measurement

Figure 2 shows that protic solvents, such as methanol, 2-propanol and 2-butanol, favors the epoxidation of propylene, whereas epoxidation reaction is slow in aprotic solvents, such as MeCN, MeCOMe and THF. From Table 1 and Fig. 2, we can find that there is no direct correlation between the propylene epoxidation and simple physical parameter of solvents (dielectric constant, dipole

moment and autoprotolysis constant) if we consider all the solvents together (protic and aprotic). But $\log r_0$ (r_0 is the initial rate of epoxidation reaction) has a linear dependence with E_T shown in Fig. 3. Therefore, propylene epoxidation is more active in the solvent with a larger E_T . This is because E_T reflects more comprehensively the over-all interaction between the solute and solvent.

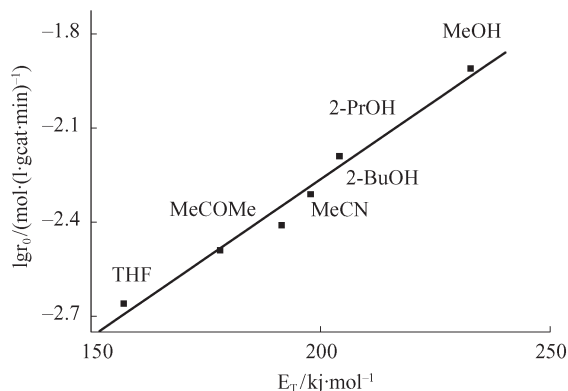


Fig. 3 Correlation between E_T and $\log r_0$ for the propylene epoxidation with H_2O_2 on TS-1

3.2.4 Physisorption and diffusion factor in solvent effect

Epoxidation of propylene on TS-1 is a heterogeneous catalytic reaction, there is a possible link between the physisorption of the reactants on TS-1 and the solvent effects in epoxidation. The partition coefficient K is defined as $K = \frac{q}{c}$, with q and c the intraporous and extraporous concentrations of the tracer, respectively [14]. As a parameter that reflects the competitive adsorption between solvent molecules and reactants molecules on TS-1, the partition coefficient shows the effect of solvent on reaction.

Langhendries [14] quantitatively studied the liquid-phase adsorption of a broad series of compounds on heterogeneous TS-1, through liquid chromatographic experimental method, and adsorption data of alkanes, alkenes, and other compounds were obtained with methanol, ethanol, 2-propanol, acetonitrile and acetone as solvents. These data indicated that, for a given adsorbent, partition coefficients decrease there is a decreasing polarity of the alcohol solvent (e.g., $K_{MeOH} > K_{2-PrOH} > K_{2-BuOH}$), which agrees with the known organophilic nature of TS-1. For a given solvent, $K_{alkane} > K_{alkene} > K_{alknol}$.

When alcohol is used as solvents, a polar network connected by hydrogen bond is formed in the outside of TS-1 pores. In this polar network, non-polar or low polar molecules are “pulled into” pores of TS-1. In epoxidation reactions with methanol, 2-propanol, and 2-butanol respectively, the order of partition coefficients of propylene is: $K_{MeOH} > K_{2-PrOH} > K_{2-BuOH}$. In this way,

for a given propylene concentration in three alcohol solvents, the intraporous propylene densities are not all the same which increases with the increasing partition coefficients. Propylene is concentrated more inside the TS-1 in a methanol solvent than in 2-propanol and 2-butanol. The higher propylene density in TS-1 pores favors an epoxidation reaction. In short, solvents have an important influence on diffusion and physisorption of reactants within pores of TS-1. Consequently, it obviously affects the reaction activity.

3.3 Other factors about solvents effect

In addition to factors above discussed, some other factors also have obvious effect on epoxidation such as reaction with solvents, deactivation of catalyst and solubility of propylene in solvents.

3.3.1 Side reaction with solvents

During the epoxidation of propylene, two kinds of reactions with alcohol solvents take place and thus some byproducts are formed. One side reaction is the oxidation of alcohol by TS-1/ H_2O_2 . Another is the ring-opening of PO under nucleophilic attack by alcohol. These side reactions increase the cost of product purification and decrease the selectivity and yield of PO. Moreover, the blocking of TS-1 pores by PO ring-opening products can cause the deactivation of TS-1. So, side reactions have an obvious negative effect on epoxidation.

The oxidation of three alcohol solvents is shown in Fig. 4. The reaction conditions are: TS-1 = 2 wt%, $T = 40^\circ C$, $H_2O_2 = 3.5$ wt%. Oxidation of 2-propanol and 2-butanol is a lot easier than methanol. 2-propanol is more easily oxidized compare to 2-butanol. The order of reactivity in oxidation is: 2-propanol > 2-butanol >> methanol. The results show that the position of OH group in the hydrocarbon chain and the chain length play an important role in oxidation of alcohol solvent. Consequently, with regards to the alcohol solvent oxidation, methanol is best one for epoxidation in comparison with 2-propanol and 2-butanol [15,16].

