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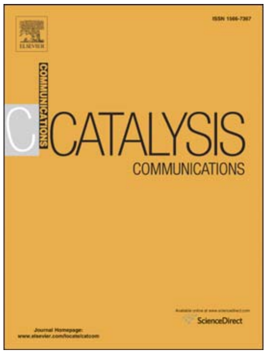

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Oxidation of cyclohexane to adipic acid catalyzed by Mn-doped titanosilicate with hollow structure

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Abstract

One-step oxidation of cyclohexane to adipic acid (AA) was carried out at 413 K over manganese-doped titanium silicalite with hollow structure (HTS) using oxygen as oxidant without any initiator or solvent. The catalyst exhibited high conversion (13.4%) and reasonable product (AA) selectivity (57.5%). Hot-separation and catalyst-recycle tests proved that the catalyst acted as a heterogeneous one and it could be reused four times without losing its activity. The synthesized materials were characterized by N_2 adsorption-desorption isotherm, FT-IR, UV-Vis and XPS techniques.

Key words: Cyclohexane, Adipic acid, Aerobic oxidation, Solvent-free, Mn-HTS

1. Introduction

The development of a simple and efficient process for the hydrocarbon activation with molecular oxygen can be one of the key technologies for synthesizing oxygenates, since some industrial processes are based on these reactions. Among them, the selective oxidation of cyclohexane to AA is an important reaction due to the fact that AA is a basic material for the production of Nylon-66 (production around million tons per year in the world) [1-3]. At present, it is commercially produced by a two-step process involving nitric acid oxidation of cyclohexanone and cyclohexanol (KA oils). These compounds generated from cyclohexane, however, limit the whole efficiency of the process owing to the low yields (8%) using homogeneous (cobalt-based) catalysts [4]. More importantly, the use of nitric acid causes some severe environmental problems in the latter process, since the emission of nitrogen oxides during the synthesis can lead to global warming and ozone depletion [1, 5]. Alternative routes for synthesis of adipic acid usually need a number of steps as shown in Scheme 1, and they are too expensive or too complicated to be used as a commercial process. The direct oxidation of cyclohexane to AA is a promising route for its application in industrial production, because it completely overcomes the major drawbacks mentioned above. Currently, direct production of AA from cyclohexane with alkyl hydroperoxide or O_3 as oxidant has been studied extensively with a catalyst consisting of cobalt salts [6, 7]. From an economic viewpoint, its cost is still prohibitive for less value-added cases. In contrast, a one-step catalytic cyclohexane oxidation to AA using molecular oxygen as a sole oxidant has been desired in view of green chemistry.

The challenge of obtaining adipic acid in a manner that is environmentally friendly with low costs has initiated the search for the direct oxidation of cyclohexane. Lu and co-workers described an aerobic catalytic system for the direct production of AA from cyclohexane based on the Anderson-type $[(C_{18}H_{37})_2N(CH_3)_2]_6Mo_7O_{24}$ catalyst [8]. Yu et al. developed a catalytic method for the direct oxidation of cyclohexane with O_2 using N-hydroxyphthalimide (NHPI) or some transition metal species as a key catalyst [9]. These catalytic processes, however, involve the homogeneous catalytic system. Furthermore, most of the NHPI is decomposed to phthalic acid and other related byproducts, and the polyoxometalate catalyst is difficult to be recycled. In contrast to the homogeneous catalytic systems, the heterogeneous systems such as metal-doped aluminophosphates [10, 11] and carbon nanotubes [12] have only a low efficiency for direct oxidation of cyclohexane to AA.

The MFI-type titanosilicate, TS-1, has been known for its remarkable catalytic activity in oxidation of cyclohexane to KA oils at mild conditions with H_2O_2 [13]. This titanosilicate-catalyzed oxidation process is believed to be a “green” route to substitute for old ones. Following Spinacé’s pioneer work with the TS-1 catalyst, Shi had developed a efficient titanosilicate catalyst with hollow structure (HTS) for use in the oxidation of cyclohexane and showed to be more active than TS-1 with H_2O_2 as oxidant [14]. This reason may be attributed to the enhancing of dimensions of the intra-particle pores and can intensify the transport of reactants and products in and out of the crystal’s channels [15]. On the basis of these results, HTS may exhibit better selectivity for AA in the aerobic oxidation of cyclohexane, since the diameter of AA (1.00 nm) is larger than these of cyclohexanone (0.51 nm) and cyclohexanol (0.58 nm). In contrast to the tremendous progress on titanosilicate catalysts for oxidation of cyclohexane to KA oils with H_2O_2, much less has been reported the titanosilicate-catalyzed aerobic oxidation of cyclohexane to AA, which is equally important to be developed from a simple bench-top procedure and to further apply it for industrial-scale applications. Herein, we explore an active, selective and green Mn-HTS catalyst to a one-step aerobic oxidation of cyclohexane to AA under mild reaction conditions (scheme 2).

