Advances and perspectives in catalytic oxidation of hydrocarbons in liquid phase*

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Abstract This review article summarizes recent advances in catalytic oxidation of hydrocarbons, especially presents two strategies for activation of C-H bonds or molecular oxygen. Based on our own research results, the applications of the two methods in the oxidation of cyclohexane, toluene and ethyl benzene, etc. are introduced, and the perspectives of the two methods are also discussed.

Keywords: hydrocarbon, oxidation, molecular oxygen, catalysis, C-H bond.

Alkanes are the main components of natural gas and petroleum. However, there is no effective method that can directly convert hydrocarbons into valuable products due to their inert reactivity[1,2]. The activation and functionalization of hydrocarbons are of great importance to both scientific research and industrial production. Among the various methods for the functionalization of hydrocarbons, partial oxidation of hydrocarbons is the most important process. According to the statistical data, about 25% organic chemicals produced by the catalytic processes came from selective oxidation. The inert reactivity of alkanes is due to the higher bond strength and the lower polarity of C-H bond. In addition, the products are more reactive than the inert alkanes and tend to be deeply oxidized to water and carbon dioxide, which leads to the large amount of energy needed, the inefficient use of starting materials and the substantial environmental burden. So, it is very significant and challenging to develop an efficient method to activate the C-H bonds[3].

The traditional alkane oxidation generally employs the toxic stoichiometric inorganic reagents as oxidants, such as permanganate, dichromate and nitric acid. However, these processes generate large amounts of inorganic salt-containing effluent along with the target products. Moreover, the strong oxidation ability of these reagents tends to cause runaway oxidation and difficult product separation. Thus, it is urgent to replace these antiquated technologies with cleaner, catalytic alternatives[4]. These defects could be avoided by using the environment friendly oxidants that include H_2O_2 or O_2. However, these oxidants cannot oxidize the inert alkanes without catalysts due to their mild oxidation abilities. Despite the catalytic hydrocarbon oxidation has received intensive attention in petrochemical field and has been applied in industry, the low conversion and selectivity and the rigorous reaction conditions are still the general problems for the catalytic alkane oxidation[5].

The reactions between alkanes and molecular oxygen are spin-forbidden from the view of molecular orbit theory. Therefore, the activation of alkanes is regarded as the Holly Grail in chemistry by Bard et al.[6] Our laboratory has conducted the search for selective oxidation of hydrocarbons and has made some advances in this field. In this paper, we introduce two strategies of activation of C-H bonds or molecular oxygen for catalytic hydrocarbon oxidation, especially for cyclohexane, toluene and ethyl benzene, etc.

1 The idea for catalytic oxidation of alkanes

The direct oxidation of alkane using molecular oxygen is difficult to occur because the triplet state of ground state O_2 and the singlet state of alkanes are spin-forbidden. So, eliminating the spin-forbidden by activation of O_2 or alkanes is necessary for the process.

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The electron configuration in molecular orbits of ground state O_2, excitation state O_2, and superoxide anion (O_2^-) is shown in Fig. 1. The ground state O_2 is triplet ($^3\Sigma_g O_2$) and the two highest occupied molecular orbits (HOMOs) of ground state O_2, π^*_{2px} and π^*_{2py}, are occupied by two electrons with the same spin orientation, respectively. The ground state O_2 has the following characteristics: (1) Free radical. It has two single-electrons in its HOMO orbits. Thus, the ground state O_2 has the free radical character and is easy to react with free radical. (2) Inert reactivity. The two single-electrons with the same spin orientation in HOMO orbits cannot bind electron-pair with the opposite spin orientation because of spin-forbidden. This is why the reactivity of the ground state O_2 is far lower than that of the free radical with a single electron although it has the radical behavior. If the ground state O_2 could directly oxidize a substrate, the substrate molecule must have two single-electrons with the same spin orientation in HOMO. Unfortunately, most molecules have electron pair in HOMO, and cannot react with the ground state O_2.

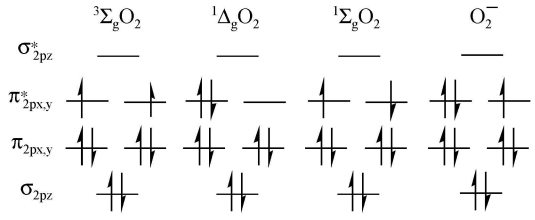


Fig. 1. The electron configuration in molecular orbits of different oxygen species.

