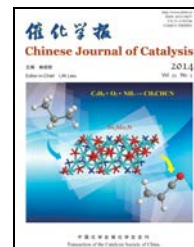




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Communication

Cyclohexane oxidation: Small organic molecules as catalysts

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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.

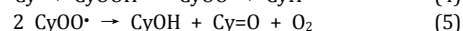
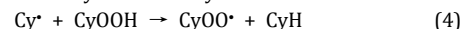
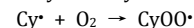
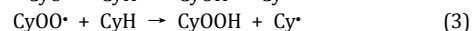
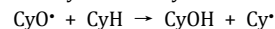
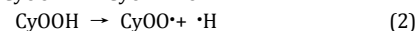
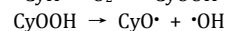
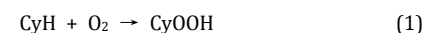
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The oxidation of cyclohexane to cyclohexanone and cyclohexanol is an important industrial process and the products are precursors for the production of caprolactam and adipic acid, which are the building blocks for nylon-6 and nylon-6, 6 [1,2]. The 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



Scheme 1. Radical chain mechanism for cyclohexane oxidation.

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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 oxida-

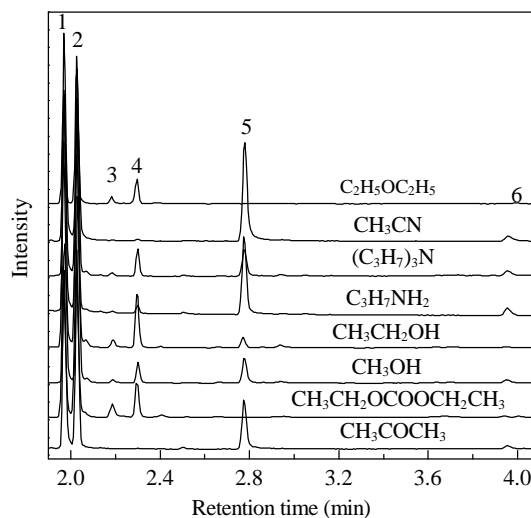


Fig. 1. GC-MS analysis of the products from cyclohexane oxidation over different small-molecule catalysts. 1, Cyclohexanol; 2, Cyclohexanone; 3, Caproic acid; 4, Cyclohexyl hydroperoxide; 5, Cyclohexanone peroxide; 6, Caprolactone.

tion 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} .

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	—	—	67	32
Ketone	cyclohexanone	11.5	8.3	40
	CH_3COCH_3	10.3	5.2	40
	$C_6H_5COC_6H_5$	2.1	2.7	58
Aldehyde	C_6H_5CHO	14.9	10.5	46
	$C_6H_5CH_2CHO$	6.2	5.1	47
Ester	$CH_3COOCH_2CH_3$	11.0	7.5	39
	$C_3H_7COOCH_2CH_3$	7.3	5.8	30
	$CH_3CH_2OCOOCH_2CH_3$	11.2	6.5	43
Alcohol	CH_3OH	9.8	2.5	54
	CH_3CH_2OH	6.5	2.6	49
	$CH_3CH_2CH_2OH$	2.1	1.3	42
	CH_2OHCH_2OH	0.6	0.3	64
Amine	$C_3H_7NH_2$	13.1	7.5	48
	$(C_3H_7)_2NH$	11.2	10.6	47
	$(C_3H_7)_3N$	17.0	22.6	48
	$(C_2H_5)_3N$	13.7	13.3	42
	CH_3CN	13.2	4.8	46
Others	$C_2H_5OC_2H_5$	8.3	6.0	43
	C_6H_5OH	0	0	—

^a Typical conditions: cyclohexane 3 mL, catalyst 10 μ L (or 10 mg), O_2 1.5 MPa, 150 $^\circ$ 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.

