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# Direct cyclohexanone oxime synthesis via oxidation-oximization of cyclohexane with ammonium acetate

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An unexpected cascade reaction for oxidation-oximization of cyclohexane with ammonium acetate was developed for the first time to access cyclohexanone oxime with 50.7% selectivity (13.6% conversion). Tetrahedral Ti sites in Ni-containing hollow titanium silicalite can serve as bifunctional catalytic centers in the reaction. This methodology not only provides a direct approach to prepare cyclohexanone oxime, but also simplifies process chemistry. Various available nitrogen sources, such as ammonium salt and even ammonia can be used as starting materials.

The catalytic functionalization of hydrocarbons from petroleum is one of the greatest challenges that must be met for inert sp<sup>3</sup> C–H bond activation to be used widely in organic synthesis.1 Cyclohexanone oxime is an important chemical intermediate for the manufacture of nylon-6, 6. Most industrial processes of cyclohexanone oxime production involve multiple steps:<sup>2</sup> (a) aerobic oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone (KA oils), (b) conversion of ammonia to NH<sub>2</sub>OH salts, (c) and finally oximization of cyclohexanone with NH<sub>2</sub>OH salts (Scheme S1). In this process, the aerobic oxidation of cyclohexane suffers from the low conversion of less than 5% by preventing the deep-oxidation of KA oils and also involves the generation of alkaline waste. In addition, the preparation of NH<sub>2</sub>OH salts requires strongly acidic conditions and precious metal catalysts for catalytic reduction of nitrate salts or nitric oxide derived from NH<sub>3</sub>, and the oximization process coproduces large volumes of inorganic salt waste. Research efforts are being directed at more direct methods to produce cyclohexanone oxime, such as the ultraviolet photonitrosation of cyclohexane using NOCI or the nitrosation of cyclohexane with NOHSO<sub>4</sub> in fuming H<sub>2</sub>SO<sub>4</sub> medium,<sup>3</sup> but these processes involve highly nitrosating reagents and/or corrosive high energy

consumptions. Recently, it was reported that, with improvements in efficiency, such a direct ammoximation of cyclohexanone with  $NH_3^4$ or hydrogenation of nitrocyclohexane (or nitrobenzene)<sup>5</sup> to cyclohexanone oxime (Scheme S1) can be less expensive than the existing multistep processes. A direct photochemical transformation of cyclohexane into cyclohexanone oxime using *t*-butyl nitrite and UV-LED diodes is also described.<sup>6</sup> To our knowledge, however, no reaction has yet been developed where cyclohexanone oxime is directly accessible from cyclohexane and ammonium salt or NH<sub>3</sub> in a single catalytic system.

Titanium-silicalite (TS-1), with MFI cages connected by 10ring pore openings, has been known for its remarkable catalytic activity in alkane oxidation,7 alkene epoxidation,8 cyclohexanone ammoxidation<sup>9</sup> and phenol hydroxylation.<sup>10</sup> The isolated Ti-O<sub>4</sub> species in the silicate frameworks have been hypothesized to be critical active sites for activation of  $H_2O_2$ . The microporous structure of the TS-1 zeolite core, more specifically its bidirectional micropore (0.55 nm), however, strongly hinders the diffusion of reactants to the Ti-O<sub>4</sub> sites and thus constrains its catalytic activity. The preparation of hollow-structured TS-1 (HTS) is therefore carried out today by using post-treatment desilication, and the formation of the intra-particle pores in the structure can intensify the diffusion and accessibility to Ti-O<sub>4</sub> sites.<sup>11</sup> Accordingly, HTS is shown to be more active than solid-structured TS-1. Meanwhile, results from the current study demonstrates that by modifying the electronic structure of Ti-O₄ sites in TS-1 the product selectivity can be tuned. Au-modified TS-1 was reported to achieve high propylene oxide selectivity in direct propene epoxidation with H<sub>2</sub> and O<sub>2</sub>.<sup>12</sup> B-doped TS-1 used in the presence of a particular sulfolane co-solvent is capable of protecting the produced phenol from over-oxidation and dramatically enhanced the reaction selectivity.<sup>13</sup> Recent studies from our laboratory have shown that the TS-1 implanted with transition metal Mn(IV) ions is more adapted for the production of adipic acid compared with KA-oil.<sup>14</sup> Therefore, designing an efficient TS-1 catalyst with prominently improved catalytic activity and product selectivity is of prime scientific and industrial importance.

