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# Octahedral-based redox molecular sieve M-PKU-1: Isomorphous metal-substitution, catalytic oxidation of *sec*-alcohol and related catalytic mechanism

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# ABSTRACT

Octahedral-based redox molecular sieves M-PKU-1 (M=Cr, Fe) were synthesized by isomorphous metalsubstitution and used as catalysts for catalytic dehydrogenation of *sec*-alcohols using H<sub>2</sub>O<sub>2</sub> as oxidant. Various characterizations, such as X-ray diffraction Rietveld refinement and XPS spectrum, confirmed that transition metals were embedded successfully inside the PKU-1 framework with a high level (about ~50 atom %) and presented in the valence state of +3. Molecular probe analyzes suggested that Cr sites catalyzed the quick formation of active 'OH radicals, however strongly suppressed the generation of superoxide 'O<sub>2</sub><sup>-</sup> ions. Under the performed reaction conditions, 10%Cr-PKU-1 exhibited excellent catalytic performances (>99 % selectivity) and kept favorable recyclable stability. A hypothetical mechanism was proposed, which involved a  $Cr^{3+}-Cr^{2+}-Cr^{3+}$  circle when the oxidative dehydrogenation reaction happened. Furthermore, qualitative and quantitative analyzes were performed to illustrate the stepwise byproducts generated in the probable pathway due to the over-oxidization, but the selectivity to the two proposed pathways seemed to be in equal portions and didn't have any obvious preference. Obviously, our preliminary results still merit further exploration; we believe however, they would provide helpful information to better understand the structure-activity relationship and the key function of Cr-PKU-1 in the catalytic activation of H<sub>2</sub>O<sub>2</sub>.

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# 1. Introduction

Liquid-phase catalytic oxidation is widely used in the manufacture industry of both bulk and fine chemicals, and the traditional process usually involves stoichiometric inorganic oxidants, thus being unfavorable due to the environmental protection [1]. Employing homogeneous catalysts, i.e. soluble metal salts or complex molecules, are conventional and usually efficient, however suffer from the disadvantages in difficult recovery, low recycling ability and easy deactivation [2]. On the other hand, heterogeneous catalytic systems using redox molecular sieves are easy to handle these issues, by incorporating metal ions into the framework of zeolites or zeolite-like materials [3,4]. The local confinement of the redox active sites in their channels/cavities can provide a microenvironment analogy with enzymes and therefore potentially endow the catalyst with unique activity and selectivity.

A typical example is TS-1 (a titanium-substituted silica-based molecular sieve), which was first synthesized by Taramaso et al.

\* Corresponding authors. *E-mail addresses:* gaowl@cqu.edu.cn (W. Gao), taoyang@cqu.edu.cn (T. Yang). in 1983 and has been extensively investigated over the past few decades [5]. This microporous material with redox sites was proved to efficiently catalyze a wide variety of oxidative transformations with H<sub>2</sub>O<sub>2</sub>, RO<sub>2</sub>H, or O<sub>2</sub> under relatively mild conditions [6–11]. Nevertheless, the titanium concentration in TS-1 is quite low (the maximum atomic ratio of Si/Ti is about 2.5 %), because of the incompatible ionic radii and different coordination numbers between Ti<sup>4+</sup> and Si<sup>4+</sup>. In fact, transition metals such as titanium prefer octahedral coordination, and along this line, octahedralbased molecular sieves (OMS) are an alternative and promising system to accommodate transition metal ions as redox sites. Till now, Todorokite-type OMS is the typical and successful case, in which the rock salt blocks of manganese oxides are interlinked forming one-dimensional tunnels via rutile-type connection [12,13]. Indeed, Todorokite-type catalysts have already exhibited good performances in some oxidation and hydration reactions [14-18].

