Electronic Supplementary Information (ESI)

An oxidation mechanism of molecular oxygen over cyclohexene catalyzed by cobalt *L*-glutamic acid complex

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The effect of various solvents in the oxidation of cyclohexene is illustrated in Table 1. Moreover, six different solvents (1.0 mL) were applied to the constant amounts of cyclohexene (1.0 mL) and catalysts (0.02 mmol) at 70°C for 24 h. It can be observed that regardless of the solvent which has been used, there was no observably appreciable increase in selectivity, as demonstrated in Table 1. Besides, it would yield a conversion rate of 82.5% and a total selectivity of 93.2%, with no solvents involved. This can be attributed to the fact that addition of solvent may cause a reduction of the contact between substrate and catalyst at the interface. Hence, no solvent could be selected for the further study.

Table 1. Effect of solvents on the oxidation of cyclohexene.

Solvents	Conversion (%)	Total selectivity (%)
Blank	82.5	93.2
Methanol	46.2	95.9
Ethanol	58.3	93
Acetone	34.2	98.1
Acetonitrile	36.5	94.4
Dichloromethane	17.2	97.6
Dichloroethane	16.4	98.5

Fig 1 displays the relationship between the selectivity of products and reaction temperature in the oxygen oxidation of cyclohexene at five temperatures, namely 40, 50, 60, 70°C and 75°C. It can be seen that the conversion would experience an increase from 82.5% to 85.4%, with the increase of the reaction temperature from 70 to 75°C. However, the volatilization of cyclohexene was strong due to the boiling point of cyclohexene being 83°C. In conclusion, to avoid any evaporation of cyclohexene, the final reaction was carried out at 70°C.

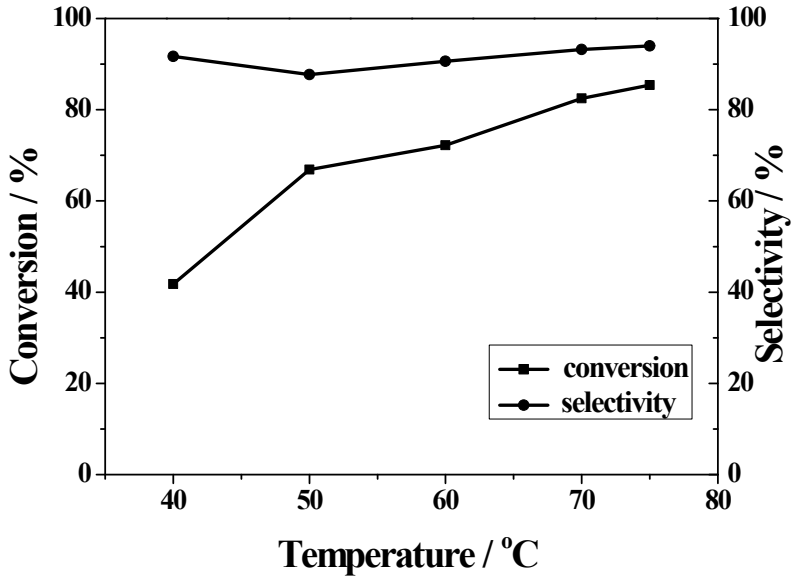

Fig 1. Effect of temperature on the oxidation of cyclohexene.

The effect of the amount of cyclohexene was also studied, while five different amounts of cyclohexene, i.e., 0.4, 0.8, 1.0, 2.0 and 3.0 mL, were considered with the other conditions kept constant. As for the highest conversion rate, it would be 82.5% in case the volume of cyclohexene was 1.0 mL, as shown in Fig 2. It is clear that the conversion of cyclohexene and total selectivity of three main products takes place with the increase in the volume of cyclohexene from 0.4 to 1.0 mL. Besides, the total selectivity of products increased with the rise of the cyclohexene amount from 1.0 to 3.0 mL, along with the decrease of the conversion of cyclohexene. This behavior may be due to the by-products created during the reaction.