Molecular oxygen can be activated by two methods: (1) Converting ground state O_2 into excitation state O_2. (2) Reducing O_2 by one electron to superoxide anion. O_2 accepts one electron and generates anionic radical O_2^- which has one electron in its HOMO and possesses higher reactivity of free radical[7,8]. Most metal catalysts can transfer one electron to O_2 to generate O_2^- and realize the activation of O_2. Therefore, the oxidation of alkanes with O_2 can be succeeded by activating O_2 to generate active O_2^- which then reacts with alkane molecules.

Despite the alkanes are reactive inert, there exists the prevalent autoxidation of C-H bonds in nature. After organic compounds are deposited in air for a long period, they can be slowly oxidized by O_2 to superoxides. The mechanism[9] is briefly shown in Fig. 2. This process takes place under very mild conditions that gives us the following inspirations: (1) Free radical can easily abstract hydrogen atom from alkane and the activation energy of the reaction is low. (2) The generated alkyl radical is easy to couple with O_2. From the above conclusions, it can be seen that although the alkane is reactive inert, the radical chain reaction can easily occur. By generating alkyl radical and the radical chain transfer, alkanes can be transformed to other species or compounds. The above facts allow us to propose a mechanism for alkane oxdation, that is, alkanes can be activated by radicals.

$$M^{n+} + O_2 \longrightarrow M^{(n+1)}OO\bullet$$
$$M^{(n+1)}OO\bullet + RH \longrightarrow M^{(n+1)}OOH + R\bullet$$
$$R\bullet + O_2 \longrightarrow ROO\bullet$$
$$ROO\bullet + M^{(n+1)}OOH \longrightarrow M^{(n+1)}OO\bullet + ROOH$$
$$ROO\bullet + RH \longrightarrow ROOH + R\bullet$$

Fig. 2. The mechanism of autoxidation of hydrocarbons.

2 Examples of O_2 and C-H bond activation

2.1 Activation of O_2

Up to now, the most studied method of the alkane oxidation has been focused on the activation of O_2. The catalysts used are mainly transition metals including Fe, Co, Mn, Cu, Ti, V, Mo, Au, etc.[10—13]. According to their forms, the catalysts can be divided into homogeneous transition metals, and heterogeneous metals and their oxides. For heterogeneous catalysts, they are mainly molecular sieves and metal oxides. The following sections mainly introduce our own research results of solid oxides as catalysts.

2.1.1 Oxidation of toluene catalyzed by metal oxides

The results of toluene oxidation by metal oxides indicate that manganese oxides have higher activity than other metal oxides. The conversion of toluene could reach 38.7% at 195 ℃ over Mn_3O_4 after 3 h reaction, and the main product is benzoic acid[13]. As shown in Table 1, the oxidation of toluene by $CuFeO_x/Al_2O_3$ gives the results of 7.4% toluene conversion and 69.4% benzaldehyde+benzyl alcohol selectivity after reaction at 190 ℃ for 2 h[14]. Addition of a small amount of pyridine to the reaction system, the selectivity of benzaldehyde and benzyl alcohol can

be greatly improved to 92.0% with the benzaldehyde selectivity of 85.9%. The promotive effect of pyridine for the benzaldehyde selectivity is probably due to the *in situ* dynamic holding of pyridine on the catalyst surface. Because pyridine (pKa=8.8) is an alkaline molecule with a lone-pair electron, it can react with the Brönsted acid site of the catalyst surface. Due to these Brönsted acid sites maybe induce the overoxidation of benzaldehyde, therefore, through the reaction of pyridine with the Brönsted acid site, the reaction of the Brönsted acid site with the benzaldehyde could be inhibited. And thus the selectivity of the target products was increased.

