Chinese Journal of Catalysis 35 (2014) 279–285

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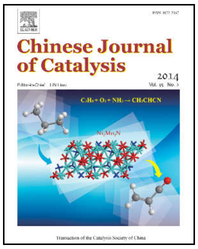

Communication

Cyclohexane oxidation: Small organic molecules as catalysts

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ARTICLE INFO

Article history:
Received 10 November 2013
Accepted 2 January 2014
Published 20 March 2014

Keywords:
Cyclohexane oxidation
Small-molecule organocatalysis
Polarization
Hydrogen bond
Radical scavenging

ABSTRACT

The catalytic activity of several small organic molecules including ketones, aldehydes, esters, alcohols and amines toward cyclohexane oxidation was investigated. The catalytic activity was found to be closely related to polarity, α-H activity, the strength of hydrogen bond formed with cyclohexane and the radical scavenging capability of these molecules. Based on the obtained results, the catalytic role of the organic solvent must be considered for cyclohexane oxidation. Tripropylamine has very high activity in cyclohexane oxidation and it might be further developed as a promising small-molecule organocatalyst for future application.

The oxidation of cyclohexane to cyclohexanone and cyclohexanol is an important industrial process and the products are precursors for the production of caprolactam and adipic acid, which are the building blocks for nylon-6 and nylon-6, 6 [1,2]. The auto-oxidation of cyclohexane is known to proceed through a complex radical chain mechanism as described in Scheme 1 [3]. Cyclohexane can react with oxygen to form cyclohexyl hydroperoxide. The chain initiation proceeds through the cleavage of cyclohexyl hydroperoxide (reaction (2)). Once oxygen-centered radicals are formed, they attack cyclohexane to form cyclohexyl radicals (reaction (3)). Cyclohexyl radicals are further oxidized to cyclohexyl peroxy radicals (reaction (4)). The cyclohexyl peroxy radicals are the main chain propagators. The chain is terminated by the mutual destruction of two cyclohexyl peroxy radicals [3]. Various byproducts are generated during the radical chain reaction. Commercially, cyclohexane oxidation is operated at a temperature of 140–160 °C and under a pressure of 1–1.5 MPa. The conversion is usually kept below 5% to prevent the deep oxidation of cyclohexane, giving 70%–85% selectivity toward cyclohexanone-cyclohexanol mixture (KA oil).

Transition-metal ions such as Co^{2+}, Cr^{3+}, or Mn^{2+}, which can accelerate free radical chain reactions [4], have been used to catalyze cyclohexane oxidation. However, these catalysts are difficult to separate from the products and can induce pipeline blocking. Heterogeneous catalysts such as modified zeolites [5–7], supported metal catalysts [8,9], metal organic frameworks [10–14] and carbon materials [15,16] have been used to catalyze cyclohexane oxidation and a certain activity can be

$$\begin{array}{cr}
\mathrm{CyH} + \mathrm{O_2} \rightarrow \mathrm{CyOOH} & (1) \\
\mathrm{CyOOH} \rightarrow \mathrm{CyO}^{\bullet} + {}^{\bullet}\mathrm{OH} & \\
\mathrm{CyOOH} \rightarrow \mathrm{CyOO}^{\bullet} + {}^{\bullet}\mathrm{H} & (2) \\
\mathrm{CyO}^{\bullet} + \mathrm{CyH} \rightarrow \mathrm{CyOH} + \mathrm{Cy}^{\bullet} & \\
\mathrm{CyOO}^{\bullet} + \mathrm{CyH} \rightarrow \mathrm{CyOOH} + \mathrm{Cy}^{\bullet} & (3) \\
\mathrm{Cy}^{\bullet} + \mathrm{O_2} \rightarrow \mathrm{CyOO}^{\bullet} & \\
\mathrm{Cy}^{\bullet} + \mathrm{CyOOH} \rightarrow \mathrm{CyOO}^{\bullet} + \mathrm{CyH} & (4) \\
2\ \mathrm{CyOO}^{\bullet} \rightarrow \mathrm{CyOH} + \mathrm{Cy{=}O} + \mathrm{O_2} & (5)
\end{array}$$

Scheme 1. Radical chain mechanism for cyclohexane oxidation.

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This work was supported by the MOE Innovation Team (IRT13022) of China, the Collaborative Innovation Center of Chemical Science and Engineering (Tianjin) and 111 Project (B12015).

DOI: 10.1016/S1872-2067(14)60024-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 3, March 2014

obtained. Combined with Mn^{2+} or Co^{2+}, N-hydroxyphthalimide (NHPI) has been successfully applied to the functionalization of different hydrocarbons. Cyclohexane can also be directly oxidized to adipic acid by oxygen using NHPI as a catalyst [17]. In most cyclohexane oxidation reactions that have been reported, a solvent has been used and it has a significant impact on the reaction results. Based on our preliminary experimental results, considerable cyclohexane conversion can be achieved in the absence of catalysts when solvents such as methanol are used. That is, the solvent may play a catalytic role in cyclohexane oxidation. Therefore, the catalytic activity of small organic molecules toward cyclohexane oxidation was investigated in this study and a catalysis mechanism is proposed.