2. Experimental

2.1 Synthesis of the catalytic materials and characterization

The HTS was prepared according to the post-synthesis method. First, TS-1 was synthesized from tetraethyl orthosilicate (TEOS), alkali-free TPAOPH solutions and titanium butoxide (TBOT) with a composition of SiO_2:0.4TPAOPH:0.01TiO_2:40H_2O. The resultant gel was hydrothermally treated at 443 K for 3 days under static conditions. The solid product was filtered, washed, dried and finally calcined at 793 K for 10 h. Secondly, the HTS solid was synthesized by treating with sulfuric acid solution with a weight ratio of the previous calcined TS-1:sulfuric acid:water = 10:1.0:140, and the acid-treated TS-1 was dispersed in TPAOPH solution in a weight ratio of molecular sieve:TPAOPH:water = 10:1.5:125. The mixture was then hydrothermally treated at 413 K for 3 days under static conditions. The solid product was filtered, washed, dried and finally calcined at 793 K for 10 h.

The manganese oxo-species (1.0 wt.% of Mn) were introduced onto the support by the wet impregnation method from EtOH and water (1:1) solution of $Mn(Ac)_2 \cdot 4H_2O$. Impregnated samples were evaporated at 373 K overnight and then calcined at 773 K in air for 3 h (with heating rate 5 °C/min). The investigated samples were denoted as xMn-HTS, where x is the manganese content in support in the weight percentage.

The characterizations of the materials were depicted in Supplementary data, including N_2 adsorption, X-ray diffraction, UV–Vis, FT-IR, XPS.

2.2 Cyclohexane oxidation

The catalytic oxidations were carried out in a 100 mL stainless steel reactor equipped with a Teflon beaker, magnetic stirrer. In a typical reaction, cyclohexane (119 mmol) was mixed with the target catalyst and then heated to the reaction temperature under a constant oxygen pressure. After reaction, the mixture was cooled down, dissolved in ethanol and filtered. Aliquots of the above mixture (25 μL) were withdrawn by a syringe. Each aliquot was diluted with 0.4 mL of toluene containing 50 mg of PPh_3 and internal standard (n-hexanol). The yield of cyclohexanol was calculated as a difference between the value obtained by GC and the concentration of cyclohexyl hydroperoxide determined iodometrically (reduction in cyclohexyl hydroperoxide with PPh_3 gives an additional amount of cyclohexanol). The obtained acid was analyzed by high-performance liquid chromatography using the external standard method.

3. Results and Discussion

3.1. Characterization of materials

Mn-HTS was characterized by N_2 adsorption-desorption, XRD, UV-Vis spectroscopy, FT-IR and XPS. N_2 adsorption-desorption images (Fig. 1A and B) depict the textural properties of the material. Apparently, the abrupt closure at $p/p_0 = 0.42$ on the desorption branch was characteristic of intra-crystalline voids in the samples, accessible only via entrances smaller than 4 nm [15]. Furthermore, Mn-HTS catalysts showed the higher pore diameter than pure HTS because Mn species with oxygen had a higher bond length than Si-O, indicating incorporation of Mn to form Si–O–Mn linkages in the zeolite framework sites [16]. XRD images (Fig. 1C) of the catalysts showed the same main diffraction peaks as those in XRD of normal TS-1 [17], indicating that the HTS is with MFI topological structure. Mn-HTS catalysts showed no additional diffraction intensity, thereby indicating that the Mn species were well dispersed either in the framework or on the internal surface of support materials. As examined by FT-IR (Fig. 1D), the intra-framework Ti and Si–O–Mn linkages formed were characteric by the absorption peak at 966 [18] and 1100 cm^{-1} [19], which further confirming that the catalysts were with MFI and had the framework Mn.

The corresponding UV–Vis spectrum showed two bands (Fig. 2A), the first band ca. 215 nm, which was assigned to a charge transfer from O^{2-} to tetrahedral Ti^{4+} in the zeolite framework, a second band around 300 nm indicated that the zeolite contained extraframework Ti species (e.g., octahedral Ti sites) [15, 20, 21]. The second assignments might be, however, somewhat hampered by overlap of signals corresponding to O^{2-} to Mn^{3+} electron transition (310 nm) [22]. Fig. 2B showed the XPS spectra for Ti 2p orbital in HTS and 1% Mn-HTS. The Ti 2p XPS spectra of the BE (binding energy) of the principal Ti 2p3/2 core electron [23] for the HTS could be deconvoluted into two contributions: one peak appeared at ca. 458.5 eV, which might be assigned to the octahedrally coordinated Ti^{4+} ion and another at ca. 460.0 eV associated Ti^{4+} in the tetrahedral coordination within the silica framework. The relative area ratio of the peak at 460.0 eV assigned to tetrahedral Ti species, however, dramatically decreased with the loading of Mn, suggesting a change in the coordination from tetrahedral to octahedral. This could be attributed to the change in the coordination number of titanium by the formation of a Ti-O-Mn bond [24]. In addition, the peaks were shifted in the higher binding energy in the Mn-HTS, which meant the change of Ti–O bonding strength with the Mn insertion [25]. Mn2p spectrum for 1.0% Mn-HTS was presented in Fig. 2C. The binding energy value of the Mn 2p3/2 peak was 641.5 eV. According to the literature [26], this value indicated that Mn was present as a mixture of Mn^{2+}, Mn^{3+} and Mn^{4+} on the surface of 1.0% Mn-HTS.

