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The Oxidation of Cyclohexene with Polymer Supported Co(II) in Supercritical Carbon Dioxide

Jun LIU, Rui ZHANG, Liang GAO, Tao JIANG, Zhi Min LIU, Jun HE, Bu Xing HAN*, Guan Ying YANG

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

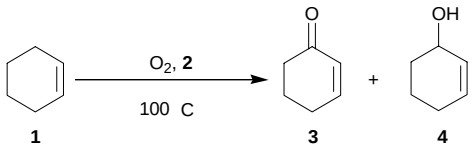
Abstract: The cyclohexene **1** was oxidized with polymer-supported 2.2'-bipyridine cobalt(II) complex in the presence of CO_2. The conversion and selectivity was sensitive to the pressure of CO_2.

Keywords: Oxidation, cyclohexene, polymer-supported, carbon dioxide.

It is known that a small change in the pressure near critical point of a fluid causes a significant change in density-dependent properties, such as the solubility parameter, viscosity, and dielectric constant[1]. Recently, there has been a growing interest in using supercritical fluids (SCFs) as reaction media[2, 3].

Homogeneous catalysts are capable of high specific activity and selectivity. But their removal from the reaction mixtures is difficult[4]. The application of reusable polymer-bond analogues of homogeneous catalysts is an interesting example of green chemistry[5]. In this work we study the oxidation of cyclohexene **1** with polymer-supported 2.2'-bipyridine cobalt(II) complex (PSBPy-Co, **2**) as catalyst in SC CO_2 (**Scheme 1**).

Scheme 1



CO_2 with a purity of 99.95% was supplied by Beijing Analytical Instrument Factory. Cyclohexene (A. R. Grade) was supplied by Beijing Chemical Factory and distilled before use. The PSBPy was prepared using the method reported by Card *et al.*[6]. And the complexation of Co(II) with PSBPy was based on the procedure of Lei *et al.*[7].

The oxidation was carried out in a 12 mL stainless steel reactor. **1** (12 mmol) and **2** (10 mg) was added into the reactor. The reactor was sealed and 12mmol O_2 was added. The reactor was then heated to 100°C in an oil bath and stirred with a magnetic stirrer.

CO_2 was added with a high-pressure pump. After 5 h, the reactor was cooled to room temperature. The reaction mixture was analyzed on HP 4890 gas chromatography.

Table 1 lists the conversion of **1** and selectivity to 2-cyclohex-1-ol **3** and 2-cyclohex-1-one **4**. It can be seen from **Table 1** that the conversion of **1** increases when CO_2 is added (entry 1 and 2). This may be the result of the increase of solubility of O_2 in the liquid substrate. However, as the pressure of CO_2 increase further, the conversion decreases rapidly. This may be ascribed to the inert gas effect of CO_2. The CO_2 molecule will block off the contact of catalyst with O_2 and substrate.

Phase behavior calculation using Peng-Robinson equation[8] shows that the **1**/O_2/CO_2 ternary mixture is in two phase region at pressures lower than 16 MPa, and becomes a single phase at higher pressures. In the two-phase region the selectivity to **3** and **4** decreases with the addition of CO_2, and then increase in the single-phase region. The most interesting is that with the addition of CO_2 the ratio of S_3 to S_4 shows a maximum in the phase-separate point. The detail mechanism of the effect of CO_2 on the oxidation of **1** needs further investigation.

Table 1 Conversion and selectivity at different conditions[a]

Entry	Conv[b] / %	P[c] / MPa	Added CO_2[d]/ mmol	S_3[e] / %	S_4[f] / %	S_3 / S_4
1	60.5	3	0	53.5	20.9	2.56
2	65.8	10	45	50.8	18.8	2.70
3	59.2	12	55	50.2	16.8	2.99
4	45.5	15	78	49.3	11.1	4.44
5	31.6	17	97	48.5	9.9	4.90
6	15.8	19	106	47.8	14.8	3.23
7	11.6	20	117	55.1	20.6	2.67

[a], 12 mmol **1**, 10 mg **2,** 12 mmol O_2, reaction temperature and time:100°C, 5 h. [b], Conversion of **1**. [c], Initial total pressure. [d], The amount of CO_2. [e], The selectivity to **3**. [f], The selectivity to **4**.

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