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We herein describe a direct, one-step approach to construct cyclohexanone oxime enabled by a modified hollow TS-1 catalyst using 30%  $H_2O_2$  as the oxidant in a suitable solvent. This one-pot strategy uses cyclohexane and ammonium salt ( or NH<sub>3</sub>) as readily available starting materials (Scheme 1), which simplifies process chemistry and obviates energy in intermediary isolation. The key element for success in this tandem reaction is a catalyst-directed selective oxidation of different reactants with in-situ generation of cyclohexanone and NH<sub>2</sub>OH intermediates, as an alternative to the oximization leading to cyclohexanone oxime.



Fig. 1 TEM images of HTS and 3% Ni/HTS.

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The structural properties of HTS and Ni/HTS catalysts are analyzed to elucidate the intrinsic reasons for the distinct catalytic activity (Table S1). XRD patterns of HTS and 3% Ni/HTS indicated that the prepared catalysts are crystalline MFI zeolite (Fig S1),<sup>15</sup> and the weak peak at 2 $\Theta$  = 43.24 ° ascribed to nickel oxide clusters (JCPDS Card No. 87-0712) can be observed. TEM imaging of HTS and Ni/HTS revealed catalyst particles with abundant intracrystalline voids, never connecting directly with the surface (Fig. 1). The nickel oxide species are uniformly dispersed in hollow cavities throughout the HTS support in the case of Ni/HTS. The presence of intracrystalline voids accessible only via entrances smaller than 4 nm is evident from abrupt closure at  $p/p_{0}$  = 0.42 on the desorption branch (Fig. 2A).<sup>16</sup> This kind of hollow cavity benefits diffusion and facilitates reactant transport to active sites and increasing the catalytic activity.

The Ti coordination state of HTS and Ni/HTS catalysts was studied by UV-visible, Fourier infrared and X-ray photoelectron spectroscopy. Compared with the silicalite-1 or Ni/silicalite-1, UV-visible spectra of HTS and Ni/HTS show a main band at 210 nm ascribed to tetrahedral TiO<sub>4</sub> species,<sup>17</sup> while a small band at 330 nm also appears, reflecting most likely the presence of ex-framework Ti species (Fig. 2B).<sup>18</sup> An additional band at 280 nm (O<sup>2-</sup> to Ni<sup>2+</sup> electron transition) is observed in Ni/HTS.<sup>19</sup> In Fig. S2, the characteristic band at 960 cm<sup>-1</sup>, not observed for silicalite-1, is attributed to the stretching vibration of Si-O-Ti bonds in the framework.<sup>20</sup> However, this peak position shifted to lower wavenumbers for Ni/HTS, which can be assigned to the presence of Ni species side-on bound to the silicon of Si-O-Ti unit, thus weakening the [Ti-O-Si] bond. Based on the Ti 2p XPS spectra (Fig. S3), the Ti 2p3/2 peak for the pure HTS is found at the binding energy (BE) of ~ 459.1 eV belonging to the tetrahedral TiO<sub>4</sub> species (with a fractional amount of 72% in Fig. S3).<sup>21</sup> This peak for the Ni/HTS, however, displays a lower BE, indicating that the Ti–O bonding strength was changed by the introduction of Ni species and influences the local chemical state of Ti<sup>4+</sup> ions. The BE of Ni 2p3/2 at 855.0°eV<sup>22</sup>/f<sup>4</sup>Ni/Hits<sup>6</sup> lower than that in Ni/silicalite-1 (856.1 eV), which indicates that the Ni species in Ni/HTS have a partial positive charge (Ni<sup>6+</sup>) due to the electron transfer between the Ti<sup>4+</sup> and Ni<sup>2+</sup> ions.





Based on the above experimental studies, the structural modification of HTS by the introduction of Ni atom is further studied by DFT calculation. Fig.S4 shows that three of the Ti–O bond lengths of framework Ti sites in Ni/HTS are found to be lengthened to 1.804–1.817 Å from 1.815–1.820 Å in pure HTS, indicating the more relaxed structure to facilitate the formation of five-membered cyclic Ti-OOH intermediate.<sup>23</sup> Meanwhile, the NBO charge of Ti atom in Ni/HTS is negatively charged with –0.027 e, which reflects that there is electron transfer from Ni to Ti. This negatively charged the Ti site in Ni/HTS leads to easier absorption and activation of H<sub>2</sub>O<sub>2</sub>, resulting in the enhancement of the rate relevant step.