3.2 Catalytic performance of the different catalyst

To understand the influence of the framework of supports, incorporated ion types, and content, the reactivity of the prepared materials has been tested comprehensively for cyclohexane oxidation using O_2 as oxidant in a solvent-free system. The results are listed in Table 1. HTS support exhibited the high catalytic activity and AA selectivity compared the reference sample Silicon-1 and TS-1(entries 2-4). These differences might be explained by the following factors [14]: i) the enrichment of the external surface Ti concentration of HTS led to the better accessibility of Ti species as a catalytic active site for cyclohexane oxidation (measured from XPS and UV-Vis spectra; ii) the characteristic hollow structure of HTS could enhance the accessibility of active centers and diffusion of reactant molecules, thus decreased or even eliminated molecular diffusions (measured from N_2 adsorption-desorption). Entries 7–10 illustrated the metal-based HTS catalysts (such as Cr-HTS, Fe-HTS, Co-HTS, Mn-HTS) for the oxidation of cyclohexane. Among them, the catalyst Mn-HMS gave the highest selectivity of AA with a relatively high cyclohexane conversion, being plausibly attributed to the nature of the metal used (entry 10) [27]. Furthermore, the reference Mn_3O_4 catalyst showed a low selectivity of AA with 5.2% cyclohexane conversion by using 100 mg dosage (entry 5), confirming the important role of Mn species in the framework of the samples as a highly active component in the oxidation of cyclohexane to AA (measured from N_2 adsorption-desorption and XPS). This assertion might also support the difference among the catalytic performance of the different content Mn supported on HTS (entries 10-12). For example, the selectivity of AA was low (36.5%) upon 0.5% Mn-HTS catalyst. The framework Mn(IV)/Mn(III) as strong Lewis acid sites and highly active components could promote the simultaneous decomposition of peroxide and the production of radicals OH• [28], thus accelerating the oxidation of cyclohexanone and enhancing the selectivity of AA. In short, the synergistic effects among framework Ti, framework Mn and characteristic hollow structure made Mn-HMS an effective catalyst for the oxidation of cyclohexane to AA under mild conditions.

3.3 Effect of various parameters

In the following experiments, the influence of the amount of catalyst 1% Mn-HTS, reaction temperature, reaction time, as well as reaction pressure on the cyclohexane-oxidation, was investigated in a solvent-free system. Fig 3A shows that an increase in the amount of catalyst from 0.03 to 0.10 g resulted in a continuous and considerable increase of cyclohexane conversion from 3.3% to 13.4% and AA selectivity from 17.7% to 57.5%, respectively, with a concomitant decrease in the selectivity of KA oil from 80.7% to 21.0%. However, beyond this amount, the conversion of cyclohexane and the selectivity of AA increased, which might be attributed to the so-called “catalyst inhibitor reaction” phenomenon [29]. Fig. 3B illustrates the effect of reaction temperature on cyclohexane reaction. The conversion of cyclohexane was found to increase with an increase in reaction temperature and passed through a maximum at 413 K. But the highest selectivity was obtained at 408 K. A further increase in the reaction temperature resulted in a decrease of both conversion and selectivity, probably owing to the deep oxidation [30]. Fig. 3C presented that cyclohexane conversion continuously increased with reaction time. Synchronously, AA selectivity increased gradually, while KA oil selectivity decreased, the decrease might be due to its further oxidation of KA oils. Above phenomena might further indicate that KA oil should be intermediate products, the cyclohexane oxidation process was composed of the process of converting cyclohexane to KA oil and that of KA oil to AA. Fig. 3D illustrated the effect of reaction pressure on cyclohexane reaction and the conversion of cyclohexane increased with the increasing in reaction pressure and passed through a maximum at 1.4 MPa. But the highest selectivity was obtained at 1.0 MPa. A further increase in the reaction pressure resulted in a darkly decrease of both conversion and selectivity, which might be explained by the solubility of oxygen in the reaction system [31].

3.4 Stability of the catalyst: hot-separation and catalyst-recycle test

Hot catalyst filtration tests [32] were performed to verify the nature of catalysis in the catalytic systems studied. A hot reaction mixture containing the solid catalyst (1% Mn-HTS) was filtrated after 3 h, and the oxidation of the mother liquor (filtrate) was followed for another 6 h. As can be seen from Fig. 4A, the cyclohexane conversion did continue to increase, albeit at a much lower rate. The persistence of a low activity could be attributed to the thermal autoxidation, initiated by the oxygenated products, present in the mother liquor [33, 34]. Similar results were observed if the hot-filtration test was performed after 6 h. Metallic ions like Ti and Mn were detected in the filtered products solution by ICP-OES analysis and found to be below the detection limit (< 0.04 ppm), implying that Mn-HTS can act as truly heterogeneous catalyst. After four consecutive uses, the stability of 1% Mn-HTS was confirmed by comparison of the FT-IR and UV─Vis spectra of the fresh and three times reused (Fig. 1D and Fig. 2A).

