

## Oxidation of Styrene with Molecular Oxygen in Supercritical CO<sub>2</sub>

Tao JIANG , Bu Xing HAN\*, Guo Ying ZHAO , Zhong Hao LI ,  
Yan Hong CHANG , Hai Xiang GAO , Jun Chun LI

Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences,  
Beijing 100080

**Abstract:** The oxidation of styrene with molecular oxygen catalyzed by PdCl<sub>2</sub>+CuCl<sub>2</sub> has been investigated in supercritical CO<sub>2</sub> with a batch reactor. The oxidative system of styrene contains four components at the beginning and seven components during the reaction. The critical temperature, critical pressure, and critical density at different conversions are determined by using a high-pressure view cell. The effect of phase behavior on the conversion and selectivity were studied. Experimental results showed that the critical parameters of the reaction mixture at fixed initial molar ratio changed with the conversion of reactant. The conversion of styrene reached maximum near the critical density of the reaction mixture. Product selectivity also varied with density of reaction mixture and could be tuned to some degree.

**Keywords:** Styrene, supercritical fluids, carbon dioxide, wacker oxidation, molecular oxygen.

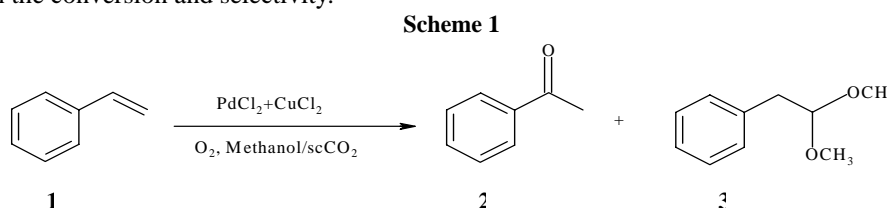
In recent years, much attention has been paid to the fundamental study and application of supercritical fluids (SCFs). In general, substances existing above its critical pressure (Pc) and temperature (Tc) are called as SCFs<sup>1-3</sup>. Among the SCFs, supercritical CO<sub>2</sub> (scCO<sub>2</sub>) has been used as a clean substitute for some toxic and volatile organic solvents because it provides mild critical conditions. In addition, CO<sub>2</sub> has many other advantages, such as non-toxic, non-corrosive, non-flammable and easy to separate with reactants and products. The application of scCO<sub>2</sub> in chemical reactions has played a significant role in enhancing conversion and improving selectivity<sup>4,5</sup>. The reaction rates and selectivity can be tuned by changing temperature and pressure.

The Wacker reaction is an important method for the functionalization of alkenes, which is usually employed in the production of aldehydes and ketones. It is well known that methyl ketone has numerous utilities. Therefore, oxidation of olefins has been studied by several groups<sup>6-11</sup>. The process is normally achieved over a Pd( ) or Cu( ) catalyst using molecular oxygen (O<sub>2</sub>) or excess hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as oxidizing agents. The Pd catalyzed Wacker oxidation of terminal olefins occupies a prominent position. From the economic and environmental points of view, the selective oxidation of organic chemicals with molecular oxygen as oxidant is beneficial and will continue to be a realm of great potential<sup>12</sup>.

---

\* E-mail: Hanbx@iccas.ac.cn

The oxidation of styrene with molecular oxygen catalyzed by PdCl<sub>2</sub>/CuCl<sub>2</sub> in supercritical CO<sub>2</sub> was studied in this work (**Scheme 1**). The phase behavior of this reaction system was first investigated in a high-pressure view cell<sup>13</sup>. Oxidative reaction of styrene was then conducted to get insight into the effects of phase behavior on the conversion and selectivity.



