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Critical Properties of the Reacting Mixture in the Selective Oxidation of Cyclohexane by Oxygen in the Presence of Carbon Dioxide

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The critical properties of binary mixture (cyclohexane + carbon dioxide) involved in the selective oxidation of cyclohexane by oxygen in the presence of carbon dioxide were measured using a high-pressure viewing cell with visual observation. Moreover, the critical properties of the nominal reacting mixture (cyclohexane + nitrogen + carbon dioxide + cyclohexanol + cyclohexanone + water, where nitrogen is regarded as the homomorphous stand-in for oxygen) were also determined with the composition representing the extent of reaction (conversion of cyclohexane) with the initial mole ratio of cyclohexane to oxygen being 1:1 and 2:1 and the mole fraction of carbon dioxide being 0.5, 0.6, and 0.7, respectively. The results indicated that the critical properties of the reacting mixture depend on the extent of reaction as well as the initial composition, and the addition of proper solvent is an effective way to tune the critical properties of the reacting mixture. Such information is essential for determining the reaction conditions when one intends to carry out the selective oxidation of cyclohexane by oxygen under supercritical conditions and/or using carbon dioxide as a solvent, which could be an interesting option to enhance the reaction rate, improve the selectivity, and prolong the catalyst lifetime compared with current processes in the gas or liquid phase.

1. Introduction

The selective oxidation of cyclohexane to cyclohexanol and cyclohexanone is of considerable importance in the chemical industry for producing nylon-6 polymers. Most of the current processes still use "sacrificial" oxidants such as nitric acid, hydrogen peroxide, and alkyl hydroperoxides, which may have low energy efficiency and selectivity as well as generate environmentally hazardous wastes and byproducts. Oxidation using molecular oxygen is very attractive because it is inexpensive, readily available, and environmentally benign.[1,2] Co, Mn, and Fe containing aluminophosphate molecular sieves proved to be effective catalysts for the alkane oxidation with molecular oxygen.[3,4] However, the relatively high amounts of unwanted byproducts such as hexanoic acid and valeric acid due to the overoxidation in the conventional two-phase process is still an urgent problem to resolve.

Supercritical fluid (SCF) technology has been developing since the 1980s in the chemical industry. Performing reactions under supercritical conditions rather than in the gas or liquid phase could be an interesting option for improving the equilibrium conversion, enhancing the reaction rate, increasing throughput, prolonging the catalyst lifetime, and making the process more environmentally benign.[5−7] Moreover, environmentally undesirable solvents and byproducts may be avoided and the yield of desired products may be improved through the addition of proper SCF media.[8−10] Several articles have been published on the oxidation of cyclohexane in the presence of compressed carbon dioxide,[11−15] which indicate that it is advantageous to conduct the reaction in supercritical carbon dioxide, one reason being that there are fewer byproducts of the reaction in compressed carbon dioxide. The reaction products can be made to condense by manipulating the phase behavior circumventing unnecessary side reactions, and the reaction rates and conversions can thus be manipulated by adjusting the operating conditions of temperature and pressure and feed composition near the mixture critical point. The reaction behavior is often very sensitive to the reaction conditions; the operation in the regions near the critical point was most desirable to make the most of the unique characteristics of supercritical fluid. Because the composition and the critical properties of the reacting mixture always change along with the extent of reaction,[9,16] it is essential to be cognizant of the critical properties of the reacting mixture along with the reaction course.

The actual reacting mixture of cyclohexane oxidation in the presence of carbon dioxide consists of three components initially and at least six during the course of the reaction when products are formed (i.e., cyclohexane, oxygen, carbon dioxide, cyclohexanol, cyclohexanone, and water). For the purpose of determining phase behavior, nitrogen is normally regarded as the homomorphous stand-in for oxygen to avoid oxidation during the measurement because the physical properties of nitrogen are most similar to those of oxygen and its concentration in the reacting mixture is low (10% to 25%). Calculations with the Peng−Robinson equation of state indicated that the difference in phase behavior between carbon dioxide + cyclohexane + nitrogen and carbon dioxide + cyclohexane + oxygen is not considerable.[13,15]

The critical properties of the reacting mixture depend on the original composition, the conversion, and the products selectivity. However, the reaction conditions are usually determined by the critical properties of the initial