In order to check the recycle of the catalyst, four reactions were carried out. After each reaction, the catalyst was separated by filtration and washed with water and ethanol for several times. Then, the catalyst was dried at 373 K for 6 h to remove water and ethanol. The regenerated catalyst was used for the recycling study under the same reaction conditions. The results on the fresh and regenerated catalyst were shown in Fig. 4B. It could be seen that the conversion of cyclohexane on the regenerated catalyst was slightly lower than that on fresh catalyst. The selectivity of AA on regenerated catalyst was almost equal with that over fresh catalyst. These results disclosed that the catalyst was stable and could be reused after the reaction.

3.5 The proposed reaction mechanism

Based on the results presented here, as well as those in previous studies [21, 35], three main conclusions emerge: (i) cyclohexane oxidation takes place on Ti sites mainly located in the external surface, (ii) the hollow structure of HTS favors the accessibility of active centers and diffusion of reactant molecules, and (iii) the reaction proceeds through radical intermediates. In the present reaction, the diameter of cyclohexane is 0.49 nm and that of the products cyclohexanol, cyclohexanone, cyclohexyl hydroperoxide (CHHP) and AA should be 0.58, 0.51, 0.69 and 1.0 nm, respectively. The hollow structure and Ti sites in the external surface therefore are more adapted for the production of bulky AA comparison of cyclohexanol and cyclohexanone. Similar reports also showed that Ti-loaded zeolites with larger channels appear more adapted for the oxidation of bulky molecules [36]. The oxidation of cyclohexane in this process first involves noncatalytic autoxidation of cyclohexane by oxygen to CHHP. Subsequently, the bulky Ti(OOCh) species was possibly formed by the reaction of TiOH with CHHP, and the homolytic fragmentation of Ti(OOCh) can yield Ti-centered radical species such as Ti(IV)-O• or Ti(IV)-OO• [21, 37]. The species was generally regarded as active centers for cyclohexane oxidation (Scheme 3). The presence of Mn^{3+} sites further increased the formation of CyOO•, which propagated the reaction with formation of cyclohexyl radical, thereby increasing the conversion. Additionally, adsorption of cyclohexanone on the Mn-doped catalyst surface might facilitate the aH-abstraction from cyclohexanone by CyOO•, by forming the cyclohexane-1,2-dione product, thus enhancing the AA formation rate [38]. This was in agreement with the observed relative high AA selectivity (84.5%)

with high cyclohexanone conversion (40.5%) in the oxidation pure cyclohexanone experiment (Table 1, entry 5).

4. Conclusion

In this paper, an efficient catalyst system for oxidation of cyclohexane to AA was developed using Mn-HTS as catalyst, molecular oxygen as oxidant in a solvent-free system. The high selectivity of AA (57.5%) and good cyclohexane conversion (13.4%) could be achieved over Mn-HTS catalyst in the optimized conditions. The catalyst could be reused with almost the same activity, with the potential industrial applications.

Acknowledgments

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Figure captions:

Fig. 1. (A) N_2 adsorption-desorption isotherms, (B) pore diameter distribution, (C) XRD, (D) FT-IR of samples parent HTS and the xMn-HTS.

Fig. 2. (A) UV-Vis, (B) Ti(2p) core level XPS, (C) Mn(2p) core level XPS of samples parent HTS and the xMn-HTS.

Fig. 3. Effect of the catalyst amount (A), reaction temperature (B), reaction time (C) and reaction pressure (D) on the conversion of cyclohexane and AA selectivity over the synthesized 1% Mn-HTS. (reaction conditions: 10 g cyclohexane, K/A oil is the cyclohexanol and cyclohexanone; Others include Glutarate acid, Succinate acid and Ester).

Fig. 4. Results of hot-separation (A) and recycle (B) test of 1% Mn-HTS catalyst at 413 K. (reaction conditions: 1.0 MPa O_2, cyclohexane 10 g, catalyst 0.1 g).

Table 1 Catalytic performance of the different catalyst[a]

Entry	Catalyst	Conversion[b] (%)	Selectivity[c] (%)					
			CyOH	Cyone	SA	GA	AA	Othes
1	Blank	1.0	32.5	46.9	--	--	5.8	14.8
2	Silicon-1	1.0	32.5	46.5	--	--	4.6	16.4
3	TS	1.7	48.4	50.5	--	--	--	1.1
4	HTS	7.6	24.4	33.2	--	--	30.7	11.7
5	Mn_3O_4	5.2	36.3	26.5	--	--	35.2	2.0
6	Mn-Silicon-1	6.2	24.5	41.5	0.9	1.1	22.7	9.3
7	Co-HTS(1%)	8.2	15.3	21.3	2.4	6.2	44.7	10.1
8	Fe-HTS(1%)	9.2	31.9	37.0	--	1.3	27.7	2.1
9	Cr-HTS(1%)	7.9	17.1	42.9	--	1.8	36.4	1.8
10	Mn-HTS(1%)	8.6	12.0	22.8	1.8	4.5	57.7	1.2
11	Mn-HTS(0.5%)	7.5	23.7	27.5	0.4	3.7	36.5	8.2
12	Mn-HTS(3%)	7.9	12.1	22.9	3.0	5.5	52.8	3.7
13[d]	Mn-HTS(1%)	43.2	--	--	1.7	11.9	85.3	1.0