Several kinds of polar molecules with different functional groups were used as catalysts for cyclohexane oxidation under solvent-free conditions. Ultra-high purity reagents (>99.99%) were used throughout the reaction. The catalytic performance of several different ketones, aldehydes, esters, alcohols, and amines are summarized in Table 1. A blank experiment without any catalyst gave a cyclohexane conversion of 1.4% after reaction for 4 h because of auto-oxidation. Cyclohexanol and cyclohexanone were detected as exclusive products. Phenol and its oxidation product, quinone, are good radical scavengers. When phenol was used as the catalyst, no cyclohexane oxidation occurred, which confirmed that this reaction proceeds by a radical chain mechanism. However, cyclohexanone and acetone exhibit significant catalytic activity; their TOF values were 8.3 and 5.2 h^{-1}, respectively. Meanwhile, their selectivity toward cyclohexanone and cyclohexanol was only 74% and 76%, respectively. GC-MS analysis results (Fig. 1) show that the main products obtained when using acetone as a catalyst are cyclohexanone, cyclohexanol and cyclohexanone peroxides, which can induce ring opening reaction and deep oxidation. The catalytic activity of cyclohexanone implies that cyclohexane oxidation is an autocatalytic reaction. The catalytic activity of diphenyl ketone is much lower than that of cyclohexanone and acetone. Cyclohexane conversion was only 2.1% after 4 h and the TOF value was calculated to be 2.7 h^{-1}.

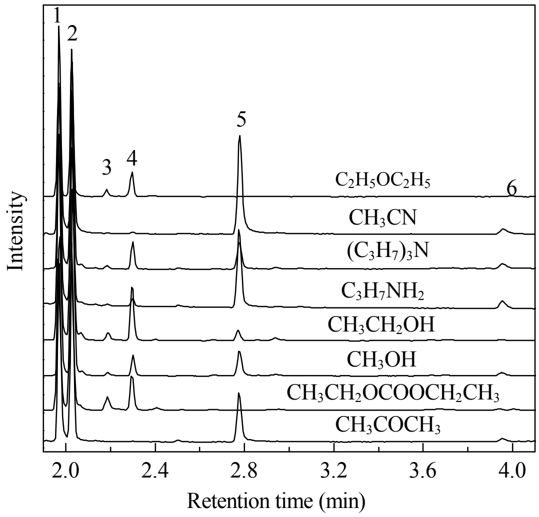

Fig. 1. GC-MS analysis of the products from cyclohexane oxidation over different small-molecule catalysts. 1, Cyclohexanol; 2, Cyclohexanone; 3, Caproic acid; 4, Cyclohexyl hydroperoxide; 5, Cyclohexanone peroxide; 6, Caprolactone.

Similar to ketones, aldehydes also have carbonyl groups and they are expected to be active in the cyclohexane conversion. Benzaldehyde and its homolog, phenylacetaldehyde, show considerable catalytic activity in cyclohexane oxidation. Cyclohexane conversion using benzaldehyde was 14.9%, which corresponds to a TOF value of 10.5 h^{-1}. In addition, the total selectivity toward cyclohexanone and cyclohexanol was 94%, which is distinctly higher than that using cyclohexanone and acetone.

Table 1

Cyclohexane oxidation catalyzed by small organic molecules.

Catalyst		C_6H_{12} conversion [a] (%)	TOF [b] (h^{-1})	$C_6H_{10}O$ selectivity (%)	$C_6H_{12}O$ selectivity (%)
Blank	—	1.4	—	67	32
Ketone	cyclohexanone	11.5	8.3	40	34
	CH_3COCH_3	10.3	5.2	40	36
	$C_6H_5COC_6H_5$	2.1	2.7	58	41
Aldehyde	C_6H_5CHO	14.9	10.5	46	48
	$C_6H_5CH_2CHO$	6.2	5.1	47	45
Ester	$CH_3COOCH_2CH_3$	11.0	7.5	39	46
	$C_3H_7COOCH_2CH_3$	7.3	5.8	30	48
	$CH_3CH_2OCOOCH_2CH_3$	11.2	6.5	43	34
Alcohol	CH_3OH	9.8	2.5	54	36
	CH_3CH_2OH	6.5	2.6	49	40
	$CH_3CH_2CH_2OH$	2.1	1.3	42	38
	CH_2OHCH_2OH	0.6	0.3	64	35
Amine	$C_3H_7NH_2$	13.1	7.5	48	34
	$(C_3H_7)_2NH$	11.2	10.6	47	32
	$(C_3H_7)_3N$	17.0	22.6	48	33
	$(C_2H_5)_3N$	13.7	13.3	42	38
Others	CH_3CN	13.2	4.8	46	32
	$C_2H_5OC_2H_5$	8.3	6.0	43	45
	C_6H_5OH	0	0	—	—

[a] Typical conditions: cyclohexane 3 mL, catalyst 10 μL (or 10 mg), O_2 1.5 MPa, 150 °C, 4 h. After the removal of peroxide by triphenyl phosphine, the reactants and products were analyzed by GC (flame ionization detector, DB-5 capillary column) using biphenyl as an internal standard.

[b] Calculated as mole of cyclohexane converted per mole of catalyst per hour.