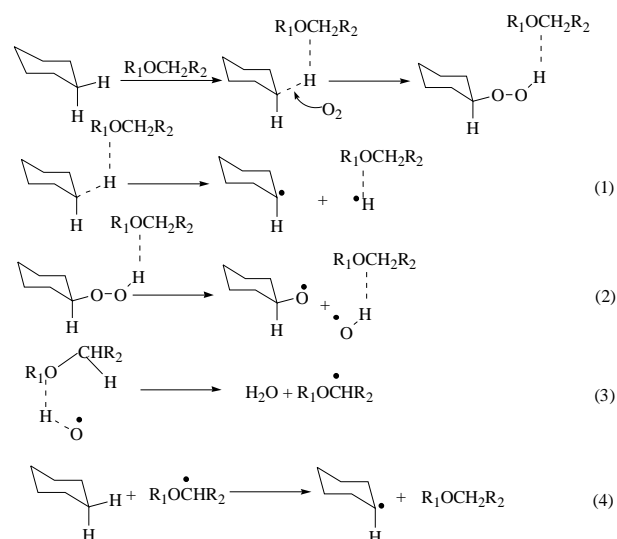
^b Calculated as mole of cyclohexane converted per mole of catalyst per hour.

The cyclohexane conversion when using phenylacetaldehyde was 6.2% (cyclohexanone and cyclohexanol selectivity of 92%), which corresponds to a TOF value of 5.1 h⁻¹. The catalytic activity of aldehydes obviously decreases with an increase in the length of the carbon chain.

Ethyl acetate, ethyl butyrate, and diethyl carbonate were used as catalysts for cyclohexane oxidation. TOF values of 7.5 and 5.8 h⁻¹ were obtained for ethyl acetate and ethyl butyrate, respectively. The catalytic activity decreased with an increase in the length of the catalyst's carbon chain. This is consistent with the results obtained when using aldehydes as the catalyst. In addition, a TOF value of 6.5 h⁻¹ was obtained for diethyl carbonate. Selectivity toward cyclohexanone and cyclohexanol was similar to that obtained when using ketones as the catalyst but lower than that obtained when using aldehydes as the catalyst. GC-MS analysis results indicate that the main products from cyclohexane oxidation are cyclohexanone, cyclohexanol, and cyclohexyl hydroperoxide when using diethyl carbonate as the catalyst. Traces of 6-hydroxy hexanoic acid and butyric acid were detected as well.

All the above-mentioned catalysts have carbonyl groups. Therefore, their activity might originate from their C=O bonds. In addition, C-O bonds are also present in the ester molecules. To investigate the role of oxygen in the C-O bonds, the ethers were evaluated as catalysts for cyclohexane oxidation. When diethyl ether was used as the catalyst, a cyclohexane conversion of 8.3% was obtained after 4 h (TOF: 6.0 h⁻¹). The selectivity toward cyclohexanol and cyclohexanone was 45% and 43%, respectively. GC-MS analysis results show that the byproducts are cyclohexyl hydroperoxide and caproic acid. These results indicate that the C-O bond in diethyl ether is also catalytically active during cyclohexane oxidation. The catalytic activity of diethyl ether is slightly less than that of ethyl acetate. Each diethyl carbonate molecule contains two C-O bonds and one C=O bond; however, the catalytic activity of diethyl carbonate and ethyl acetate is quite similar. Obviously, the catalytic activity of small organic molecules is not simply determined by the amount of functional groups but also by other physicochemical properties.

All the active small organic molecules mentioned above are polar molecules with O atoms. Hydrogen bonds can be formed between the H atoms in cyclohexane and O atoms in the catalysts. Therefore, we propose that polarity and hydrogen bonding play important roles in the cyclohexane oxidation reaction. The catalysis mechanism is proposed and described in Scheme 2. The C-H bond in cyclohexane becomes longer and weaker because of the induced polarization of polar molecules and hydrogen bond formation. Therefore, the C-H bond can be broken to produce a cyclohexyl radical. The formed cyclohexyl radical can react with molecular oxygen to produce CyOO radical. Alternatively, the oxygen atom can attack the weakened C-H bond to form a hydroperoxide, which is similar to cyclohexane auto-oxidation (Scheme 1). Obviously, a strongly polar catalyst will better conduct the reaction and higher catalytic activity might be expected. As for the evaluated catalysts, the polarity decreases with an increase in the length of the carbon chain and, therefore, the catalytic activity also decreases with it.