[a] Reaction conditions: 0.1 g of catalyst; 119 m mol (10 g) of substrate; 1.0 MPa O_2; 413 K; 6 h.

[b] Cyclohexane conversion = (the amount (mmol) of starting cyclohexane □ the amount (mmol) of cyclohexane recovered)/the amount (mmol) of starting cyclohexane × 100%.

[c] Product selectivity = content of this product/Σ content (mmol) of each product) × 100%, CyOH: cyclohexanol, Cyone: cyclohexanone, SA: Succinate acid，GA: Glutarate acid，AA: Adipic acid, Others: Ester and Cyclohexyl hydroperoxide.

[d] Reactant is the cyclohexanone, reaction temperature: 373 K, oxygen pressure: 0.6 MPa.

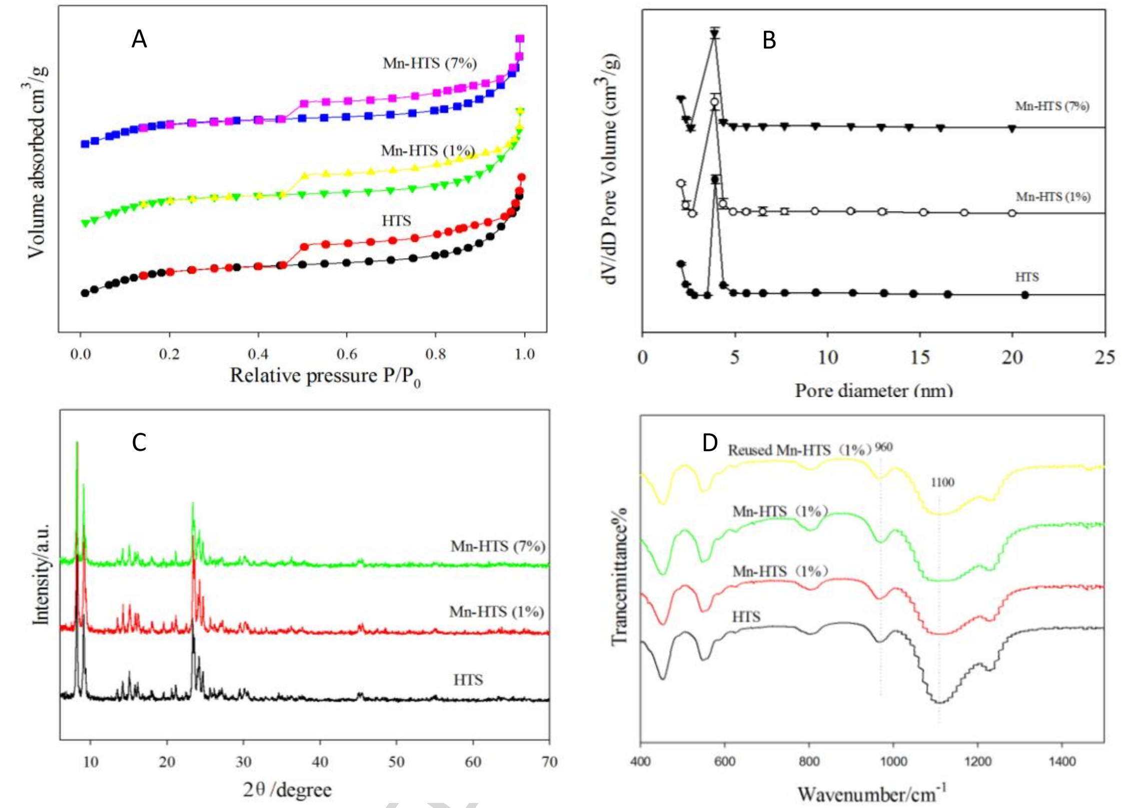

A
Volume absorbed cm^3/g
Mn-HTS (7%)
Mn-HTS (1%)
HTS
0.0
0.2
0.4
0.6
0.8
1.0
Relative pressure P/P$_0$
B
dV/dD Pore Volume (cm^3/g)
Mn-HTS (7%)
Mn-HTS (1%)
HTS
0
5
10
15
20
25
Pore diameter (nm)
C
Intensity/a.u.
Mn-HTS (7%)
Mn-HTS (1%)
HTS
10
20
30
40
50
60
70
2θ /degree
D
Reused Mn-HTS (1%)
960
1100
Mn-HTS (1%)
Mn-HTS (1%)
HTS
Trancemittance%
400
600
800
1000
1200
1400
Wavenumber/cm^{-1}