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reacting mixture and sometimes even by the critical properties of one pure substance in the reactants. Ignorance of the change in the critical properties in a reacting system can cause a misinterpretation of the solvent effect. Although much work has focused on the critical properties of the related mixtures,[17−21] the experimental data for ternary and more complex mixtures are scarce. Shibata and Sandler[19] carried out an investigation on the high-pressure vapor−liquid equilibria of mixtures of nitrogen, carbon dioxide, and cyclohexane; Mukhopadhyay and Srinivas[20] reported the muticomponent solubility of reactants and products of cyclohexane oxidation in supercritical carbon dioxide. On the basis of that, the phase envelope of the ternary system nitrogen + carbon dioxide + cyclohexane and the influence of the thermodynamic state on the reaction kinetics was examined.[13] Recently, the phase equilibrium of the reaction system was determined, and the oxidation of cyclohexane in compressed carbon dioxide and other liquid solvents using oxygen as the oxidant was conducted,[15] which proved the advantage of the reaction in supercritical carbon dioxide and the importance of a cosolvent. However, a systematical study of the critical properties of the reacting mixture for cyclohexane oxidation by oxygen in carbon dioxide along the reaction course is still imperative, which will be of benefit to the determination of the phase behaviors of the reacting mixture and the operating parameters for the reaction under supercritical conditions as well as to the understanding of the inherent effects of supercritical solvent on the reaction thermodynamics and kinetics.

In this work, the critical properties of the binary mixture (cyclohexane + carbon dioxide) involved in the selective oxidation of cyclohexane with oxygen in the presence of carbon dioxide were measured using a high-pressure viewing cell with visual observation. Moreover, the critical properties of the nominal reacting mixture (cyclohexane + nitrogen + carbon dioxide + cyclohexanol + cyclohexanone + water, where nitrogen is regarded as the homomorphous stand-in for oxygen) were also determined with the composition representing the extent of reaction (conversion of cyclohexane) with the initial mole ratio of cyclohexane to oxygen being 1:1 and 2:1 and the mole fraction of carbon dioxide being 0.5, 0.6, and 0.7, respectively. The determination of the operating conditions for cyclohexane oxidation with molecular oxygen in the presence of carbon dioxide was hereby discussed, and the solvent effects of carbon dioxide on the reaction were clarified.

2. Experimental Section

Cyclohexane (>99.5 mass %), cyclohexanol (>99.6 mass %), and cyclohexanone (>99.5 mass %) were purchased from Beijing Chemical Corporation. Deionized water was supplied by Taiyuan Chemical Corporation. Carbon dioxide (>99.95 mol %) from the Beijing Analytical Instrument Corporation and nitrogen (>99.99 mol %) from Shanxi-Yihong Corporation of Gas Reagents were used without further treatment. All of the liquid reagents were further purified by distillation. The purity of all chemicals was checked by gas chromatography and proved to be >99.5 mol %.

For the selective oxidation of cyclohexane in the presence of carbon dioxide, only small amounts of byproducts are observed,[4,12,15] so they are neglected in the study of phase equilibrium. Moreover, the selectivity for cyclohexanone is analogous to that for cyclohexanol and the critical properties of the two products are also very close (cyclohexanone, 392 °C, 4.6 MPa; cyclohexanol, 376.9 °C, 4.26 MPa),[22,23] so the following reaction scheme is assumed to prepare the nominal reacting mixture for measuring the critical properties:

Table 1. Critical Properties of the Pure Substances

	t_c/°C		P_c/MPa		ρ_c/g·cm^{-3}	
substance	this work	lit[24,25]	this work	lit[24,25]	this work	lit[24,25]
carbon dioxide	31.8	30.9	7.38	7.38	0.473	0.469
cyclohexane	283.2	280.6	4.20	4.08	0.280	0.273

Table 2. Critical Properties of the Binary Mixture Cyclohexane (1) + Carbon Dioxide (2)

x_2	t_c/°C	P_c/MPa	x_2	t_c/°C	P_c/MPa
0	283.2	4.20	0.704	188.6	13.64
0.177	269.8	6.02	0.792	161.3	14.17
0.311	256.2	7.73	0.899	103.3	12.77
0.402	245.6	8.86	1	31.8	7.38
0.558	219.5	11.50			

$$2C_6H_{12} + \frac{3}{2}O_2 \rightarrow C_6H_{12}O + C_6H_{10}O + H_2O$$

The composition of the nominal reacting mixture was then determined according to the initial reactants constituents (cyclohexane, oxygen/nitrogen, carbon dioxide) and the extent of reaction (conversion of cyclohexane).