Oxidation-oximization of cyclohexane to cyclohexanone oxime with CH<sub>3</sub>COONH<sub>4</sub> as nitrogen source over the assynthesized Ti catalysts was initially investigated in the presence of 30% H<sub>2</sub>O<sub>2</sub>. After extensive screening, the hollow HTS was found to be active for this reaction, and the selectivity to oxime was 41.8%, with the byproduct being KA-oil and nitroso ester (Table 1, entry 2). Similarly, solid-structured TS-1 is composed of Ti species existing in tetrahedral coordination. However, the low activity observed in the reaction using TS-1 in place of HTS (entry 3), indicates that the hollow structure of HTS facilitates reactant transport since the reactant molecules such as cyclohexane (0.48 nm),  $H_2O_2$  (0.26 nm) and CH<sub>3</sub>COONH<sub>4</sub> (0.54 nm) can easily come into the intracrystalline voids to active sites via the crystal's channels (0.55 nm). In contrast, another Ti-containing catalyst (entry 6), which lacks a tetrahedral environment of the Ti atoms with very low oxime selectivity (1.7%). As a result, the tetrahedral  $Ti-O_4$  species in HTS are responsible for the same activation of cyclohexane and CH<sub>3</sub>COONH<sub>4</sub>, the associated catalytic activity for the formation of oxime. With the aim to tune the catalytic selectivity of Ti-O<sub>4</sub> active sites, we further studied a new electronic structure modification of Ti-O<sub>4</sub> sites by implanting transition metal ions. As shown in Table 1 (entry 5), incorporation of the  $\mathrm{Ni}^{2+}$  species in the HTS is able to significantly enhance the oxime selectivity (from 41.8% to 50.7%). On the contrary, adding Al3+, Mo3+, Cr3+ and Mn2+ species to HTS can suppress the formation of oxime (entries 8-10). The increased selectivity over Ni-modified HTS may be due

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to the formation of this  $Ti-O_4$  species with favorable electronic effects, which was confirmed by calculating the Ni-modified HTS and the pure HTS structure (Fig.S4).

Table 1 Direct oxidation-oximization of cyclohexane to oxime over the different catalysts.  $^{\rm a}$ 