Fig. 1

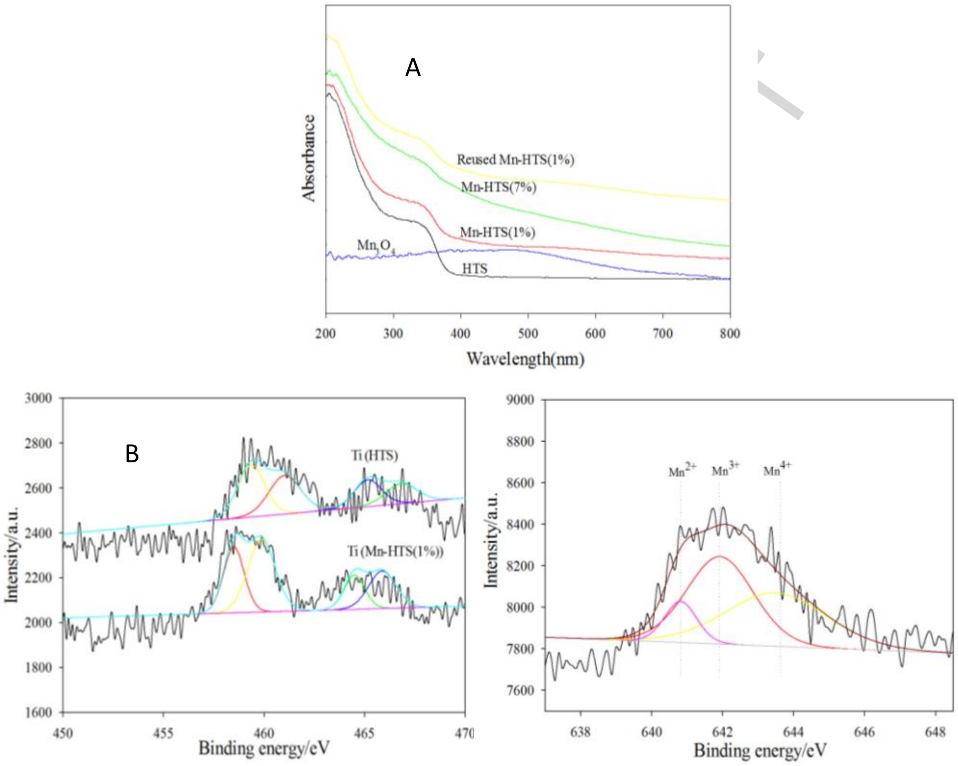

A
Absorbance
Reused Mn-HTS(1%)
Mn-HTS(7%)
Mn-HTS(1%)
Mn3O4
HTS
200
300
400
500
600
700
800
Wavelength(nm)
B
Intensity/a.u.
3000
2800
2600
2400
2200
2000
1800
1600
Ti (HTS)
Ti (Mn-HTS(1%))
450
455
460
465
470
Binding energy/eV
Intensity/a.u.
9000
8800
8600
8400
8200
8000
7800
7600
Mn2+
Mn3+
Mn4+
638
640
642
644
646
648
Binding energy/eV