Scheme 2. Reaction mechanism for cyclohexane oxidation with small organic molecule as the catalyst. R₁, R₂ = H or alkyl.

Under our reaction conditions, the formed hydroperoxide is easily converted to a CyO radical and a hydroxyl radical via hemolytic cleavage. The hydroxyl radical is so active that it can easily abstract an α -H from the hydroperoxide of cyclohexanone to produce new radicals. Once new radicals form, β -cleavage begins and leads to ring-opened byproducts [18]. However, the activity of hydroxyl radicals decreases when they are attached to polar molecules by hydrogen bonds. Moreover, the α -H activity of polar molecules is usually higher than that of cyclohexane. Radical rearrangement and dehydration may occur (reaction (3)). The activity of the newly formed R₁OCHR₂ radicals is much lower than that of hydroxyl radicals. R₁OCHR₂ radicals can abstract H atoms from cyclohexane to produce Cy radicals, accompanied by the recovery of catalyst molecules. Diphenyl ketone has a large electronic conjugated system, which can stabilize free radicals. Therefore, when diphenyl ketone is used as a catalyst, the formed radicals will be captured and hinder subsequent reactions.

The O atoms in alcohols can also form hydrogen bonds with the H atoms in cyclohexane and, therefore, alcohols might be active in the cyclohexane oxidation reaction. Several kinds of alcohols were used as catalysts for cyclohexane oxidation and the results are shown in Table 1. Alcohols were found to be poor catalysts for cyclohexane oxidation and the catalytic activity of methanol (TOF: 2.5 h⁻¹) and ethanol (TOF: 2.6 h⁻¹) is very similar. Alcohols have a strong radical scavenging ability. Radicals can abstract H atoms from alcohols to produce alkoxy radicals, which will lose H atoms to aldehydes and can be further oxidized. Glycol has very low catalytic activity (TOF: 0.3 h⁻¹) because polyhydric alcohols are good free radical scavengers, which impedes this reaction. The products obtained using methanol or ethanol as the catalyst were identified by GS-MS. As shown in Fig. 1, cyclohexanol, cyclohexanone, cyclohexyl hydroperoxide and cyclohexanone peroxide were detected in both cases. ϵ -Caprolactone was detected when using methanol as the catalyst while more cyclohexyl hydroperoxide was detected when using ethanol as the catalyst.

Acetonitrile is a commonly used solvent for cyclohexane oxidation. However, its catalytic role has never been studied and, in fact, we found that acetonitrile is very active in cyclohexane oxidation. A cyclohexane conversion of 13.2% was obtained after 4 h using acetonitrile as the catalyst (TOF: 4.8 h⁻¹). The total selectivity toward cyclohexanol and cyclohexanone was 78% and the selectivity toward cyclohexanone peroxide was 18%. Traces of ϵ -caprolactone were also identified by GC-MS. The catalytic activity of acetonitrile was comparable with that of other heterogeneous catalysts. Acetonitrile is a strong polar molecule with active α -H, and hydrogen bonds can be formed between the H atoms of cyclohexane and the N atoms of acetonitrile. Therefore, the reaction pathway described in Scheme 2 also operates when acetonitrile is used as a catalyst. In another experiment, a cyclohexane conversion of 35% was obtained after 4 h when 4.5 mL acetonitrile and 0.5 mL cyclohexane were mixed and reacted at 140 °C under a pressure of 1.5 MPa (cyclohexanol 15%, cyclohexanone 66%, cyclohexyl hydroperoxide 1%, hexanol 8%, cyclohexanone peroxide 8%, ϵ -caprolactone 1%). Based on these experimental results, acetonitrile should be used as a solvent with caution for cyclohexane oxidation and the catalytic role of acetonitrile cannot be neglected.