$\begin{array}{c c c c c c c c c c c c c c c c c c c $								
Entry      Catalyst      (%) <sup>b</sup> A      B      C      D        1      None      3.1      72.5      17.6      10.0      0        2      HTS      14.9      43.1      4.3      10.9      41.8        3      TS-1      7.4      47.3      6.5      11.7      34.5        4      Silicalite-1      5.2      64.0      22.1      11.4      2.6        5      3%Ni/HTS      13.6      31.2      3.2      14.9      50.7        6      2%Ti/silicalite-1      1.1      62.7      29.4      6.3      1.7        7      3%Ni/silicalite-1      4.4      55.8      35.1      9.1      0        8      3%Mo/HTS      9.5      24.5      7.3      33.2      35.1        9      3%Al/HTS      13.7      42.6      4.3      11.7      41.4        10      3%Cr/HTS      9.2      41.6      5.5      17.1      35.9        11      3%Mn/HTS      2.0      39.3      18.7      3.6	Entry	Catalyst	Conv.	Sel. (%)				
1      None      3.1      72.5      17.6      10.0      0        2      HTS      14.9      43.1      4.3      10.9      41.8        3      TS-1      7.4      47.3      6.5      11.7      34.5        4      Silicalite-1      5.2      64.0      22.1      11.4      2.6        5      3%Ni/HTS      13.6      31.2      3.2      14.9      50.7        6      2%Ti/silicalite-1      1.1      62.7      29.4      6.3      1.7        7      3%Ni/silicalite-1      4.4      55.8      35.1      9.1      0        8      3%Mo/HTS      9.5      24.5      7.3      33.2      35.1        9      3%Al/HTS      13.7      42.6      4.3      11.7      41.4        10      3%Cr/HTS      9.2      41.6      5.5      17.1      35.9        11      3%Mn/HTS      2.0      39.3      18.7      3.6      38.4			(%) <sup>b</sup>	А	В	С	D	
2      HTS      14.9      43.1      4.3      10.9      41.8        3      TS-1      7.4      47.3      6.5      11.7      34.5        4      Silicalite-1      5.2      64.0      22.1      11.4      2.6        5      3%Ni/HTS      13.6      31.2      3.2      14.9      50.7        6      2%Ti/silicalite-1      1.1      62.7      29.4      6.3      1.7        7      3%Ni/silicalite-1      4.4      55.8      35.1      9.1      0        8      3%Mo/HTS      9.5      24.5      7.3      33.2      35.1        9      3%AI/HTS      13.7      42.6      4.3      11.7      41.4        10      3%Cr/HTS      9.2      41.6      5.5      17.1      35.9        11      3%Mn/HTS      2.0      39.3      18.7      3.6      38.4	1	None	3.1	72.5	17.6	10.0	0	
3      TS-1      7.4      47.3      6.5      11.7      34.5        4      Silicalite-1      5.2      64.0      22.1      11.4      2.6        5      3%Ni/HTS      13.6      31.2      3.2      14.9      50.7        6      2%Ti/silicalite-1      1.1      62.7      29.4      6.3      1.7        7      3%Ni/silicalite-1      4.4      55.8      35.1      9.1      0        8      3%Mo/HTS      9.5      24.5      7.3      33.2      35.1        9      3%AI/HTS      13.7      42.6      4.3      11.7      41.4        10      3%Cr/HTS      9.2      41.6      5.5      17.1      35.9        11      3%Mn/HTS      2.0      39.3      18.7      3.6      38.4	2	HTS	14.9	43.1	4.3	10.9	41.8	
4      Silicalite-1      5.2      64.0      22.1      11.4      2.6        5      3%Ni/HTS      13.6      31.2      3.2      14.9      50.7        6      2%Ti/silicalite-1      1.1      62.7      29.4      6.3      1.7        7      3%Ni/silicalite-1      4.4      55.8      35.1      9.1      0        8      3%Mo/HTS      9.5      24.5      7.3      33.2      35.1        9      3%Al/HTS      13.7      42.6      4.3      11.7      41.4        10      3%Cr/HTS      9.2      41.6      5.5      17.1      35.9        11      3%Mn/HTS      2.0      39.3      18.7      3.6      38.4	3	TS-1	7.4	47.3	6.5	11.7	34.5	
5      3%Ni/HTS      13.6      31.2      3.2      14.9      50.7        6      2%Ti/silicalite-1      1.1      62.7      29.4      6.3      1.7        7      3%Ni/silicalite-1      4.4      55.8      35.1      9.1      0        8      3%Mo/HTS      9.5      24.5      7.3      33.2      35.1        9      3%Al/HTS      13.7      42.6      4.3      11.7      41.4        10      3%Cr/HTS      9.2      41.6      5.5      17.1      35.9        11      3%Mn/HTS      2.0      39.3      18.7      3.6      38.4	4	Silicalite-1	5.2	64.0	22.1	11.4	2.6	
62%Ti/silicalite-11.162.729.46.31.773%Ni/silicalite-14.455.835.19.1083%Mo/HTS9.524.57.333.235.193%Al/HTS13.742.64.311.741.4103%Cr/HTS9.241.65.517.135.9113%Mn/HTS2.039.318.73.638.4	5	3%Ni/HTS	13.6	31.2	3.2	14.9	50.7	
7    3%Ni/silicalite-1    4.4    55.8    35.1    9.1    0      8    3%Mo/HTS    9.5    24.5    7.3    33.2    35.1      9    3%Al/HTS    13.7    42.6    4.3    11.7    41.4      10    3%Cr/HTS    9.2    41.6    5.5    17.1    35.9      11    3%Mn/HTS    2.0    39.3    18.7    3.6    38.4	6	2%Ti/silicalite-1	1.1	62.7	29.4	6.3	1.7	
8      3%Mo/HTS      9.5      24.5      7.3      33.2      35.1        9      3%Al/HTS      13.7      42.6      4.3      11.7      41.4        10      3%Cr/HTS      9.2      41.6      5.5      17.1      35.9        11      3%Mn/HTS      2.0      39.3      18.7      3.6      38.4	7	3%Ni/silicalite-1	4.4	55.8	35.1	9.1	0	
9      3%Al/HTS      13.7      42.6      4.3      11.7      41.4        10      3%Cr/HTS      9.2      41.6      5.5      17.1      35.9        11      3%Mn/HTS      2.0      39.3      18.7      3.6      38.4	8	3%Mo/HTS	9.5	24.5	7.3	33.2	35.1	
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11 3%Mn/HTS 2.0 39.3 18.7 3.6 38.4	10	3%Cr/HTS	9.2	41.6	5.5	17.1	35.9	
	11	3%Mn/HTS	2.0	39.3	18.7	3.6	38.4	

<sup>a</sup> Conditions: 0.08g catalyst, cyclohexane 0.15 g (1.78 mmol), CH<sub>3</sub>COOH/CH<sub>3</sub>CN (7.5 ml, V=1:4), ammonium acetate as an ammonium source, cyclohexane: ammonium acetate =1:18 (molar ratio), cyclohexane:H<sub>2</sub>O<sub>2</sub> = 1:6 (molar ratio), reaction time 4 h at 110 °C. A = cyclohexanol; B = cyclohexanone; C = cyclohexyl nitrite; D = cyclohexanone oxime.