Fig. 2

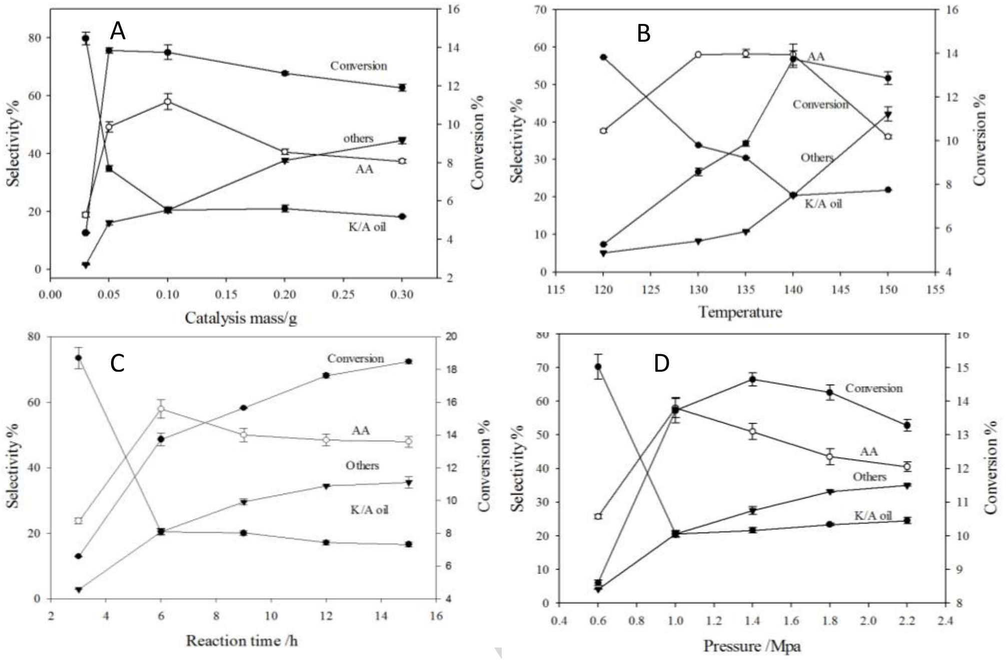

A
Selectivity %
Conversion %
Catalysis mass/g
Conversion
others
AA
K/A oil
B
Selectivity %
Conversion %
Temperature
AA
Conversion
Others
K/A oil
C
Selectivity %
Conversion %
Reaction time /h
Conversion
AA
Others
K/A oil
D
Selectivity %
Conversion %
Pressure /Mpa
Conversion
AA
Others
K/A oil

Fig. 3

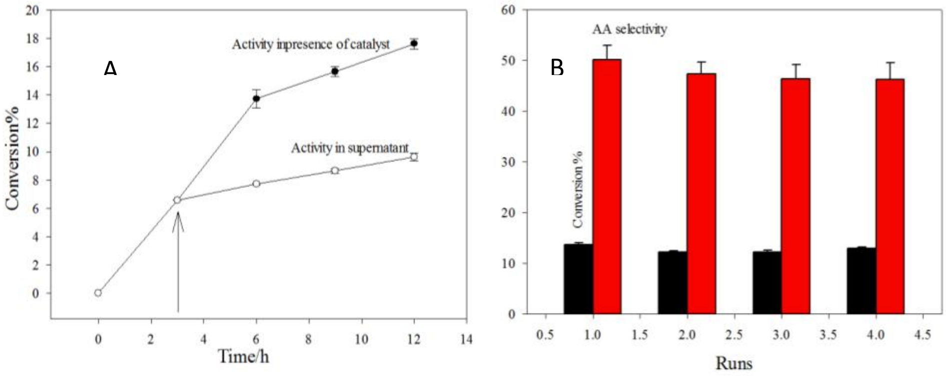
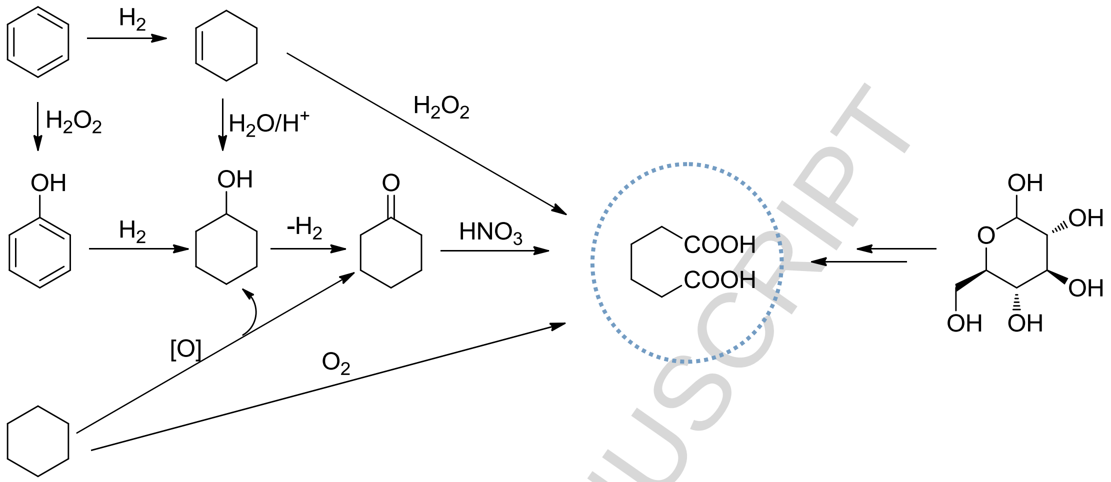
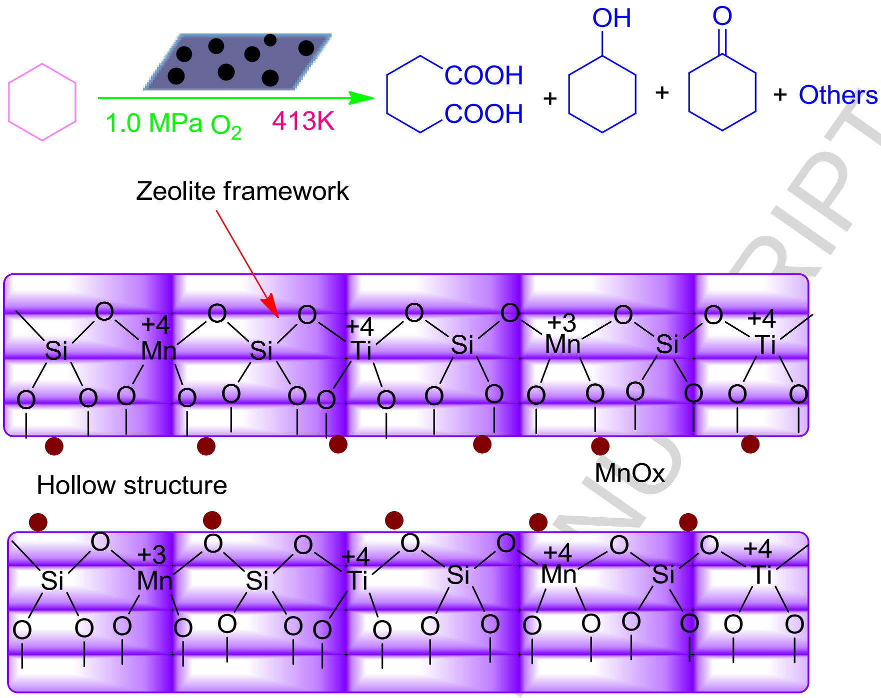