Table 1. Oxidation of cyclohexane with different catalysts[a)]

Catalyst	Conversion (%)	Product distribution (%)				
		A	K	CHHP	Acid	Ester
Blank	1.2	7.3	35.9	53.6	2.3	0.9
Co_3O_4	7.6	39.6	49.5	0.8	4.8	5.3
Co_3O_4[b)]	1.3	60.4	33.7	2.9	3.0	0
Co_3O_4[c)]	3.5	38.3	31.4	10.7	14.6	5.0
Co_3O_4/Al_2O_3	2.3	41.0	35.7	12.4	5.4	5.5
$Co(OAc)_2$	4.7	32.6	28.7	0.8	22.5	15.4

a) Reaction time: 6 h, reaction temperature: 393 K. A, cyclohexanol; K, cyclohexanone; acid, mainly adipic acid; ester, dicyclohexyl adipate, hexanolactone and other ester.

b) Co_3O_4 was prepared by calcination of the precipitation obtained from $Co(NO_3)_2$ and Na_2CO_3 solution.

c) Co_3O_4 was prepared by air-calcination of cobalt nitrate

2.1.2 The applications of nano-metal oxides in oxidation of cyclohexane

Metal oxide nanoparticles exhibit unique chemical properties due to their limited size and high density of corner or edge surface sites, and they may have high activity in hydrocarbon oxidation[15, 16]. We compared the activity of Co_3O_4 nanocrystal catalysts with the conventionally prepared catalyst and homogeneous cobalt catalyst for the liquid phase oxidation of cyclohexane using molecular oxygen as oxidant, and the results are shown in Table 2. The conversion of cyclohexane over Co_3O_4 prepared by the conventional precipitation or air-calcination of cobalt nitrate method was 1.3% and 3.5%, respectively. The 2.3% conversion of cyclohexane was obtained over Co_3O_4/Al_2O_3. Further, the reaction was carried out in the absence of catalyst, and a low conversion with cyclohexyl peroxide as the main product was observed. Remarkably, Co_3O_4 nanocrystals exhibited the best performance with a cyclohexane conversion of 7.6%, K/A oil selectivity of 89.1% and yield of 6.7%, which was higher than Co_3O_4 catalysts prepared by the conventional method. The homogeneous cobalt catalyst, adopted in industry, showed a cyclohexane conversion of only 4.7% and a selectivity of 61.3% to K/A oil under comparable reaction conditions. These results revealed that the nanocatalyst undoubtedly possesses higher activity than that of the conventional catalyst, and reducing the particle size of the metal oxides to nanometer scale is an effective method for increasing their catalytic activity in hydrocarbon oxidation.

2.1.3 Surface modification with organic groups

Catalyst modified by methyl was prepared for studying the influence of surface modification with organic groups on its catalytic performance. To examine and compare the hydrophobic property of the catalysts, Au/CH_3-MCM-41 and Au/MCM-41 were added to an immiscible mixture of water and cyclohexane, which gave a visible demonstration of this property. After the mixture was shaken, Au/CH_3-MCM-41 was totally dispersed in organic layer and the water layer was clear. On the contrary, Au/MCM-41 mixed with the water and deposited at the bottom of the water, and the organic layer was clear. The phenomena indicate that the surface of Au/CH_3-MCM-41 is highly hydrophobic while that of Au/MCM-41 is hydrophilic[17].

The results of cyclohexane oxidation over Au/CH_3-MCM-41 and Au/MCM-41 at different reaction time using molecular oxygen as oxidant are shown in Fig. 3. It can be seen that the reaction efficiency on Au/CH_3-MCM-41 is higher than that over Au/MCM-41. For example, the cyclohexane conversion of 5.68% was obtained over Au/CH_3-MCM-41 at reaction temperature of 130 ℃ and reaction time of 2 h; whereas, under the same reaction conditions the cyclohexane conversion was only 3.77% over Au/MCM-41. The selectivity of mono-oxygenated products decreased with the increase of cyclohexane conversion. So, the selectivity of different catalysts must be compared under similar cyclohexane conversion. The selectivity (83.9% at 3.2% cyclohexane conversion) of mono-oxygenated products over Au/CH_3-MCM-41 is a little higher than that (79.7% at

3.4% cyclohexane conversion) of Au/MCM-41.

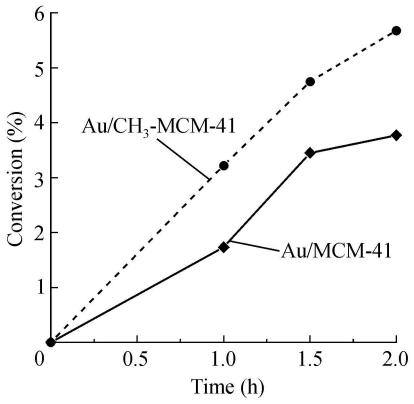


Fig. 3. The catalytic performance of Au/CH_3-MCM-41 and Au/MCM-41 in cyclohexane oxidation.