On the other hand, there is another interesting system of octahedral-based molecular sieves (denoted as PKU-n), which consist of cost-effective elements such as aluminum and boron [19–24]. Among them, PKU-1 was the most extensively







investigated both in structure and in catalytic properties, [25–29] beneficial from its easy preparation, high thermal stability, substantial specific acidic sites, and most importantly, Al<sup>3+</sup> in PKU-1 can be replaced by  $Cr^{3+}$ ,  $Fe^{3+}$  or  $Ga^{3+}$  in a very high level [19]. Single crystal X-ray diffraction revealed that PKU-1 is consisted of AlO<sub>6</sub> octahedra by edge-sharing exclusively, affording 18-ring channels along the *c*-axis. Borates groups, in the forms of BO(OH)<sub>2</sub>, BO<sub>2</sub>(OH) and B<sub>2</sub>O<sub>4</sub>(OH), attach to AlO<sub>6</sub>-framework by sharing vertex oxygen atoms. The BO(OH)<sub>2</sub> and BO<sub>2</sub>(OH) groups reside within the 18-ring channels and narrow these channels along the [001] direction (Fig. 1a), while B<sub>2</sub>O<sub>4</sub>(OH) groups attach to the walls of 10-ring channels and almost block the channels along the [100] direction (Fig. 1b).

In this study, we synthesized metal-incorporated PKU-1 (denoted as M-PKU-1, M=Cr or Fe) and Cr-PKU-1 was proved to be quite efficient to catalyze the oxidation of *sec*-alcohols into the corresponding ketone compounds with a high selectivity (99% using  $H_2O_2$  as the oxidant), which is considered as one of the important transformations because of the wide utility in pharmaceutical syntheses and fine chemical engineering [30–32]. Obviously, homogeneous catalysis on this reaction hold several drawbacks in reactor corrosion and catalyst recovery et al. [33–36] therefore a green oxidation system using recyclable heterogeneous catalysts is desired [37–40].

The systematic survey on the catalysis conditions of M-PKU-1 suggests that 10%Cr-PKU-1 is the most efficient catalyst for a variety of *sec*-alcohols. The transformation from cyclohexanol to cyclohexanone (abbreviated as CHOL and CYC for clarity, hereinafter) was selected as the model reaction to understand the catalytic mechanism. The results indicate the presence of  $Cr^{3+}$  in the framework of PKU-1 promotes the activation of  $H_2O_2$  into OH radicals exclusively (prohibiting the formation of  $O_2^-$  ions in the meantime). An appropriate concentration of OH radical is the key to the high selectivity (99%) to CYC under mild conditions, and the oxidation process was speculated accordingly, during which a  $Cr^{3+}-Cr^{2+}-Cr^{3+}$  cycle was involved.

As proved in the following, a low-level Cr in PKU-1 tends to provide lower concentration of OH radical and thus results into a long reduction period, while the over-high concentration of  $Cr^{3+}$  in PKU-1 (i.e. 30 atom %) generated excessive 'OH radicals and side-reactions/over-oxidation were therefore unavoidable. For example, CHOL was degraded successively into some low-molecular-weight

organic molecules through multistep oxidative reactions. We also performed qualitative and quantitative analyzes on over-oxidized products in order to better understand the function of Cr-PKU-1 in  $H_2O_2$  activation, the results indicate a gentle generation rate of 'OH (from  $H_2O_2$ ) would lead to the high selectivity of ketone, but a higher 'OH concentration could lead to diverse by-products such as adipic acid or cyclic lactone. In general, this study is a preliminary study on the controllable and selective activation of  $H_2O_2$  catalyzed by Cr-PKU-1, and considering the significant capacity to accommodate desired metals, M-PKU-1 catalysts really holds high potentials, for example, on catalyzing other redox reactions, probably with additional loading of cocatalysts.

# 2. Experimental section

## 2.1. Syntheses of Cr-PKU-1, Fe-PKU-1 or Fe-Cr-PKU-1 catalyst

The syntheses of M-PKU-1 were carried out in a closed Teflon autoclave by the boric acid flux method as described in the literature [19]. Typically,  $Cr(NO_3)_3 \cdot 9H_2O$  (0.5 mmol),  $Al(NO_3)_3 \cdot 9H_2O$ (4.5 mmol) and concentrated HNO<sub>3</sub> (0.3 mL) were first loaded to a 25 mL Teflon container and slowly heated until a homogeneous solution was formed. Then, a large amount of boric acid (100 mmol), functioned as both reaction medium and reactant, was charged into the autoclave. Next, the autoclave was sealed and heated at 513 K for 120 h. After the reaction, the autoclave was naturally cooled to room temperature and the resultant solid was washed with warm water (343 K) in order to completely remove residual boric acid or other soluble components. The as-synthesized Cr-PKU-1 powder is greenish.