Encouraged by this result, different nitrogen sources, such as NH<sub>4</sub>Cl, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>HCO<sub>3</sub>, HCOONH<sub>4</sub>, ammonia and ammonia gas, were examined under the present reaction conditions (Table 2). Remarkably, ammonia was also a suitable substrate with providing the highest selectivity (57.2%), albeit resulting in low conversion. Generally, ammonia gas and ammonium salt from weak acids also reacted to give the desired oxime product at 22~30% selectivity. Other ammonium salts from strong acids such as  $\mathsf{NH}_4\mathsf{Cl}$  and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> gave only trace amounts of oxime products. This is likely because ammonia can be conveniently generated in situ through the dissociation of ammonium salt from weak acids due to the larger N–H bond distance of the NH<sup>4+</sup> connecting a weak acid anion established by DFT calculations (Table S2). Meanwhile, the N atom of ammonium salt from weak acids with high NBO charge is more easily activated to form NH<sub>2</sub>OH by electropositive Ti sites. The oxidation-oximization of cyclohexane to oxime with H<sub>2</sub>O<sub>2</sub> was also investigated using different solvents by 3% Ni/HTS catalyst. With these solvents such as acetonitrile, CF<sub>3</sub>COOH, CH<sub>3</sub>COOH and C<sub>2</sub>H<sub>5</sub>COOH, the selectivity of oxime was higher than 20% under the reaction conditions. A dramatic decrease of selectivity was observed with ethanol. Even worse results were obtained with ethyl acetate and t-butanol solvent, which are usually used as solvents in cyclohexanone ammoximation reaction. Conversely, as shown in Table S3, a dramatic improvement of selectivity was obtained by using a mixed solvent of CH<sub>3</sub>CN and CH<sub>3</sub>COOH, which allowed a conversion of cyclohexane close to 13.6% with a selectivity of oxime higher than 50%. Analysis of the UV-Vis spectra (Fig. S5A) and the continuum solvation model of DFT calculations (Fig. S6) reveals that the beneficial co-solvent effect can be rationalized by considering the interaction of solvents with each other, which can modify the CH<sub>3</sub>COOH

structure with electric charge and acid strength<sub>Vi</sub> in Addition, this may be due to the formation of the stellar formation of the HTS intracrystalline voids via the crystal's channels (0.55 nm) as an entrance, allowing oxime to remain relatively protected towards further oxidation. This is identified in solution by UV-Vis spectra and calculating the diameters of the free oxime molecule (0.51 nm) and complex (0.63 nm), as shown in Fig. S5B and Fig. S7.

Table 2 Direct oxidation-oximization of cyclohexane to oxime with different nitrogen sources.  $^{\rm a}$ 

Entry	Nitrogen	Temp.	Conv.	Sel. (%)			
	source	(°C)	(%) <sup>b</sup>	А	В	С	D
1	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	110	36.4	63.4	28.7	5.1	2.8
2	NH <sub>4</sub> Cl	110	18.0	65.7	29.4	2.1	2.7
3 <sup>b</sup>	$NH_3 \cdot H_2O$	90	4.1	21.3	17.0	4.5	57.2
4	NH <sub>4</sub> HCO <sub>3</sub>	90	0.1	48.4	14.1	20.9	16.6
5	HCOONH <sub>4</sub>	125	1.4	60.5	10.6	9.1	19.7
7	$CH_3COONH_4$	110	13.6	31.2	3.2	14.9	50.7
8	NH <sub>3</sub>	90	9.9	43.5	23.4	4.0	29.1

<sup>a</sup> Conditions: 0.08g 3%Ni/HTS catalyst, cyclohexane 0.15 g (1.78 mmol), CH<sub>3</sub>COOH/CH<sub>3</sub>CN (7.5 ml, V=1:4), ammonium acetate as an ammonium source, cyclohexane: ammonium acetate =1:18 (molar ratio), cyclohexane:H<sub>2</sub>O<sub>2</sub> = 1:6 (molar ratio), reaction time 4 h at 110 °C. A = cyclohexanol; B = cyclohexanone; C = cyclohexal nitrite; D = cyclohexanone oxime. <sup>b</sup> Using TFA instead of CH<sub>3</sub>COOH.