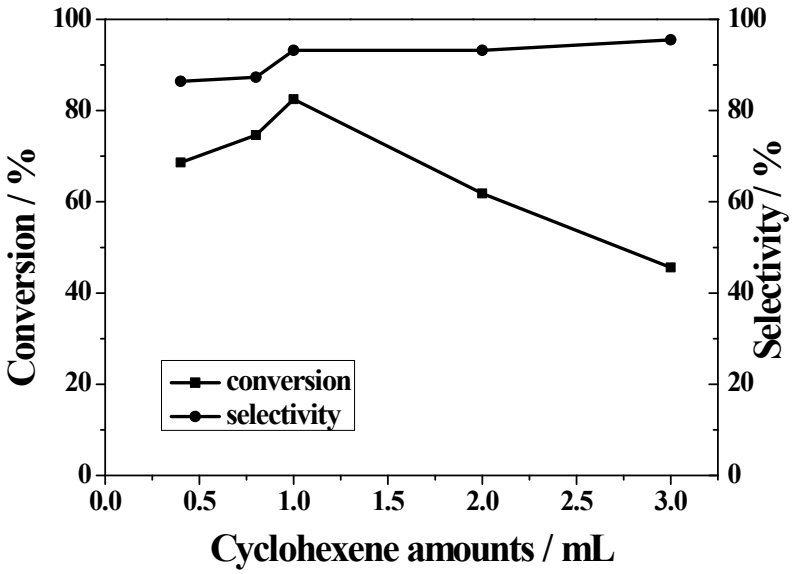

Fig. 2. Effect of cyclohexene amount on its oxidation.

Fig 3 describes the effect of the reaction time on the oxidation of cyclohexane; experiments were carried out with 0.02 mmol catalysts at 70°C with 1.0 mL cyclohexene for durations of 8, 12, 16, 20, 24 h and 36 h. This process was accompanied by a significant conversion of cyclohexene which has increased from 34.1% to 83.1% with an increase of the reaction time to 36 h. Besides, it would yield the highest total selectivity of 98.6%, despite of which the conversion rate of cyclohexene increased by only 0.6% with the increase of the reaction time from 24 h to 36 h. As a result, it can be noticed that there is no clear advantage in terms of increasing the reaction time. Therefore, the optimized reaction time was 24 h.

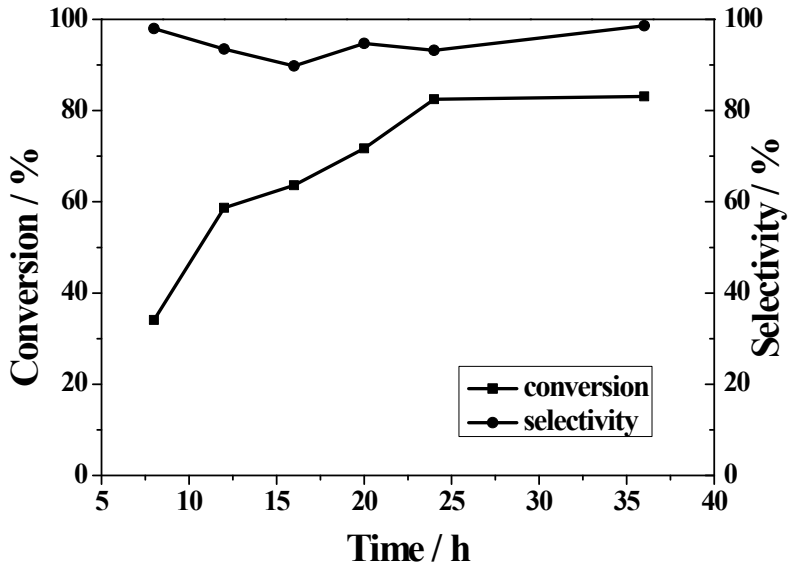

Fig. 3. Effect of reaction time on the oxidation of cyclohexene.

In summary, the optimized conditions were as follows: without any solvents; reaction temperature = 70°C; catalyst amount = 0.02 mmol; cyclohexene amount = 1.0 mL; reaction time = 24 h. Under these optimized reaction conditions, the L-Glu-Co (II) catalysts would yield a conversion rate of 82.5% and a total selectivity of 93.2%.