In the literature, the molecular formula of PKU-1 was identified to be  $HAl_3B_6O_{12}(OH)_4$  [19]. Therefore, as for Cr-PKU-1, for example with 10 atom % substitution, the exact formula is  $HCr_{0.3}Al_{2.7}B_6O_{12}$ (OH)<sub>4</sub>. For simplicity, these as-synthesized Cr-PKU-1 samples were denoted sequentially as 0%, 6%, 10%, 20%, 30%, 40% or 50%Cr-PKU-1, according to the increase *x*.

The syntheses of Fe-PKU-1 and Fe-Cr-PKU-1 samples were similar with those of Cr-PKU-1. Fe(NO)<sub>3</sub>·9H<sub>2</sub>O was used as the Fe<sup>3+</sup> source. According to the initial loading amount of transition metals, the as-obtained Fe-PKU-1 samples were marked as 0%, 5%, 10%, 20% or 30%Fe-PKU-1, while bimetal-substituted PKU-1



Fig. 1. Octahedral-based framework of PKU-1 stabilized with three types of borate hydroxyl groups along 18-ring (a) and 10-ring (b) windows; red octahedron, AlO<sub>6</sub>; green octahedron, CrO<sub>6</sub>; cyan, yellow and grey spheres represent O, B and H atoms, respectively.

samples were denoted as 0%Fe-5%Cr, 5%Fe-5%Cr, 10%Fe-5%Cr or 20%Fe-5%Cr-PKU-1, respectively.

#### 2.2. Catalyst characterizations

2.2.1 Powder X-ray diffraction data were collected at room temperature on a PANalytical X'pert powder diffractometer equipped with a PIXcel 1D detector under Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å). The operating voltage and current were 40 kV and 40 mA, respectively. Le Bail fitting was performed using the TOPAS software package [41]. In order to *in-situ* observe the phase transformation under higher temperature, a high-temperature powder XRD experiments were carried out on a Bruker D8 Advance diffractometer (Cu K $\alpha$  radiation,  $\lambda$  = 1.5406 Å) with a computer-controlled furnace. The sample was loaded on a platinum strip and heated from room temperature to 1300 K in air at a heating rate of 5 K/min, and the XRD data were collected after the temperature was stabilized for 1 h at each chosen temperature.

2.2.2 X-ray photoelectron spectra (XPS) were acquired with UK Kratos Axis Ultra spectrometer with Al K $\alpha$  X-ray source operated at 15 kV and 15 mA. Kinetic energies of photoelectrons were measured using a hemispherical electron analyzer working at the constant pass energy (40 eV). The pressure in the chamber was less than  $5.0 \times 10^{-9}$  Torr. The XPS data were collected in increments of 0.1 eV with dwell time of 500 ms. Electron binding energies were calibrated against the C 1 s emission at  $E_{\rm b}$  = 284.6 eV to correct the contact potential differences between the sample and the spectrometer.

2.2.3 Cyclic voltammetry (CV) was performed to identify the redox behavior of Cr-PKU-1. To prepare the testing electrode, a viscous slurry containing 74 wt % Cr-PKU-1, 18.5 wt % acetylene black, and 7.5 wt % PTFE was mixed and pressed onto a nickel foam current collector. After that, the electrode was dried in vacuum and maintained at 333 K for 24 h in prior to measurements. Electrochemical tests were examined on an electrochemical workstation (Autolab Pgstat302N, Switzerland). The working solution was prepared by mixing CH<sub>3</sub>CN (80 mL), dimethyl sulphoxide (DMSO) (0.5 mL) and 0.1 M KCl solution (10 mL). In a three-electrode cell, Pt foil, Ag/AgCl and the above loaded nickel foam were used as the counter, reference and working electrodes, respectively. Cyclic voltammetry curves were obtained in the potential range of  $-1.0 \sim 0$  V vs. Ag/AgCl by varying the scan rate from 5 to 100 mV·s<sup>-1</sup>.