2.2 The method of C-H bonds activation—organocatalysis

In recent years, there appeared a new research field—organocatalysis[18], which is completely different from metal catalysis. Organocatalysis has shown good catalytic performance and potential applications, and it is also a new strategy for designing catalysts[19]. Organocatalysis is defined as accelerating a chemical reaction with a small organic molecule that does not contain metal atom, and its catalytic active center is the organic group. Ishii system, which combines *N*-hydroxyphthalimide (NHPI) with a cocatalyst (variable valence metal), is an effective catalytic system, and it oxidizes a broad range of organic substrates, e.g., alkylaromatics and alkanes, under mild conditions[20]. Ishii system has lots of merits, but the product selectivity for some process is still lower and metal cannot be completely omitted. Biological oxidation via free radical can be accelerated by enzyme, and exhibits high efficiency and high product selectivity. Based on the following three elementary factors of biomimetic oxygenation model, we developed a new biomimetic system for oxidation reaction via free radical:

(1) Redox center

In biological oxygenation process of C-H bond via free radical, abstracting a hydrogen atom from C-H bond of reactant is the initial and key step, and is the characteristic of the free radical reaction. The active redox center of enzymes is free radical or the similar species, which has the single-electron property.

The free radical that can abstract a hydrogen atom from C-H bond must be highly electrophilic[21]. However, the life of most of the highly electrophilic free radical is short-lived, and it usually exists as an intermediate in reaction. So, for designing a free radical as the active redox center, we should consider the potential material that is not a free radical but can generate radical. Moreover, the material should easily undergo singe electron transfer under certain conditions and generate electrophilic radical for abstracting a hydrogen atom from C-H bond.

NHPI was proved to be such a material that satisfies the above criterion. Fig. 4 shows the scheme of the generation of phthalimide *N*-oxyl radical (PINO) from NHPI via the transfer of an electron. PINO is a highly electrophilic radical that can abstract a hydrogen atom from C-H bond under mild conditions. So, we selected NHPI as the potential redox active site in our biomimetic catalytic system.

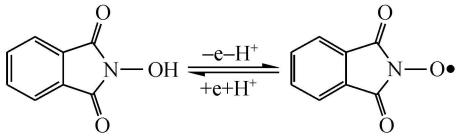


Fig. 4. The transform between PINO and NHPI.

(2) Accelerant for singe electron transfer

The transformation from NHPI to PINO involves electron transfer and there should exist an electron acceptor. Moreover, the deoxidized state of acceptor formed by receiving an electron should be able to return to its oxidized state by losing an electron. In other words, the electron acceptor should possess single electron redox character. The chain of electron transfer in an organism is composed of various coenzymes. Ubiquitous quinone derivative is proved to be one of the units of the electron-transfer chain[22]. The coenzyme Q is the mostly familiar quinone coenzyme, and the structure of Q is shown in Fig. 5.

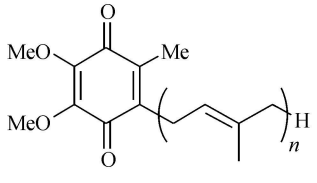


Fig. 5. The structure of Q.

Fig. 6 shows the redox process of quinone. Quinone accepts electrons to form hydroquinone, which is a process with two electrons transfer. Actu-

ally, this process contains two steps of single electron transfer, and the semi-hydroquinone is an unstable intermediate. However, since semi-hydroquinone is unstable, if the reaction is stopped, quinone and hydroquinone will be the final forms and exist stably.

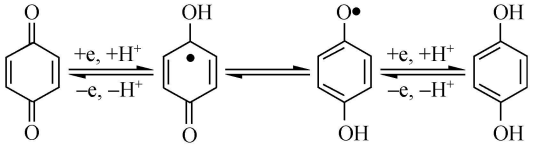


Fig. 6. The redox process of quinone.