Inspired by the catalytic role of small organic molecules in cyclohexane oxidation, we attempted to design highly active organocatalysts for this reaction. Since amines are strong polar molecules with active α -H, they were developed as possible catalysts for cyclohexane oxidation. As shown in Table 1, all the amines studied gave very high catalytic activity and the activity increased with an increase in the number of substituent groups. The TOF value was calculated to be 7.5, 10.6, and 22.6 h⁻¹ for propylamine, dipropylamine and tripropylamine, respectively. Compared with alcohols, amines cannot scavenge radicals and, therefore, exhibit much higher catalytic activity toward cyclohexane oxidation. Although the total selectivity toward cyclohexanol and cyclohexanone was similar (Ca 80%), the selectivity toward cyclohexyl hydroperoxide and cyclohexanone peroxide was quite different. The selectivity toward cyclohexyl hydroperoxide increased with an increase in the number of substituent groups at the N atom while selectivity

toward cyclohexanone peroxide decreased. Moreover, triethylamine (TOF: 13.3 h⁻¹) had lower catalytic activity than tripropylamine (TOF: 22.6 h⁻¹). In a general sense, triethylamine has a lower steric hindrance effect and stronger polarity, which should be good for the reaction. This can be explained by the different electron densities of the nitrogen atoms. The ethyl substituent has a far lower ability to supply an electron to the N atom than propyl and, therefore, the electron density of the N atom in triethylamine is lower than that in tripropylamine. The strength of the hydrogen bond decreases with a decrease in the electron density of the N atom, which influences the activation of cyclohexane.

In summary, several polar molecules such as ketones, aldehydes, esters, alcohols and amines were used as catalysts for cyclohexane oxidation and specific activity was observed. We propose a mechanism for cyclohexane oxidation by small organic molecule catalysis as follows. A hydrogen bond is formed between the catalyst and cyclohexane. The C-H bond in cyclohexane becomes longer and weaker because of polarization effects and hydrogen bond formation. The C-H bond can be broken to produce cyclohexyl radicals or the weakened C-H bond can be attacked by oxygen to produce COOH, which can undergo hemolytic cleavage to a CyO radical and a hydroxyl radical. The catalytic activity is controlled by the strength of the polarity and the hydrogen bond formed with cyclohexane, the activity of α -H and the radical scavenging ability. A strongly polar catalyst and hydrogen bonding are beneficial for cyclohexane oxidation. A specific α -H activity is also beneficial for the reaction while a high enough α -H activity resulting in free radical scavenging will impede the reaction.

The catalytic role of the organic solvent must be taken into account for cyclohexane oxidation. Small-molecule organocatalysts can be developed for use in industrial cyclohexane oxidation.

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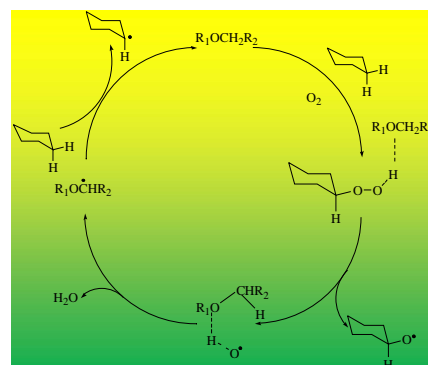
Graphical Abstract

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Cyclohexane oxidation: Small organic molecules as catalysts

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N- or O-containing small organic molecules were used as catalysts for cyclohexane oxidation. The polarity, α -H activity, strength of the hydrogen bond formed with cyclohexane and the radical scavenging capability of these molecules determine their catalytic activity.