2.2.4 Sample morphology was examined with a field emission scanning electron microscopy (JEOL, JSM-7800F) equipped with an energy dispersive spectrometer (EDS) analyzer. Samples were prepared by dispersing dry powder on double-sided conductive adhesive tape followed by coating with a gold film. The recorded SEM image shown in this work was at a magnification of  $1300 \times$ .

2.2.5 UV–Vis diffuse reflectance spectrum (UV–Vis DRS) was collected using a Shimadzu UV-3100 spectrometer equipped with an integrating sphere and using  $BaSO_4$  as a reflection standard. Spectra were recorded in the range of 190–1000 nm in 0.5 nm steps with a scan speed of 60 nm/min and time constant of 2 s. In the visible range, a constant slit width of 2 nm was used for the monochromator, and the reflected radiation was detected with a photon multiplier detector. The wet pastes were placed on the window of the integrating sphere for testing.

2.2.6 Combined thermogravimetric (TG) and differential scanning calorimeter (DSC) analyzes were performed on a Mettler-Toledo TGA/DSC1 instrument at a heating rate of 10 K/min from room temperature to 1173 K. Its temperature precision was  $\pm 0.5$  K and microbalance sensitivity was less than  $\pm 0.1$  µg. Blank experiments without samples were carried out to obtain the base-lines to calibrate the experiments with samples at different heating rates. Under an inner atmosphere of high purity nitrogen (a flow

rate of 80 mL/min), the samples were heated from room temperature to 378 K, keeping at 378 K for 10 min to remove the moisture content, and then further heated up to 1173 K. Besides, all samples were kept at 10  $\pm$ 1 mg for avoiding heat transfer limitations.

2.2.7 Photoluminescence (PL) spectroscopy was used to detect OH radicals formed over Cr-PKU-1 catalyst using terephthalic acid (TA) as a probe molecule. In a typical run, 40 mg of 10%Cr-PKU-1 was dispersed in a mixed aqueous solution containing 3 mmol TA, 20 mmol CHOL, 20 mL CH<sub>3</sub>CN, and 40 mmol H<sub>2</sub>O<sub>2</sub>. After stirring for a specified interval of time, the suspension was withdrawn and then centrifuged to remove the powder. The upper and transparent solution was used for the PL measurement with an excitation irradiation at 328 nm on a Hitachi F4600 fluorescence spectrometer. PMT voltage was fixed to be 700 V, and the width of excitation and emission slit were both set to 2.5 nm.

2.2.8 UV–Vis absorption spectra were used to detect superoxide ion  $(\cdot O_2^-)$  formed over Cr-PKU-1 catalyst using nitroblue tetrazolium (NBT) as a probe molecule. In a typical run, 40 mg of 10% Cr-PKU-1 was dispersed in a mixed aqueous solution containing 3 mmol NBT, 20 mmol CHOL, 20 mL CH<sub>3</sub>CN, and 40 mmol H<sub>2</sub>O<sub>2</sub>. After stirring for a specified interval of time, the suspension was withdrawn and then centrifuged to remove the catalyst. The upper solution was diluted for 20 times with DMSO and then used for UV–Vis absorption measurement in a UV–Vis spectrometer (PUXI TU-1810, China).

## 2.3. Catalytic dehydrogenation

All organic solvents were purified by distillation method, other substrates such as *sec*-alcohol were used as received. Catalytic dehydrogenation of *sec*-alcohols was performed in a 50 mL single-neck round-bottom flask immersed into a silicon oil bath and stirred with a magnetic stirrer. In a standard run, 20 mmol CHOL, 20 mL CH<sub>3</sub>CN, 40 mg 10%Cr-PKU-1 catalyst and 40 mmol H<sub>2</sub>O<sub>2</sub> (30 wt %) were mixed in the flask. After heated at 353 K for 8 h, reaction mixture was extracted with a syringe to transfer to a centrifuge tube, and subsequently centrifuged to remove the solid catalyst. Finally, the obtained transparent solution was analyzed qualitatively or quantitatively with chromatography-mass spectrometry (GC–MS), gas chromatography (GC) and high performance liquid chromatography (HPLC), respectively.