Ring-opening of PO with alcohol solvents is catalyzed by weak acidic Ti center, the order of activity is: methanol > isopropanol > butanol. This order is resulted from the effect of alcohol molecule on the acidity of intermediate and steric factor of alcohol in the pore of TS-1 [17].

3.3.2 Effect of solvent on deactivation

In the epoxidation of propylene catalyzed by TS-1, deactivation of catalyst is mainly caused by blockage of TS-1 channels due to by-products produced in the ring-opening of PO with alcohol solvents catalyzed by the acidity of TS-1/ H_2O_2 . The larger the alcohol molecule is, the more steric hindrance in etherification of PO on TS-1

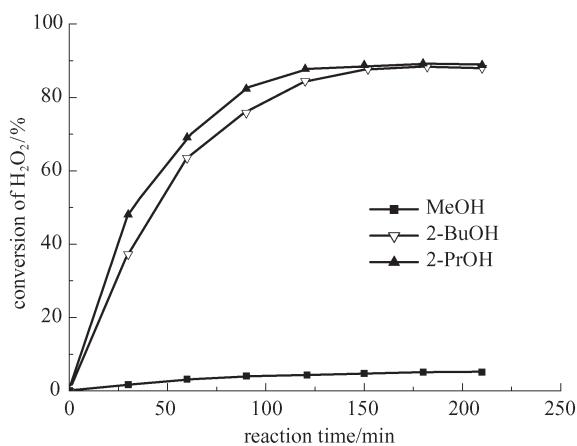


Fig. 4 Kinetics of oxidation of three alcohols with H_2O_2 on TS-1

occurs and the slower TS-1 deactivation happens. The order of catalyst life of epoxidation in the three alcohol solvents is: 2-butanol > 2-propanol > methanol [18,19].

3.3.3 The solubility of propylene in alcohol solvent

It is well known that the rate of the epoxidation reaction of propylene with H_2O_2 is significantly influenced by the gas-liquid mass transfer because it is a gas-liquid-solid three-phase reaction. A relatively high solubility of propylene in the liquid medium has a beneficial effect on the epoxidation reaction. The propylene solubility in the three alcohols is in the order of: 2-butanol > 2-propanol > methanol. Fig. 5 shows the solubility of propylene in alcohol solvents with a mass ratio of alcohol and water of 9:1, in which y -axis, i.e. x_1 , is the mass ratio concentration of propylene in solvent. The difference of solubility of propylene in the three alcohols is mainly due to the molecular properties of alcohols and the interaction between propylene and alcohol molecules [20].

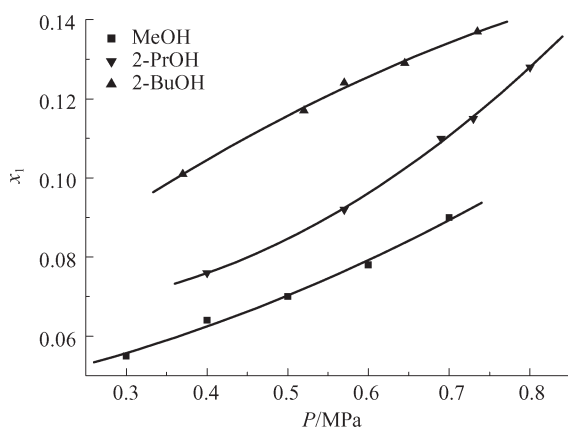


Fig. 5 Solubility of propylene in three alcohols

4 Conclusions

This work discussed in detail the various influencing factors responsible for the solvent effects on epoxidation of propylene on TS-1, including the electronic factor, steric constraints, solvent polarity, physical diffusion and partition, side reaction with solvents, deactivation of catalyst and propylene solubility in solvents. In these factors, electronic factor, solvent polarity, steric constraints, physical diffusion and partition play a major role with the rest being minor factors.

In practical processes, methanol, 2-propanol and 2-butanol are often used as the epoxidation solvents. By taking the electronic factor, steric constraints, solvent polarity, physical diffusion and partition into account, the order of activity is methanol > 2-propanol > 2-butanol. This is consistent with experimental results. Whereas from the point of view of ring-opening of PO, deactivation of catalyst and propylene solubility, the activation is in the order: 2-butanol > 2-propanol > methanol. In the end, considering oxidation of solvents, the order is: methanol > 2-butanol > 2-propanol. The final relative reactivity is the combined results of these different effects.

Different factors exert their influence in different aspects, of which electronic factors and steric factors have a more important effect on epoxidation than the other factors. The electronic factor reflects the inherent mechanism of the reaction, while steric factor determines the extent to realize the inherent mechanism. Solubility of propylene and physisorption of reactants affect epoxidation by influencing the reactant concentration in the active site of TS-1. Side reactions, including oxidation of alcohol and ring-opening of PO, influence the selectivity and yield of the main reaction. Deactivation of TS-1 relates with the sustainability of epoxidation and product cost. In short, the final choice of solvent needs a comprehensive consideration of these factors.

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