The critical properties of the mixtures were measured with the same view cell and procedures as described previously.[9,16] Briefly, the preevacuated cell was charged with a known mass of a liquid mixture based on the composition of the nominal reacting mixture, and then the cell was pressurized with carbon dioxide and nitrogen through a sampling tube. The amount of the mixture in the cell was controlled in such a way that the density of the mixture should be close to or slightly higher than its critical density. The temperature and pressure readings were made by the occurrence of strong red-glow critical opalescence and the reappearance of a meniscus on slow cooling through the critical point. The critical properties of the nominal reacting mixture remained stable during the period of measurement, which indicated that the change in composition due to the reactions during the measurement is negligible. The uncertainties of the critical temperature, critical pressure, and mole fraction were estimated to be within ±0.3 K, ±0.03 MPa, and ±0.003, respectively.

Results and Discussion

3.1. Pure Substances. As shown in Table 1, a comparison of the critical properties of pure cyclohexane and carbon dioxide measured in this work with those in the literature proved that the agreement of critical temperatures and pressures was satisfactory.[24,25] The difference between our measured density and the literature values indicated that the critical temperature and pressure could be obtained within the required uncertainty using a relatively wide range of density of the mixture provided that it was higher than the critical density. The measured critical density is the fluid density at which the critical properties were obtained; therefore, it is not very accurate (usually a little higher than the real value). Nevertheless, it was not addressed in the current work.

3.2. Binary Mixture. The critical properties of the binary mixture cyclohexane (1) + carbon dioxide (2) are listed in Table 2. Figure 1 also shows that the critical lines are continuous over the whole composition range between

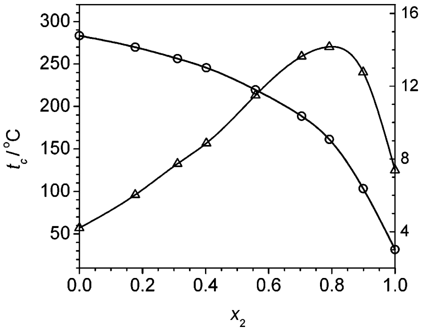

Figure 1. Critical properties of the binary mixture cyclohexane (1) + carbon dioxide (2): ○, critical temperatures; Δ, critical pressures.

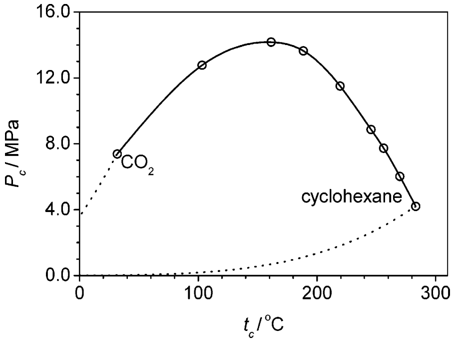

Figure 2. Projection of the critical pressure vs the critical temperature for the binary mixture of cyclohexane (1) + carbon dioxide (2): ○, critical points in this work; ···, the vapor pressure of each pure component below the critical temperature.[24]

the critical points of the two pure components; the critical temperature decreases monotonically with the mole fraction of carbon dioxide (x_2), whereas the critical pressure passes through a maximum at $x_2 \approx 0.79$. The critical point locus in the $P-T$ projection is shown in Figure 2, which should belong to type I fluid phase behavior according to the classification of van Konynenburg and Scott.[26]

The critical temperature of the binary mixture decreases with increasing carbon dioxide content, which indicates that the addition of carbon dioxide is an effective way to reduce the critical temperature of the reacting mixture. However, the critical pressure greatly increases with the addition of carbon dioxide, shows a maximum at $x_2 \approx 0.79$, and then decreases with further increases of x_2, which suggests that the content of carbon dioxide x_2 in the vicinity of 0.79 should be avoided when high critical pressure is not anticipated.