GC–MS was performed on an Agilent 7890N gas chromatograph coupled with a capillary column (DB-5: length, 30 m; inner diameter, 0.25 mm) and mass spectrum system (Agilent 5975C). Helium was used as both the carrier (1 mL/min) and make-up gas (40 mL/min). GC–MS spectra were identified by comparing the *m/z* value of each peak with the NIST Mass Spectral database.

GC was used to determine the concentration of the substrates and products on a Techcomp GC 7800 gas chromatograph equipped with a flame ionization detector (FID). A capillary column (CP-43: length, 25 m; inner diameter, 0.53 mm; film thickness, 1.0  $\mu$ m) was chosen to separate the mixed components at the following condition: 423 K for capillary column, 473 K for injector port, and 523 K for FID detector.

An Agilent 1260 infinity HPLC system coupled with an autosampler, quaternary pump, and ultraviolent detector was used to determine the concentration of adipic acid and glutaric acid in the study. The HPLC was performed on a COSMOSIL 5C18-PAQ column (length, 250 mm; inner diameter, 4.6 mm) and the column was held at 298 K. The mobile phase was a combination of solvent A (20 mM potassium phosphate dibasic in water adjusted pH to 3.0 with phosphoric acid) and solvent B (methanol). The gradient analysis was performed using 84 % solvent A and 16 % B solvent. The injection volume was 20  $\mu$ L. For all gradient segments, the elution flow rate was 1.2 mL/min, and the detection wavelength was set at 510 nm.

# 3. Results and discussion

## 3.1. Isomorphous substitution by transition metals

Fig. 2 gives the XRD patterns of the as-synthesized Cr-PKU-1 samples and the Le Bail fitting for the pattern of 10%Cr-PKU-1, as a representative. XRD patterns for all Cr-containing PKU-1 samples (the right inset of Fig. 2) are almost the same with that of the parent PKU-1, suggesting that Cr incorporations do not change their host structures. In addition, Le Bail fitting to XRD pattern of 10% Cr-PKU-1 gives a good convergence, and the refined cell parameters are *a* = 22.06 Å, *c* = 7.06 Å and *V* = 2978 Å<sup>3</sup>. The refined unit cell volumes give a linear dependence on the incorporated Cr content, and the up-limit amount of incorporated Cr is in the high level and reaches up to ~50 atom %. The expansion of unit cell volumes coincides with the fact that Cr<sup>3+</sup> ion has a larger radius (0.615 Å, coordination number (CN) = 6) than Al<sup>3+</sup> (0.535 Å, CN = 6) [42].

In one sense, Cr-PKU-1 can be regarded as a solid solution formed by the substitution of Al<sup>3+</sup> with Cr<sup>3+</sup>. However, under the present synthetic conditions, only partial solid solutions can be prepared, namely that purely Cr-substituted PKU-1 cannot be prepared. Nevertheless, the significant changes of cell parameters definitely confirmed the successful incorporation of Cr<sup>3+</sup> into the PKU-1 framework (UV-vis spectra also give another evidence for the successful Cr-incorporation, which was shown in Fig. S1 in the Supporting information, S1). In some tetrahedral-based molecular sieves, their unit cell parameters generally have no obvious change due to the extra-framework insertion or low-concentration-type incorporation in the framework, so the framework substitution by transition metal was often doubtful and cannot be conclusively drawn [43,44].

Besides Cr-PKU-1 catalysts, Fe-PKU-1 and Fe-Cr-PKU-1 were also prepared, whose powder XRD patterns as well as refined cell volumes were provided in Figs. S2–S5, SI. The XRD analyzes indicate these as-prepared catalysts are successful and phase-pure (with no impurity); the refined unit cell volume from Le Bail fitting also give a linear expansion along with the increasing doped metal cations.