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环己烷氧化反应：有机小分子的催化作用

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摘要: 考察了酮、醛、酯、醇与胺等几类有机小分子在环己烷氧化反应中的催化作用。结果表明, 有机小分子催化剂的活性与其极性的强弱、与环己烷形成氢键的强弱、 α -氢的活性及清除自由基的能力有关。因此, 对于环己烷氧化反应, 溶剂很可能存在催化作用。三丙胺在环己烷氧化反应中表现出较高的催化活性, 具有进一步开发应用的前景。

关键词: 环己烷氧化; 有机小分子催化; 极化作用; 氢键; 自由基清除

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环己烷氧化是化工生产中非常重要的反应, 其氧化产物环己醇和环己酮是制备尼龙重要材料己二酸和己内酰胺的前躯体^[1,2]. 环己烷氧化是一个复杂的自由基反应. 该反应机理如图式1所示^[3], 环己烷上的C-H键首先被氧化成过氧化氢键(反应(1)); 然后环己基过氧化氢发生均裂或异裂反应生成自由基(反应(2)). 后者可以夺取环己烷上的氢原子而生成环己基自由基(反应(3)). 环己基自由基可进一步被氧化成CyOO自由基(反应(4)), 该自由基是链增长的重要一环. 链终止反应为两分子的CyOO自由基生成环己醇和环己酮以及氧气(反应(5)). 在自由基的链式反应中会产生大量的副产物. 实际的生产过程中, 为了降低副反应的进行, 环己烷氧化反应常在140–160 °C, 1–1.5 MPa下进行, 环己烷的转化率需控制在5%以下, 环己醇和环己酮的总选择性为70%–85%.

一些过渡金属离子, 如Co²⁺, Cr³⁺和Mn²⁺等, 可以加速自由基反应^[4], 可用作环己烷氧化的催化剂, 但很难将它们从反应体系里分离出来. 另外, 这些金属阳离子会慢慢形成一些难溶的物质, 黏在管道上而引起管道堵塞. 一些非均相催化剂如改性分子筛^[5–7]、金属负载型催化剂^[8,9]、金属有机骨架结构^[10–14]和炭材料^[15,16]也被用作环己烷氧化的催化剂, 表现出一定的活性. 与Co²⁺或Mn²⁺

等一起使用时, 羟基邻苯二甲酰亚胺(NHPI)在碳氢化合物的官能化反应中具有较好的催化活性; 在特定的溶剂中, 它可催化氧气直接氧化环己烷为己二酸^[17]. 另外, 环己烷催化氧化反应大多使用溶剂, 从而可能影响反应结果. 我们的前期结果表明, 不加任何催化剂, 环己烷在甲醇、水等溶剂中都有很高的转化率, 溶剂本身可能对该反应具有一定的催化活性. 在此基础上, 我们初步探索了有机小分子催化环己烷氧化的可能性, 同时对其反应历程进行推测.

本文选用几种具有不同官能团的痕量极性有机小分子用于无溶剂下环己烷氧化反应, 所用试剂均为高纯试剂. 几种酮、醛、酯、醇和胺的催化活性如表1所示. 可以看出, 无催化剂时, 反应4 h环己烷的转化率为1.4%, 产物为环己醇与环己酮. 苯酚及其氧化产物苯醌是良好的自由基捕获剂, 当以苯酚为催化剂时, 环己烷没有转化, 这进一步确认环己烷氧化为自由基反应. 环己酮和丙酮等酮类催化活性较高, TOF值分别为8.3和5.2 h⁻¹, 但环己酮和环己醇的选择性仅为74%与76%. 气质联用分析结果(图1)表明, 当以丙酮为催化剂时, 主要产物中有环己醇、环己酮与环己酮过氧化物, 其中环己酮过氧化物容易发生开环反应, 进一步被深度氧化; 环己酮催化

活性表明, 环己烷氧化是一个自催化反应. 另外, 二苯酮的催化活性远低于环己酮和丙酮, 反应4h环己烷的转化率为2.1%, 对应TOF值仅为2.7 h⁻¹.

醛与酮类似, 都含有羰基, 可能存在催化活性. 当以苯甲醛及其同系物苯乙醛为催化剂时, 环己烷氧化反应活性较高. 苯甲醛为催化剂时, 环己烷转化率为14.9%, TOF值为10.5 h⁻¹, 环己醇与环己酮的总选择性可达94%, 明显高于丙酮和环己酮为催化剂时的选择性. 当以链长更长的苯乙醛为催化剂时, 环己烷转化率降低, 其TOF值为5.1 h⁻¹, 环己醇与环己酮的选择性达92%. 醛的催化活性随着碳链长度增加而明显降低.