O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> were supplied by Beijing Analytical Instrumental Factory, and the purities were 99.95%, 99.999% and 99.95%, respectively. Methanol with a purity of 99.5% was produced by Beijing Chemical Plant. Styrene was first washed with 10% NaOH solution then with distilled water, and finally distilled under reduced pressure. Other reagents were used as received. The apparatus for determining the phase behavior of oxidative system of styrene is described elsewhere<sup>13</sup>. It consists of a constant temperature water bath, a high-pressure view cell, a temperature controller (Haake D8, accuracy  $\pm 0.05$  K), a pressure transducer (accuracy  $\pm 0.01$  MPa), and a magnetic stirrer. The view cell has a piston, which can be moved up and down by a screw to change the volume of the cell.

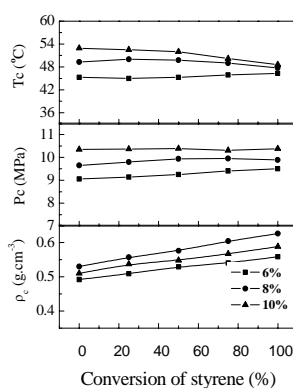
In this study, methanol is used as a cosolvent. The main products of the reaction are methyl phenyl ketone and phenylacetaldehyde dimethyl acetal (**2** and **3**). Therefore, at the start of the reaction, there are four components in the system, CO<sub>2</sub>, O<sub>2</sub>, methanol, and styrene, and the reaction system contains seven components during the reaction, *i.e.* CO<sub>2</sub>, O<sub>2</sub>, methanol, styrene, water, **2** and **3**. To avoid reactions, catalysts were not introduced in the system and N<sub>2</sub> was used to replace O<sub>2</sub><sup>14</sup> during the determination of phase behavior of reaction mixture. The method for determining the critical properties of reaction mixture was also described previously<sup>13</sup>.

The oxidation of styrene with molecular oxygen in scCO<sub>2</sub> was carried out in a batch stainless steel reactor (12.1 mL) equipped with a magnetic stirrer. In the experiment, the air in the reactor was replaced with CO<sub>2</sub>. Methanol, styrene, and catalysts were loaded into the reactor. O<sub>2</sub> and CO<sub>2</sub> were then charged. Then the reactor was heated to 55°C under stirring. After a suitable reaction time, the reactor was cooled in an ice bath, and the gases were released slowly. The experiments indicated that the liquid substances entrained by the gases were negligible. The liquid sample was analyzed by GC.

It is known that the critical temperature and critical pressure of a multi-component system is a function of its composition. The composition of the system at a fixed initial reactant concentration can easily be calculated from the conversion. The critical parameters and phase behavior at a selected conversion can be determined by preparing the mixture with pure chemicals. In this work, the critical parameters of the reaction system are determined by simulating the composition of the reaction system in the absence of catalysts because it is very important to avoid reactions in this process. The

molar ratio of methanol: styrene: N<sub>2</sub> was 3: 1: 1 and the total molar concentration of the three components in the mixture is 6%, 8% and 10% respectively. The dependence of the critical temperature, critical pressure, and critical density of the system on the conversion of styrene is given in **Figure 1**. It can be seen that the critical density increases with increasing styrene conversion at all the initial reactant concentrations. The critical temperature and pressure change a little with conversion of styrene in the conversion range studied. But the critical temperature, critical pressure, and critical density increase with increasing the reactant concentration.

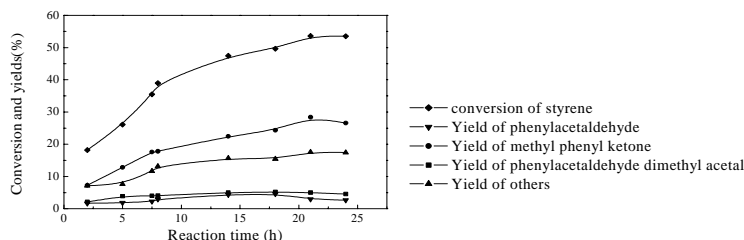
**Figure 1** Critical properties of reaction mixture at different initial content of reactants



Results in **Figure 1** allow us to choose suitable conditions to conduct the reaction occurring in two-phase or homogeneous regions. At the critical temperature of the mixture, there exist two phases in the system when the pressure is lower than the critical pressure, and becomes one phase at higher pressures. The density is “apparent” when two phases exist in the system because the density and the composition of the two phases are different.