The physicochemical properties of the as-synthesized M-PKU-1 catalysts were also characterized by many measurements. For example, as for Cr-PKU-1 catalysts, SEM was employed to observe their morphology (and homogeneity), *in-situ* high temperature XRD patterns and TGA-DSC analysis were performed to monitor their thermal behaviors, and XPS spectrum was collected to

identify their chemical compositions and valence states for Cr-PKU-1. The detailed discussions about these characterizations were placed in the Figs. S6–S9, SI.

#### 3.2. Catalytic performance

#### 3.2.1. Optimizations of reaction conditions

In this study, Cr-PKU-1 catalysts were applied in the liquidphase oxidation of several selected *sec*-alcohols with 30 wt %  $H_2O_2$  as oxidant (see Fig. 3). Under the given conditions, 10%Cr-PKU-1 was demonstrated to have a high selectivity for all *sec*alcohols to ketones. For example, when CHOL was used as reaction substrate, the corresponding ketone (CYC) was obtained with a high selectivity (>99 %) along with the highest turnover frequency (TOF). The cyclic *sec*-alcohols were easily converted to the corresponding carbonyl compounds comparing to acyclic ones. Maybe, cyclic structure is beneficial to stabilize the corresponding fatty ketones and to lower its activation energy in dehydrogenation process. Owing to the highest TOF in CHOL-to-CYC, CHOL was chosen as the model reaction substrate in the following investigations.

Reaction medium is a key factor for catalytic reactions both in homogeneous and in heterogeneous systems. An appropriate solvent can effectively reduce the surface Gibbs energy and minimize side reactions. Therefore, 7 polar solvents, including acetonitrile (CH<sub>3</sub>CN), tetrahydrofuran (THF), dimethyl formamide (DMF), ethyl alcohol (EtOH), methyl alcohol (MeOH), acetone and water (H<sub>2</sub>O) were chosen as reaction media due to their miscibility with reactants, while nonpolar solvents such as toluene, hexane and dichloromethane were not the appropriate candidates because of the formation of two immiscible phases. As shown in Fig. 4, nearly 100 % selectivity to CYC was achieved in all cases, however, the reaction rates differed a lot. Experimentally, the maximum TOF was obtained when CH<sub>3</sub>CN was chosen as the solvent.

The influence of temperature on the reaction rate and CYC selectivity was also investigated in the range of 298–354 K. As shown in Fig. 5, the reaction rate was enhanced significantly with increasing temperatures, which means this dehydrogenation reaction was temperature-sensitive. In the meantime, the selectivity to CYC almost remained in a very high level (ca. >95 %) in the whole range of reaction temperature. The above results indicated a high temperature is beneficial to the selective oxidation of CHOL. Therefore, in the current study, the reaction mixtures were heated at their reflux temperature (about 354 K) in order to achieve a better reaction rate and CYC selectivity simultaneously.



Fig. 2. Le Bail fitting of powder XRD for 10%Cr-PKU-1, blue circles  $\bigcirc$  represents the observed data and red solid line is the calculated pattern; the marks below are the expected reflections. The inset is the XRD patterns of Cr-PKU-1 samples with different Cr contents.



**Fig. 3.** The reaction rate of 6 different *sec*-alcohol substrates and the selectivity to corresponding ketones over 10%Cr-PKU-1. Reaction conditions: 20 mmol *sec*-alcohol substrates, 40 mg catalyst, 20 mL CH<sub>3</sub>CN, 2 equivalent H<sub>2</sub>O<sub>2</sub> oxidant, and refluxed at 354 K for 18 h. Noting: Turnover frequency (TOF) is calculated with the division of the moles of consumed substrate by the moles of used catalyst and reaction time.



**Fig. 4.** Reaction rate of CHOL and CYC selectivity in the different solvents over 10% Cr-PKU-1. Reaction conditions: 20 mmol CHOL, 40 mg catalyst, 20 mL solvent, 2 equivalent  $H_2O_2$  oxidant, and refluxed at the individual boil point for 8 h.