本文还考察了乙酸乙酯、丁酸乙酯和碳酸二乙酯等小分子酯催化剂的环己烷氧化反应性能. 结果表明, 乙酸乙酯和丁酸乙酯的TOF值分别为7.5 h⁻¹和5.8 h⁻¹. 这与小分子醛为催化剂时的规律相同: 催化剂活性随着其碳链数的增长而减小. 另外, 碳酸二乙酯的TOF值为6.5 h⁻¹. 以酯为催化剂时, 环己醇与环己酮的选择性与小分子酮的相当, 比小分子醛的略低. 气质联用分析结果(图1)表明, 以碳酸二乙酯为催化剂时, 环己烷氧化产物主要为环己醇、环己酮和环己基过氧化氢, 另外还含有少量的6-羟基己酸和己酸副产物.

酮、醛、酯催化剂均含有羰基, 在环己烷氧化反应中表现出较高的催化活性. 因此推测催化剂活性可能与C=O存在一定关系. 酯中除了C=O键外还存在C–O单键, 为了研究C–O单键中的氧是否具有活性, 选取乙醚作为催化剂. 结果表明, 反应4h环己烷的转化率为8.3%, 环己醇和环己酮的选择性分别为45%和43%. 气质联用分析结果显示, 副产物为环己基过氧化氢和己酸. 由此可见C–O对该反应也有一定的催化作用. 乙醚的TOF值为6.0 h⁻¹, 略低于乙酸乙酯. 另外, 每个碳酸二乙酯中含有两个C–O键和一个C=O双键, 其TOF值却与乙酸乙酯的相当. 可见催化剂TOF值与官能团的数量不呈线性关系, 它不仅取决于特定的官能团的数量, 还可能与有机分子的某些特性有关.

前文所用的酮、醛、酯与醚催化剂均为极性分子, 并且都含有O原子, 可与环己烷上的H原子形成氢键. 据此我们认为, 催化剂分子的极性及氢键的形成是其影响活性的重要因素, 可能的反应历程如图式2所示: 在氢键和极性分子的诱导作用下, 环己烷的C–H键变长, 键能减小, 易于断裂生成环己基自由基, 再与氧气反应生成CyOO自由基. 或是氧原子更容易与环己烷反应生成环己烷的过氧化物, 从而有利于后续反应的进行和转化率

的提高. 催化剂的极性越高, 越有利于反应的进行. 随碳链的增长, 分子的极性减小, 因此催化剂所表现出来的TOF值随碳链的增长而减小.

在本文反应条件下, 环己基过氧化氢容易发生均裂反应生成CyO自由基和通过氢键连接到极性分子上的羟基自由基. 羟基自由基具有非常高的活性, 它可以夺取环己酮过氧化物的 α -H而生成新的自由基, 该自由基容易发生 β 裂解而导致开环反应, 并生成一系列的深度氧化产物^[18]. 然而, 当羟基自由基通过氢键连接到较大的极性分子上时, 其活性将会降低. 另外, 上述所用催化剂极性分子均具有 α -H, 比环己烷的H原子更容易被夺取. 因此, 如图式2反应(3)所示, 与极性分子相连的羟基自由基发生重排反应并脱去一分子水而生成新的自由基. 新生成的R₁OCHR₂自由基继续夺取环己烷上的H而恢复到原先的催化剂分子. 二苯酮具有较大的共轭体系, 可以稳定自由基分子. 因此, 当以二苯酮为催化剂时, 反应过程中生成的自由基与二苯酮发生加成反应, 从而不利于反应的继续进行.