(3) Multiple binding effect

The specificity for products and materials of biosynthesis is from some noncovalent binding of the substrate and the intermediate with the enzymatic protein domain. The multiple-noncovalent binding is mainly from hydrogen bond, electrostatic attraction, Van der Waals force and hydrophobic interaction between amino-acid residue and substrate. These interactions lead to the substrate orientationally surrounded by enzymatic proteins, and result in the orientational selectivity of the products. Fig. 7(a) shows the molecular model of the substrate surrounded by an enzymatic protein domain[23].

For designing the multiple-noncovalent binding sites, the following two basic factors should be considered: (1) polar groups in catalytic system, (2) similar environments with the protein domain, which can form host-guest composites.

Molecular sieves are a kind of porous materials that have uniform pores and cages, and can adsorb molecules into its pores or cages. There are some acid/basic sites and polar groups in the inner surface of molecular sieves and these groups can catalyze the reaction of substrate via noncovalent binding effect. Fig. 7(b) shows the molecular model of the substrate entering the pores of molecular sieves[24]. Molecular sieves and their catalytic properties are very similar with the enzyme and the catalytic behavior of enzyme, respectively. The similarity can be obviously observed from the comparison of Fig. 7(a) and 7(b). This property has been accepted[25] and applied in some biomimetic catalytic synthesis[26].

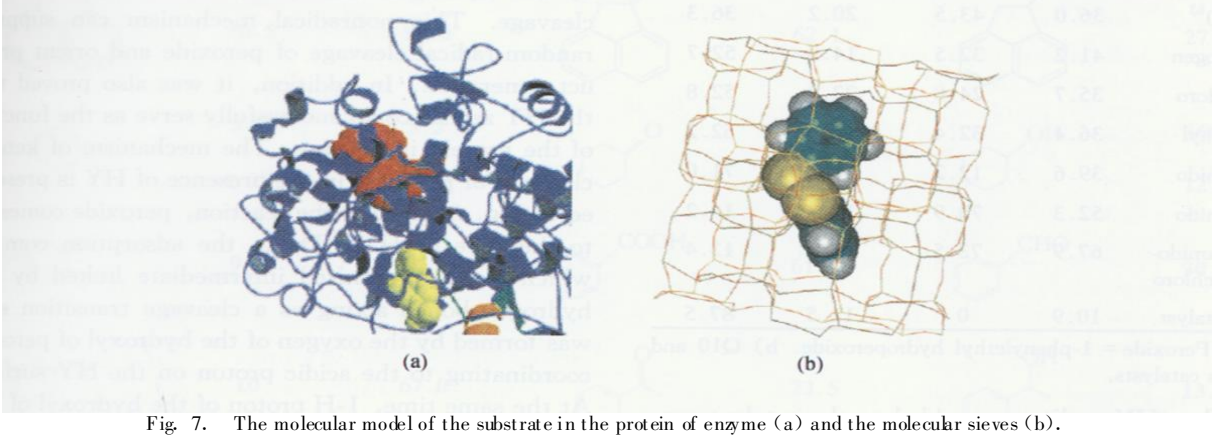


Fig. 7. The molecular model of the substrate in the protein of enzyme (a) and the molecular sieves (b).

Based on the above three elements, we established a model of biomimetic catalytic oxidation of hydrocarbons. The following shows the details:

(i) NHPI was selected as the potential redox active site in our biomimetic catalytic system. In the reaction process, NHPI transforms into PINO via *in situ* transfer of single electron with the assistance of the accelerant. Thus, abstracting H atom from C-H bond by PINO could be realized under mild conditions.

(ii) A natural ubiquitous quinone (coenzyme Q10) and derivatives of anthraquinone were used as the cocatalysts to accelerate the electron transfer of NHPI to generate PINO.

(iii) Two methods were designed to fulfill multiple-noncovalent binding sites. One was that NHPI and quinone were substituted by polar functional groups which supplied binding sites. The other was that inorganic molecular sieves were used to simulate the surrounding environment formed by the enzyme.