The reaction experiments are conducted at the initial molar ratio CO<sub>2</sub>: methanol: styrene: O<sub>2</sub>=92: 4.8: 1.6: 1.6, and the temperature is slightly above the critical temperature of the system (55°C). The apparent density of the system varied from much less than critical density to higher than critical density.

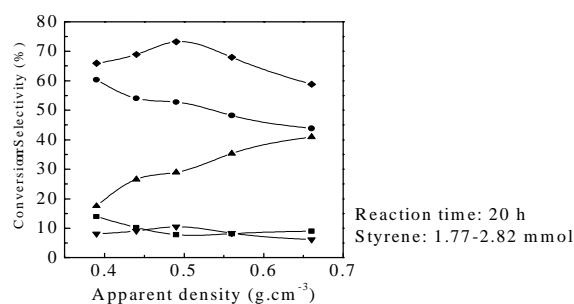
**Figure 2** Dependence of conversion of styrene on reaction time (Styrene, 2.65 mmol)



Reaction temperature 55°C; Initial content of reaction mixture 8 mol%; Methanol: styrene: O<sub>2</sub>=3:1:1; PdCl<sub>2</sub>: styrene=3 mol%; CuCl<sub>2</sub>: PdCl<sub>2</sub>=13:1.

**Figure 2** shows the effect of reaction time on styrene conversion and product yields at an apparent density of  $0.60 \text{ g cm}^{-3}$ . It can be seen that the conversion of styrene and the yields of products increase with reaction time and remain constant after about 20 hrs. The highest conversion of styrene was higher than 50% and the yield of methyl phenyl ketone was about 25%.

**Figure 3** Effect of apparent density of reaction mixture on the oxidation of styrene



**Figure 3** illustrates the dependence of conversion of styrene and yields on the apparent density of the reaction mixture. The styrene conversion reaches maximum near the critical density, as is shown in the figure. The selectivity also changes with the variation of the apparent density. It is obvious that the conversion and selectivity can be tuned by varying the apparent density. In other words, the yields of products can be tuned to a certain degree by varying the apparent density.

### Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (20073056).

### References

1. P. E. Savage, S. Gopalan, T. L. Mizan, *et al.*, *AIChE J.*, **1995**, *41* (7), 1723.
2. P. G. Jessop, W. Leitner, *Chemical Synthesis Using Supercritical Fluids*, Weinheim, Wiley-VCH, **1999**.
3. S. L. Wells, J. DeSimone, *Angew. Chem. Int. Ed.*, **2001**, *40*, 518.
4. N. S. Isaacs, N. Keating, *J. Chem. Soc., Chem. Commun.*, **1992**, 876.
5. G. Musie, M. Wei, B. Subramaniam, *et al.*, *Coord. Chem. Rev.*, **2001**, *219-212*, 789.
6. E. Monflier, E. Blouet, Y. Barbaux, *et al.*, *Angew. Chem. Int. Ed. Engl.*, **1994**, *33*, 2100.
7. H. Pellissier, P. Y. Michellys, M. Santelli, *Tetrahedron Lett.*, **1994**, *35*, 6481.
8. T. Money, M. K. C. Wong, *Tetrahedron*, **1996**, 6307.
9. G. Barak, Y. Sasson, *J. Chem. Soc., Chem. Commun.*, **1987**, 1266.
10. H. Ito, T. Kusakawa, M. Fujita, *Chem. Lett.*, **2000**, 598.
11. H. Jiang, L. Lia, J. Li, *Green Chem.*, **2000**, *2*, 161.
12. A. Hewmann, B. Akermark, *Angew. Chem. Int. Ed. Engl.*, **1986**, *23*, 453.
13. H. F. Zhang, Z. M. Liu, B. X. Han, *J. of Supercritical Fluids*, **2000**, *18*, 185.
14. Z. S. Hou, B. X. Han, L. Gao, *et al.*, *Green Chem.*, **2002**, *4* (5), 426.

Received 12 March, 2003