A
Conversion%
20
18
16
14
12
10
8
6
4
2
0
0
2
4
6
8
10
12
14
Time/h
Activity inpresence of catalyst
Activity in supernatant
B
AA selectivity
Conversion %
60
50
40
30
20
10
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Runs

Fig. 4

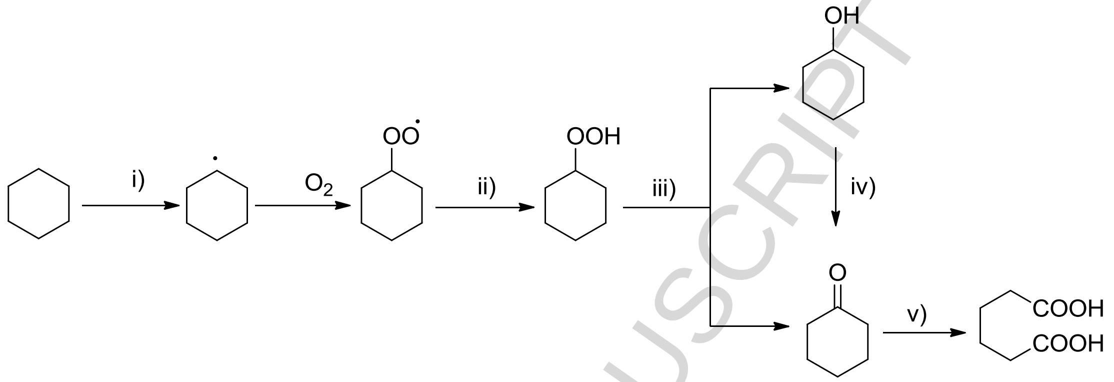
Scheme 1 Some alternative routes to adipic acid.



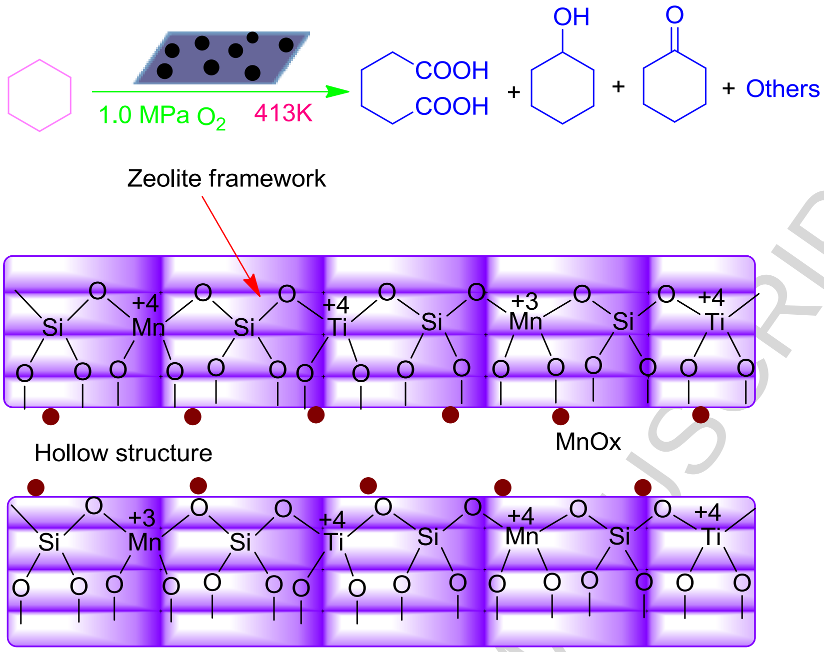
Scheme 2 Illustration for the cyclohexane oxidation over the synthesized catalysts.



Scheme 3 A possible reaction path for oxidation of cyclohexane to AA over Mn-HTS



i) O_2 or Ti-oxygen complex; ii)R-H; iii)Ti or Mn active site; iv)Ti-O_2 or Mn-O_2; v) Ti/Mn-O_2;



Graphical abstract

Highlights

- ▸Mn-HTS exhibits high selectivity for the one-step oxidation of cyclohexane to adipic acid.
- ▸The catalyst can be reused and easily separated from the reaction system.
- ▸Using molecular oxygen as oxidant without any initiator and solvent.