3.3. Critical Properties of the Nominal Reacting Mixture. For the oxidation of cyclohexane in the presence of carbon dioxide, the consumption of cyclohexane and oxygen during the reaction will produce cyclohexanol, cyclohexanone, and water; the composition of the reacting mixture depends on the extent of reaction (conversion of cyclohexane or oxygen) as well as the initial ratio of cyclohexane to oxygen and the content of carbon dioxide. To clarify the variance of critical properties of the reacting mixture with the extent of reaction and the content of carbon dioxide, the critical properties of the hexahydroxy mixture (nominal reacting mixture with carbon dioxide as an additional solvent and nitrogen as the homomorph of oxygen) of cyclohexane (1) + nitrogen (2) + carbon dioxide (3) + cyclohexanol (4) + cyclohexanone (5) + water (6) were determined with the composition representing the extent of reaction (conversion of cyclohexane) with the initial mole ratio of cyclohexane to oxygen (x_1/x_2) being 1:1 and 2:1 and the mole fraction of carbon dioxide (x_3) being 0.5, 0.6, and 0.7, respectively, as shown in Table 3.

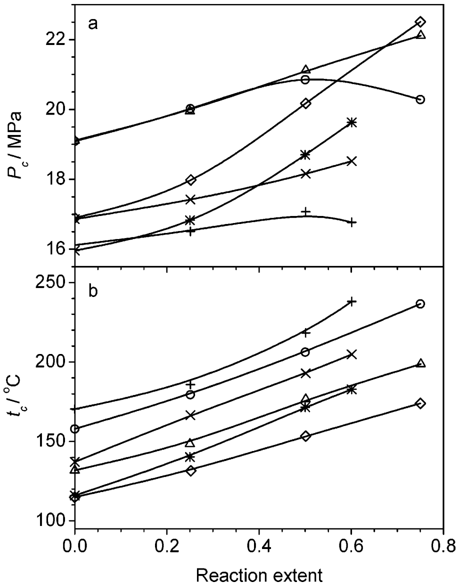

Figure 3. (a) Critical pressure and (b) critical temperature of the nominal reacting mixture (cyclohexane (1) + nitrogen (2) + carbon dioxide (3) + cyclohexanol (4) + cyclohexanone (5) + water(6)) along the reaction course of cyclohexane oxidation in the presence of carbon dioxide with the initial mole fraction $x_1/x_2 = 1$ (x_3 = ○, 0.5; Δ, 0.6; ◇, 0.7) and $x_1/x_2 = 2$ (x_3 = +, 0.5; ×, 0.6; *, 0.7).

Table 3. Critical Properties of the Nominal Reacting Mixture (Cyclohexane (1) + Nitrogen (2) + Carbon Dioxide (3) + Cyclohexanol (4) + Cyclohexanone (5) + Water (6)) along the Reaction Course of Cyclohexane Oxidation in the Presence of Carbon Dioxide

extent of reaction	x_1	x_2	x_3	x_4	x_5	x_6	t_c/°C	P_c/MPa
Initial Mole Fraction $x_1/x_2 \approx 1$ and $x_3 \approx 0.5$								
0	0.252	0.226	0.522	0	0	0	157.8	19.09
0.251	0.188	0.209	0.508	0.032	0.031	0.031	179.4	20.02
0.500	0.127	0.160	0.522	0.065	0.063	0.064	206.2	20.85
0.750	0.064	0.129	0.518	0.096	0.096	0.097	236.6	20.28
Initial Mole Fraction $x_1/x_2 \approx 1$ and $x_3 \approx 0.6$								
0	0.200	0.198	0.602	0	0	0	131.8	19.11
0.250	0.151	0.162	0.611	0.026	0.024	0.025	148.4	19.95
0.501	0.102	0.111	0.632	0.052	0.051	0.052	176.5	21.12
0.751	0.052	0.094	0.618	0.079	0.078	0.079	198.7	22.11
Initial Mole Fraction $x_1/x_2 \approx 1$ and $x_3 \approx 0.7$								
0	0.151	0.152	0.696	0	0	0	114.8	16.90
0.252	0.110	0.125	0.708	0.019	0.019	0.019	131.5	17.98
0.501	0.075	0.101	0.710	0.038	0.038	0.038	153.3	20.17
0.750	0.039	0.069	0.716	0.059	0.058	0.059	173.9	22.51
Initial Mole Fraction $x_1/x_2 \approx 2$ and $x_3 \approx 0.5$								
0	0.339	0.155	0.506	0	0	0	170.3	16.12
0.251	0.248	0.099	0.529	0.042	0.041	0.041	185.8	16.51
0.501	0.171	0.054	0.517	0.087	0.086	0.085	218.3	17.07
0.601	0.145	0.020	0.508	0.109	0.109	0.108	238.1	16.77
Initial Mole Fraction $x_1/x_2 \approx 2$ and $x_3 \approx 0.6$								
0	0.254	0.135	0.611	0	0	0	137.1	16.86
0.251	0.205	0.085	0.608	0.034	0.034	0.034	166.5	17.42
0.501	0.134	0.030	0.634	0.067	0.067	0.068	192.9	18.16
0.601	0.110	0.012	0.629	0.083	0.083	0.083	204.8	18.52
Initial Mole Fraction $x_1/x_2 \approx 2$ and $x_3 \approx 0.7$								
0	0.200	0.112	0.688	0	0	0	114.9	15.96
0.250	0.149	0.060	0.716	0.025	0.025	0.026	140.2	16.83
0.500	0.099	0.029	0.721	0.050	0.050	0.051	171.5	18.70
0.601	0.082	0.009	0.723	0.062	0.062	0.062	182.8	19.63

