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Oxidation of *n*-Butanol and 2-Pentanol with Molecular Oxygen in Supercritical CO_2

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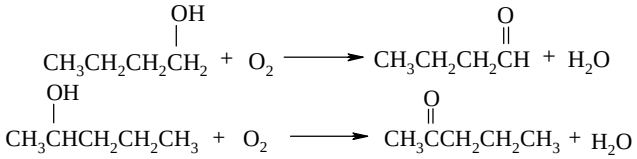
Abstract: Oxidation of *n*-butanol and 2-pentanol using molecular oxygen in supercritical (SC) CO_2 with and without co-solvent is investigated. The results showed that the reaction selectivity is high when the reaction is carried out in SC CO_2. It has been observed that co-solvent affects conversion and selectivity of the reaction considerably.

Keywords: Oxidation, *n*-butanol, 2-pentanol, supercritical CO_2, co-solvent.

The oxidation of primary and secondary alcohols, especially partial oxidation into aldehydes and ketones is a ubiquitous transformation in organic chemistry[1]. Utilizing molecular oxygen as oxidant is a more attractive route from both economic and environmental points of view. In recent years, increasing number of chemists has begun to study chemistry reaction in SC CO_2[2]. Copper-based catalyst is regarded as one of the most efficient catalysts as it can oxidize a wide range of alcohols into the corresponding aldehydes and ketones under mild condition and is cheaper[3]. Unfortunately, the aerobic catalytic oxidation of alcohols usually utilizes organic solvents, which may hinder practical applications. In this paper, using copper chloride/ phenanthroline catalytic system, we study the oxidation of *n*-butanol and 2-pentanol in SC CO_2 with and without co-solvent, and the reaction in liquid fluorobenzene was also studied for comparison. The reactions are shown in **Scheme 1**.

Scheme 1



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CO_2 was supplied by Beijing Analytical Instrument Factory with a purity of 99.995%. *n*-Butanol and 2-pentanol, fluorobenzene, CuCl, K_2CO_3, diethylazodicarboxylate and 1, 10-phenanthroline were A.R. grade and produced by Beijing Chemical Plant. All the chemicals were used without further purification. For all the experiments the molar ratio of CO_2:O_2: alcohol was 94:2:4, and that of alcohol: CuCl: diethylazodicarboxylate: phenanthroline: K_2CO_3 is 100:5:5:5:5. A batch reactor was used, which was equipped with the electric heating and magnetic stirrer and its inner volume was 12.74 mL. The products were analyzed by GC (Agilent 4890D, Agilent Technologies Inc.) with a FID detector.

The results of the reaction at different conditions are listed in **Table 1**. The reaction rate of the reactions in the organic solvent is larger than that in SC CO_2, as is shown in **Table 1**. However, the selectivity of desired products, *n*-butyraldehyde and 2-pentanone, in SC CO_2 is much higher. The main reason is that the diffusivity of SC CO_2 is higher than that of the organic solvent. Therefore, they can escape from the catalyst surface more easily, which avoids further oxidation of the products. The other reason may be that the reactants have stronger polar group –OH. Their polarity is stronger than the products. Thus, CO_2 has more significant effect on adsorption of the products at the catalyst surface, which also reduces the degree of further oxidation of the products. The conversion of alcohols decreases with increasing the pressure of SC CO_2 although the selectivity is still high. We think the reason is that high pressure CO_2 affects the adsorption of reactant on the surface of the catalyst.

The data in **Table 1** also illustrate that the conversion of alcohols in SC CO_2 is improved considerably by adding small amount of co-solvent (fluorobenzene) and the selectivity for the desired products is still very high. Study on the mechanism is a very interesting topic. It is reported that in a SC solution the concentration of the co-solvent around the solute can be much higher than that in the bulk [4], which is often referred to as "clustering". The clustering between the co-solvent and the reactants or products may be the main reason for the significant improvement of the reaction rate.

In conclusion, it is advantageous to carry out the oxidation reaction in SC CO_2 with copper-based catalyst.

Table 1 Effect of different solvents on conversion and selectivity at 333 K after reaction of 6 hrs

	Solvent	Alcohol Conversion (%)	Desired product Selectivity (%)
n-butanol	Fluorobenzene	15.3	71.0
	SC CO_2 (14.8MPa)	4.72	89.5
	SC CO_2 (13.5 MPa)	5.02	87.1
	SC CO_2+ Fluorobenzene [a]	10.3	86.3
2-pentanol	Fluorobenzene	7.37	62.2
	SC CO_2 (14.8MPa)	1.04	94.3
	SC CO_2 (13.5 MPa)	1.86	89.2
	SC CO_2+ Fluorobenzene [a]	5.86	92.1

a. P_{CO2} = 13.5MPa , the amount of co-solvent in CO_2 is 0.5 mol%.

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