醇中的O原子也可以与环己烷中的H原子形成氢键, 因而醇可能也有一定的催化活性. 本文选取了一些醇作为环己烷氧化的催化剂, 结果见表1. 根据上面所提到的规律, 甲醇的TOF值应该大于乙醇与丁醇的, 而实际上它与乙醇非常相近, 分别为2.5 h⁻¹和2.6 h⁻¹. 甲醇也是一种很好的自由基清除剂, 醇羟基上的氢被自由基夺取后生成的甲氧基仍然不稳定, 还可以继续失去一个氢而生成甲醛. 甘油的TOF值只有0.3 h⁻¹. 这是因为甘油是一种多羟基醇, 具有非常好的自由基捕获能力, 不利于反应进行. 以甲醇和乙醇为催化剂时, 所得产物经由气质联用分析, 结果如图1所示, 两者产物中均未检测到己二酸, 产物中都含有环己醇、环己酮、环己基过氧化氢与过氧化环己酮, 其中以甲醇做催化剂时, 产物中还可检测出己内酯, 以乙醇为催化剂时, 产物中环己基过氧化氢的比率远高于甲醇的.

乙腈经常用作环己烷氧化反应的溶剂, 但关于乙腈对该反应的影响却未见报道. 本文结果表明, 以乙腈为溶剂时, 反应4h后环己烷的转化率达13.2%, TOF值可达4.8 h⁻¹, 环己醇和环己酮的选择性为78%, 副产物过氧化环己酮的选择性可达18%, 产物中还含有少量的己内酯. 可见, 乙腈的催化活性与大多数多相催化剂的接近. 乙腈是一种强极性分子, 并且具有活泼的 α -H, 也可以形成氢键, 因此以乙腈为催化剂时, 图式2所描述的历程仍然成立. 我们将4.5 mL的乙腈和0.5 mL的环己烷在140 °C、

氧气分压为1.5 MPa下反应4 h后, 环己烷转化率可高达35%(产物: 环己醇15%, 环己酮66%, 环己基过氧化氢1%, 己烯醇8%, 过氧化环己酮8%, 己内酯1%). 因此, 当以乙腈作为环己烷氧化的溶剂时, 其自身催化活性不容忽视.

在上述研究基础上, 我们试图设计高活性有机小分子催化剂应用于环己烷氧化过程. 由于有机胺是极性分子且具有活泼的 α -H, 因此本文研究了几种典型有机胺的催化活性, 结果列于表1. 可以看出, 有机胺小分子均表现出很高的催化活性. 正丙胺的TOF值为 7.5 h^{-1} , 且随着胺中N上取代基的增加, 催化剂的TOF也在增加: 二丙胺的TOF值为 10.6 h^{-1} , 三丙胺的TOF值可高达 22.6 h^{-1} . 由于小分子胺不与自由基直接作用, 没有任何清除自由基的能力, 因此活性高. 尽管环己酮和环己醇的总选择性差别不大(约80%), 过氧环己酮和环己基过氧化氢的选择性却有较大的差别: 随N上取代基的增加, 环己基过氧化氢的选择性增加, 过氧化环己酮的选择性减小. 三乙胺在环己烷氧化反应中的TOF值为 13.3 h^{-1} , 明

显低于三丙胺. 与三丙胺相比, 三乙胺的空间位阻减小、极性也强, 但催化活性却较低. 这可能是由于N上电子云密度的影响, 取代基的碳链变短, 给电子能力越弱, N上电子云的密度减小, 氢键也随之减弱, 影响了环己烷的活化.

总之, 几种酮、醛、酯、醇和胺的有机分子均具有一定的催化环己烷氧化活性, 推测其催化反应历程如下: 催化剂与环己烷形成氢键, 在催化剂的诱导极化和氢键的作用下, 碳氢键变长变弱, 断裂成环己基自由基或被氧化成COOH, 而COOH均裂生成CyO自由基或与催化剂通过氢键相连的羟基自由基, 进一步实现环己烷氧化为环己醇与环己酮. 催化剂的活性与其极性的强弱、与环己烷形成氢键的强弱、 α 氢的活性及清除自由基的能力有关: 当催化剂的极性大、形成的氢键能力强时, 转化率较高; α 氢的活性高有利于反应进行, 但过高则容易清除体系内的自由基, 反而抑制反应的进行. 另外, 对于环己烷催化氧化反应, 必须考虑溶剂的催化效应. 总之, 有机小分子有望应用于环己烷氧化的催化剂.