2.2.1 The application of nonmetal catalytic system in the oxidation of ethylbenzene

Ethylbenzene oxidation can be effectively proceeded using coenzyme Q10 and NHPI as the catalyst system. Conversion of ethylbenzene reached 36.0% under 0.3 MPa O_2 at 80℃ for 10 h[27]. The biomimetic catalyst model of the combination of anthraquinone derivates and NHPI could effectively oxygenate hydrocarbons by O_2 under mild conditions. For example, when 1,4-diamino-2,3-dichloro-anthraquinone (DACAQ) and NHPI were employed, 67.9% conversion of ethylbenzene could be obtained for 10 h without over-oxidation products (the results of ethylbenzene oxidation catalyzed by other anthraquinone derivates and NHPI are listed in Table 2). However, the selectivity of acetophenone was relatively low and there were plenty of 1-phenylethyl hydroperoxide and 1-phenylethanol in products.

Table 2. Results of ethylbenzene oxidation catalyzed by anthraquinone derivates and NHPI

The substituted group of anthraquinone	Conversion (%)	Selectivity (%)		
		Acetophenone	Phenylethanol	Peroxide[a]
Q10[b]	36.0	43.5	20.2	36.3
hydrogen	41.2	32.5	14.8	52.7
2-chloro	35.7	24.8	22.4	52.8
2-ethyl	36.4	32.4	15.4	52.2
1-amido	39.6	12.2	16.8	71.0
2-amido	52.3	70.9	12.9	16.2
1,4-diamido-2,3-dichloro	67.9	73.5	13.1	13.4
No catalyst	10.9	0	12.5	87.5

a) Peroxide = 1-phenylethyl hydroperoxide. b) Q10 and NHPI as catalysts.

When HY zeolite was added to the catalyst system to simulate the surrounding environment formed by the enzyme protein, the orientation and high selectivity of the products were realized without influence on the activity of the catalyst. As shown in Table 3, the selectivity of acetophenone was above 91% after adding HY zeolite, and it was elevated 2.8 times of that without HY. On the other hand, the selectivity of 1-phenylethyl hydroperoxide was below 5%, which was only 10% of that without HY[27]. Obviously, these results were higher than those of other catalyst systems[20].

Table 3. The results of ethyl benzene oxidation catalyzed by anthraquinone derivates/NHPI/zeolite

Catalyst[a]	Conversion (%)	Selectivity (%)[b]			Yield[c] (%)
		Ace	Phe	Peroxide	
AQ/NHPI/HY	37.3	92.8	3.8	3.4	33.2
EAQ/NHPI/HY	36.9	91.8	3.1	5.0	32.5
CAQ/NHPI/HY	41.7	92.9	5.8	1.3	36.5
DACAQ/NHPI/HY	66.2	95.8	4.2	0	61.1
AQ/NHPI	41.2	32.5	14.8	52.7	12.5
EAQ/NHPI	36.4	32.4	15.4	52.2	—
CAQ/NHPI	35.7	24.8	22.4	52.8	—
DACAQ/NHPI	67.9	73.5	13.1	13.4	48.4

a) AQ = anthraquinone; EAQ = 2-ethyl anthraquinone; CAQ = 2-chloro anthraquinone; DACAQ = 1,4-diamino-2,3-dichloro-anthraquinone.

b) Ace = Acetophenone, Phe = phenylethanol, peroxide = 1-phenylethyl hydroperoxide.

c) The isolated yield of acetophenone; "—" denotes "absence of the isolated yield".

Based on the analysis of the catalytic performance of HY zeolite, it was verified that peroxide was orientably decomposed to acetophenone by the catalysis of HY zeolite and the decomposition proceeded synergistically via a protonized intermediate linked by two hydrogen bonds, but not a random radical cleavage. This nonradical mechanism can suppress random radical cleavage of peroxide and orient product generation. In addition, it was also proved that the HY zeolite could successfully serve as the function of the protein in enzyme. The mechanism of ketonic cleavage of peroxide in the presence of HY is presented in Fig. 8. During the reaction, peroxide comes into the pore of HY. Then, the adsorption complex which was a protonized intermediate linked by two hydrogen bonds acting as a cleavage transition state was formed by the oxygen of the hydroxyl of peroxide coordinating to the acidic proton on the HY surface. At the same time, 1-H proton of the hydroxyl of peroxide coordinated to the neighboring framework oxygen of HY. Afterward, the complex synergetically decomposed, resulting in dehydrolysis of the protonized hydroxyl, 1-H proton transferred onto HY surface, and ketonization of peroxide.