**Fig. 5.** The reaction rate of CHOL and CYC selectivity under different reaction temperatures over 10%Cr-PKU-1 catalyst. Reaction conditions: 20 mmol CHOL, 40 mg catalyst, 20 mL CH<sub>3</sub>CN, 2 equivalent  $H_2O_2$  oxidant, and heated at different temperature for 8 h.

For an oxidation reaction, an appropriate equivalence of oxidant will generally ensure a high yield of the product, while an excessive amount of oxidant tends to induce an over-oxidization, which means reduced selectivity to the targeted product. According to the stoichiometric equation, the dehydrogenation of one mole of CHOL requires one mole of H<sub>2</sub>O<sub>2</sub>. Herein, the influence of H<sub>2</sub>O<sub>2</sub>/substrate molar ratio (varying from 0.25/1 to 4/1) was investigated as shown in Fig. 6. Apparently, the reaction rate increased significantly with the increase in  $H_2O_2$ /CHOL molar ratio; differently, the selectivity to CYC remained high (>99 %) until H<sub>2</sub>O<sub>2</sub>/CHOL molar ratio reached 2/1 and decreased thereafter. Despite of promoting turnover frequency, the larger stoichiometry of H<sub>2</sub>O<sub>2</sub> will also result into a deeper oxidation, which will be discussed in later sections. Here, the optimal ratio of H<sub>2</sub>O<sub>2</sub>/CHOL (about 2/1) was higher than the stoichiometry, because some of  $H_2O_2$  would decompose into  $O_2$  which is chemically inert to oxidize CHOL.

#### 3.2.2. Screening of metal-incorporated PKU-1 and their recyclability

In this study, three types of catalysts, i.e. Cr-PKU-1, Fe-PKU-1 and Fe-Cr-PKU-1, were synthesized. Dehydrogenation reactions indicated the type and amount of incorporated transition-metals played a crucial role on the reaction rate of CHOL and CYC selectivity. Briefly, Cr-substituted PKU-1 samples were more active than Fe-substituted ones; on the contrary, for bimetal-substituted catalysts Fe-Cr-PKU-1, the incorporated iron ions are detrimental to CHOL transformation and CYC selectivity.

First, the catalytic performance of Cr-PKU-1 samples with 5 different Cr contents was examined, and the reaction rate of CHOL and CYC selectivity was presented in Fig. 7. Chromium-free PKU-1 catalyst did not show any obvious catalytic activity, while Cr ions were evidenced to act as active sites and played an essential role in catalytic dehydrogenation of CHOL. With the increase of Cr/(Cr + Al) atom ratio from 0 to 30 atom %, the TOF was enhanced dramatically from 0.25 to 18.25  $mol_{Sub}$ - $mol_{Cat}^{-1}$ . The selectivity to CYC, however, was not linearly dependent on the Cr content. The high CYC selectivity (ca. 99 %) was only achieved when Cr content was below 10 atom %, beyond which, the excessive chromium would greatly accelerate the side-reactions and reduce CYC selectivity. As a consequence, 10%Cr-PKU-1 sample was selected as the model catalyst in order to further discuss the catalytic mechanism.

Iron ion sometimes was reported to act as an efficient active metal for some redox reactions, such as the case of Fe/AIPO-5 [45,46]. However, Fe-substituted PKU-1 samples in this study did not give a positive catalytic capacity for the dehydrogenation of



**Fig. 6.** Reaction rate of CHOL and CYC selectivity under the different stoichiometric proportions of  $H_2O_2/CHOL$  over 10%Cr-PKU-1 catalyst. Reaction conditions: 20 mmol CHOL, 40 mg catalyst, 20 mL CH<sub>3</sub>CN, and refluxed at 354 K for 8 h.



Fig. 7. The influence of Cr amount incorporated in PKU-1 on reaction rate of CHOL and CYC selectivity. Reaction conditions: 20 mmol CHOL, 40 mg catalyst, 20 mL CH<sub>3</sub>CN, 2 equivalent  $H_2O_2$  oxidant, and refluxed at 354 K for 8 h.