To understand the reaction mechanism, control experiments were performed (Table S4). When cyclohexane was explored under standard reaction conditions in the absence of CH<sub>3</sub>COONH<sub>4</sub>, cyclohexanone and cyclohexanol were obtained as major products. The treatment of cyclohexanol in the same pot resulted in the formation of the amounts of cyclohexanone on this Ni/HTS catalyst. As stated above, it can be deduced that the formation of cyclohexanone and cyclohexanol should occur over Ti-O<sub>4</sub> species from cyclohexane, and the further conversion of cyclohexanol to cyclohexanone should also occur over Ti-O<sub>4</sub> species, which is also consistent with the observation of the cyclohexanone and cyclohexanol byproducts. On the other hand, NH<sub>2</sub>OH as a possible intermediate was detected via Ti-catalyzed activation of ammonia from CH<sub>3</sub>COONH<sub>4</sub> in the absence of cyclohexane by spectrophotography.

The reaction mechanism was also confirmed with *in situ* FT-IR observation. By adding  $H_2O_2$  to the reaction system (Fig S8), the characteristic peaks of NH<sub>2</sub>OH appeared at 1023, 1227 and 1510 cm<sup>-1</sup> assigned for the v(N-O), v(N-O-H) and v(NH<sub>2</sub>), respectively.<sup>24</sup> Besides these, the appearance of the characteristic band at 1701 cm<sup>-1</sup>, attributed to v(C=O),<sup>25</sup> was taken as evidence of cyclohexanone formation. As the reaction proceeded, these peak strengths began to increase gradually and then reduced rapidly, indicating that cyclohexanone and NH<sub>2</sub>OH were formed and further transformed as intermediates. At the same time, the new characteristic modes of v(C=N) and v(N–O) of cyclohexanone oxime at 1667 and 985 cm<sup>-1</sup> coalesced,<sup>24C,26</sup> which confirms the occurrence of the oximization to oxime. In addition, the very small v(C=N) vibration around 1655 cm<sup>-1</sup> indicates the imine formation.<sup>25</sup> *In*-

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situ FT-IR spectra further allowed monitoring the NH<sub>2</sub>OH formation in absence of cyclohexane (Fig. S8). A band developing initially at 1101 cm<sup>-1</sup> can be assigned to NH<sub>3</sub> from the dissociation of CH<sub>3</sub>COONH<sub>4</sub> before reaction in CH<sub>3</sub>CN- $CH_3COOH$  co-solvent. After the addition of  $H_2O_2$ , the characteristic band of NH<sub>2</sub>OH shows that NH<sub>2</sub>OH is generated. On the basis of the above results and previous reports,<sup>23a,27</sup> a plausible mechanism is proposed in Fig S9. In this mechanism, framework Ti in HTS interacted with  $H_2O_2$  giving rise to the formation of Ti-OOH species,<sup>28</sup> which was responsible for the C–H bond activation of cyclohexane to produce cyclohexanone and cyclohexanol. Meanwhile, an initial attack of Ti-OOH species onto the N-H of ammonia from CH<sub>3</sub>COONH<sub>4</sub> affords the intermediate NH<sub>2</sub>OH, followed by oximization of cyclohexanone to generate oxime as a major pathway.<sup>27b</sup> Alternatively, the formed cyclohexanone directly condenses with ammonia to form imine, which is then oxidized to product oxime.

In summary, direct oxidation-oximization of cyclohexane to cyclohexanone oxime with 30%  $H_2O_2$  was achieved by using a peculiar  $CH_3CN-CH_3COOH$  cosolvent and an improved HTS catalyst by means of the introduction of Ni ((Ni/HTS). Mechanistic studies indicated that NH<sub>2</sub>OH and cyclohexanone as possible intermediates involved in our catalytic system. The simplicity of this one-step process, and the demonstrated possibility of the raw material transformation, make this methodology particularly attractive for a possible industrial development.

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#### **Conflicts of interest**

There are no conflicts to declare.

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#### **Figure-abstract**



### Highlights

► One-step preparation of cyclohexanone oxime from cyclohexane and ammonium acetate.

- ▶ 13.6% cyclohexane conversion and 51% cyclohexanone oxime selectivity are achieved.
- ► Tetrahedral TiO<sub>4</sub> sites allows to activate simultaneously the different reactants.
- ► Varieties of different ammonias as readily available starting materials.