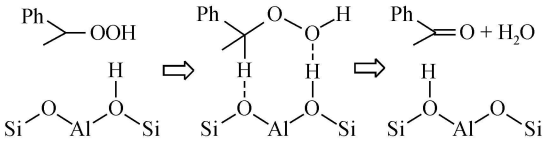
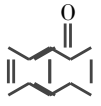
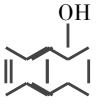
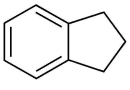
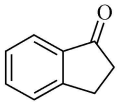
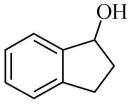
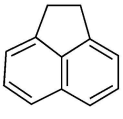
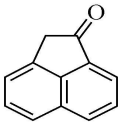
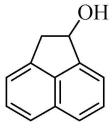
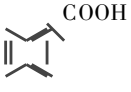
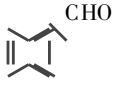
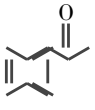
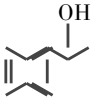
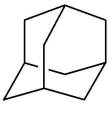
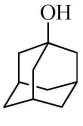
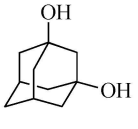
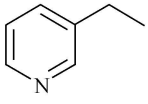
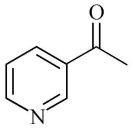
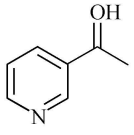


Fig. 8. Mechanism of ketonic cleavage of peroxide on HY.

2.2.2 Other applications of nonmetal catalytic system in hydrocarbons oxidation

The combination of NHPI and DACAQ catalyst system not only has good catalytic activity but also can increase the product selectivity in the oxygenation of hydrocarbons. In the oxygenation of fluorene, 84.8% fluorene was converted with 100% selectivity to 9-fluorenone when the reaction was carried out for 25 h. Organocatalysis system of the combination of NHPI and DACAQ could selectively oxidize various hydrocarbons including alkylaromatics and inert saturated alkanes, and the catalytic activity increased with elevating the reaction temperature. Tetralin was oxygenated with 91% conversion with the 98.1% selectivity of tetralone at 80 ℃ for 10 h. In the oxidation of cyclohexane, the conversion was only 5.2% at 80 ℃ for 5 h; whereas, when the reaction temperature was increased to 100 ℃ for 4 h, 14.9% conversion of cyclohexane could be obtained. The results of oxygenation of other hydrocarbons catalyzed by DACAQ and NHPI are listed in Table 5[28].

Table 5. Oxygenation of different hydrocarbons catalyzed by DACAQ/NHPI[a)]

Substrates	Time (h)	Conversion (%)	Selectivity (%)			
	5.0	85.1		63.9		25.7
	10.0	91.1		98.1		1.6
	6.0	91.2		65.8		16.2
	10.5	91.6		62.1		27.0
	5.0	5.2		31.8		36.4
	4.0[b)]	14.9		78.7		12.7
	9.0	16.7		61.8		30.6
	10	67.0		73.5		13.1
	7.0	82.4		66.5		21.5
	8.0	2.6		33.3		66.7
	7.0[c)]	13.0		76.3		23.7

a) Reaction conditions: 1.25% DACAQ and 5.0% NHPI, 80 ℃, 0.3 MPa O_2;
b) Reaction temperature: 100 ℃;
c) Reaction temperature: 120 ℃.

2.2.3 The reaction mechanism of hydrocarbons catalyzed by quinone and NHPI

Through investigating the interaction between NHPI and 2-ethylanthraquinone (EAQ) by *in situ* FT-IR, the single electron transfer mechanism of the hydrocarbons oxidation catalyzed by biomimetic model of the combined quinone and NHPI was suggested[27]. The carbonyl peak of EAQ was in the region of 1677 cm^{-1}, and the peak strength remarkably decreased in the FT-IR spectrum of the mixture of NHPI and EAQ. At the same time, two broad peaks at 3632 and 3544 cm^{-1} assigned to the -OH stretching vibration appeared in the spectrum. These indicated that EAQ reacted with NHPI and was converted to semihydroquinone or hydroquinone. The 3226 cm^{-1} peak, belonging to the stretching vibration of -OH of NHPI, disappeared in the FT-IR spectrum of the mixture of NHPI and EAQ. Concomitantly, a strong peak appeared at 1290 cm^{-1}. It might be assigned to the stretching vibration of N-O bond of PINO since its vibration often shows a broad and strong peak in this frequency region. These changes indicated that a majority of NHPI was converted to PINO by reacting with EAQ. And the electron transfer reaction between NHPI and EAQ is shown in Fig. 9.