The critical properties of the reacting mixture change with the extent of reaction, as shown in Figure 3. With the reaction proceeding to higher conversion, the critical temperature increases significantly because all of the products have higher critical temperatures than the reactants. Moreover, the critical temperature increases with the initial ratio of cyclohexane to nitrogen but decreases with the increase of carbon dioxide content, which proves that the addition of carbon dioxide and the adjustment of the ratio of alkane to oxygen are effective measures to regulate the critical temperature of the reacting mixture.

In general, the critical pressure of the reacting mixture shows a slight increase with the extent of reaction (Figure 3). The critical pressure increases with the decrease of the initial ratio of cyclohexane to nitrogen, indicating that the nitrogen/oxygen content affects the critical pressure significantly. However, the effects of carbon dioxide content on the critical pressure are much more complicated. With the initial mole fraction of carbon dioxide of $x_3 = 0.5$ and 0.6, the critical pressure of the reacting mixture is much more stable along the reaction course than that with $x_3 = 0.7$. The reason may be that the carbon dioxide content of $x_3 = 0.7$ is close to the composition at which the maximum critical pressure occurs, as indicated in the binary mixture of cyclohexane + carbon dioxide (Figure 1).

It was reported that carrying out the reaction under supercritical conditions near the critical point often gives special performance on the yield, selectivity, and catalyst stability,[7,9–16] and this work shows that the critical properties change with the extent of reaction. Therefore, to ensure that the reaction was carried out under supercritical conditions near the critical point, the reaction conditions should be tuned according to the critical properties of the reacting media along the reaction course. The reaction conditions should be a compromise of both the initial reactants and final products when the reaction is carried out at a fixed temperature and pressure.

The oxidation of cyclohexane with oxygen is an exothermic and volume-contracting reaction; the increase in temperature with the reaction course to cater to the critical temperature of the reacting mixture can be achieved by controlling the amount of heats educed from the reactor. With the addition of carbon dioxide, the critical properties of the reacting mixture depend largely on the content of carbon dioxide. The proper content of carbon dioxide could decrease the critical temperature of the reacting mixture and alleviate the extensive change in the critical pressure with the extent of reaction, which is helpful in adapt the reaction conditions in the vicinity of the critical point of the reacting mixture.

It should be noted that some side reactions such as overoxidation may occur along with the selective oxidation and the reacting mixture may also contain certain side products. The reaction is also not strictly stoichiometric. The critical properties of the actual reacting mixture should be reevaluated by considering these factors.

4. Conclusions

The critical properties of the binary mixture (cyclohexane + carbon dioxide) and the nominal reacting mixture (cyclohexane + nitrogen + carbon dioxide + cyclohexanol + cyclohexanone + water) involved in the selective oxidation of cyclohexane by oxygen in the presence of carbon dioxide were determined using a high-pressure viewing cell with visual observation.

The critical properties of the reacting mixture change with the extent of reaction. To ensure that the reaction is carried out under supercritical conditions near the critical point, the reaction conditions should be tuned according to the critical properties of the reacting mixture along the reaction course.

The addition of carbon dioxide is an effective way to tune the critical properties of the reacting mixture. With the addition of carbon dioxide, the critical properties of the reacting mixture depend largely on the content of carbon dioxide. The proper content of carbon dioxide could decrease the critical temperature of the reacting mixture and alleviate the extensive change in the critical pressure with the extent of reaction, which is helpful in adapt the reaction conditions in the vicinity of the critical point of the reacting mixture.

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