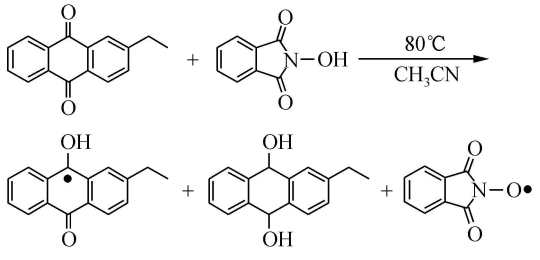


Fig. 9. The electron transfer reaction between NHPI and EAQ.

In organisms, the quinone coenzyme forms of QH_2 and QH as antioxidant can be easily abstracted a hydrogen atom by oxygen free radical. At the same time, QH_2 and QH are reduced to its oxidized state Q, and oxygen free radical is removed[29]. In the free radical reaction, QH_2 and QH are unstable and are generally used as the H feeder to radical and to generate the stable conjugate structure[30]. Thus, in the reaction catalyzed by NHPI and quinone, the generated QH_2 and QH can be easily re-abstracted H atom by other radicals and return to Q.

According to the above two kinds of reactions, the oxidation process of hydrocarbon by the Q/NHPI system can be elucidated, and the redox cycle is shown in Fig. 10. At first, NHPI is abstracted a hydrogen atom by Q to form PINO and Q is reduced to QH_2 and QH. The formed PINO abstracts a hydrogen atom from hydrocarbon to produce alkyl radical, and then reverts to NHPI. Alkyl radical interacts with O_2 and converts to alkylperoxyl radical. After further H-abstraction from QH or QH_2, alkylperoxyl radical converts to peroxide; simultaneously QH or QH_2 transforms to Q. Therefore, the redox cycle of the hydrocarbon oxidation is created.

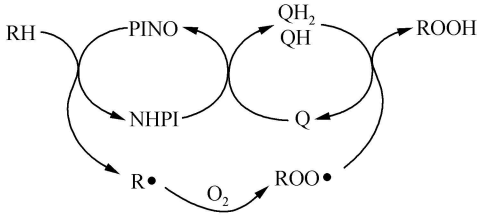


Fig. 10. Redox cycle for the oxidation of hydrocarbon by the Q/NHPI system.

3 Future scope

Nano-catalysts show higher catalytic activity than that prepared by conventional methods. For the oxidation of hydrocarbons, the substrate is nonpolar or weak polar molecule and is easily adsorbed on the hydrophobic catalyst surface. On the contrary, the oxygenation products are high polar molecules and are easily adsorbed on hydrophilic catalyst surface, which results in over-oxidation to byproducts. So, hydrophobic catalyst would benefit the process of hydrocarbon oxidation. The above ideas gave us a strategy for the further investigation of hydrocarbon oxidation. New catalyst research should be focused on the proper components, the proper surface properties that can recognize the substrate and the products, and the proper particle size of the catalyst.

Designing a highly efficienct catalyst, which is comparable with enzyme, is the dream for chemists and one of the frontiers of natural science. The next study should aim at mimicing the enzyme catalysis and developing new and highly efficienct catalysts to deal with the different substrates with special characteristics, which requests that the catalyst should comprise redox center, the accelerant for electron transfer, and multiple binding sites. This multi-functional catalyst has similar properties with the combination of different enzymes in organisms, so that it will bring higher efficiency and more convenient applications.

Organocatalysis is a new strategy and domain for synthetic chemistry. However, the application of organocatalysis in hydrocarbon oxidation is few. The catalyst, combined DACAQ with NHPI and developed by us, showed excellent activity, selectivity, broad substrates applicability, and good potential application in the oxidation of hydrocarbons. The outstanding catalytic performance of DACAQ confirmed the idea that the polar group of catalyst provided the multiple bonding sites in biocatalysis model. The further study on the catalytic mechanism of anthraquinone derivates and NHPI, and the relationship between the structure and catalytic behavior, will direct the design, development and application of the new organocatalysts that have a new structure and special catalytic behavior. Consequently, the new progress in the green synthesis of oxy-compounds will come true in the near future.

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