CHOL. As shown in Fig. 8 (left side), all Fe-PKU-1 samples exhibited poor catalytic activities, and the maximum TOF was only 1.08 mol<sub>Sub</sub>·mol<sub>Cat</sub>·h<sup>-1</sup> when using 30 atom % Fe-PKU-1 as the catalyst, which was much smaller than the ones of Cr-substituted PKU-1 catalysts. Leithall et al. reported that bimetal-substituted molecular sieves VTiAlPO-5 have exhibited a superior performance than the monometallic analogues in the epoxidation of cyclohexene, in which V and Ti ions were proved to give a cooperative and synergistic effect [47]. In our present study, Fe-Cr-PKU-1 catalysts with different Fe/Cr molar ratio were successively synthesized, and their catalytic performances in CHOL dehydrogenation were assessed, but were rather poor. In other words, the introduction of iron ions had a negative impact on CHOL transformation and CYC selectivity (see right side of Fig. 8). When increasing the amounts of iron ions, their catalytic activity decreased dramatically. It can be drawn that iron ions are unfavorable to liquid phase dehydrogenation for secalcohol.

The powder catalysts can be easily separated from the reaction solution by simple filtration followed by washing with acetone and water. After that, the reusability of 10%Cr-PKU-1 catalyst was evaluated. As shown in Fig. 9, 10%Cr-PKU-1 maintained its original framework structure and did not exhibit any obvious loss of catalytic activity after 5 runs, evidencing the excellent framework



**Fig. 8.** Reaction rate of CHOL and CYC selectivity over Fe-substituted PKU-1 and Fe-substituted 5%Cr-PKU-1 with different Fe contents. Reaction conditions: 20 mmol CHOL, 40 mg catalyst, 20 mL CH<sub>3</sub>CN, 2 equivalent  $H_2O_2$  oxidant, and refluxed at 354 K for 8 h.

stability. However, the further ICP analysis on reaction solution indicated there was a slight release of Cr active metal into the solution, the metal loss was about 4.13 %. Though unavoidable sometimes, active metal leakage seems to be greatly influenced by the performed reaction conditions, especially the type and concentration of the used oxidant. For example, when the oxidant TBHP with weak oxidizing power was used to take place of  $H_2O_2$ , the released amount of active metal Cr was trace and can be ignorable.

## 3.3. Discussions about reaction mechanism

3.3.1. Effect of Cr sites on the formation of active intermediate species As mentioned above, chromium ions in Cr-PKU-1 were assumed to function as active sites to quickly active  $H_2O_2$  into oxygenatedintermediate species during the *sec*-alcohols oxidation. In order to confirm this statement, the following experiments were designed. First, a certain amount of  $H_2O_2$  (30 wt %) and CH<sub>3</sub>CN were transferred into a test tube; next, a trace of Cr-PKU-1 powder was added into the above solution; then, the test tube was semi-sealed by Parafilm; finally, the residual amount of  $H_2O_2$  after 4 h activation was determined by redox titration using KMnO<sub>4</sub> as standard solution.

A photograph was taken to monitor  $O_2$  bubbling rate and displayed in Fig. 10a, where bubbles were observed and some of them attached to the wall of the test tube. In fact, the gas was identified as  $O_2$  and should be originated from the catalytic decomposition of  $H_2O_2$  over Cr-PKU-1. This means Cr-PKU-1 can significantly activate the peroxide bond (-O--O-) of  $H_2O_2$  and thus give an even more active oxygen-inclusive intermediate species, either 'OH radicals or superoxide ions ' $O_2^-$ . If these highly-active species were not completely consumed by the reaction substrates (like in this experiment), they would therefore prefer to deactivate quickly and combine with each other to form  $O_2$ . As for the reaction of CHOL dehydrogenation, these highly-active oxidative species are supposed to efficiently capture the hydrogen from CHOL, and largely accelerate dehydrogenation process.

Quantitative analyzes on the residual  $H_2O_2$  were performed by redox titration using KMnO<sub>4</sub> as oxidant, where the amount of consumed KMnO<sub>4</sub> was shown in Fig. 10b. Apparently, the O<sub>2</sub> evolution rate shows a positive dependence on the concentration of Cr<sup>3+</sup>. In other words, a higher chromium concentration in Cr-PKU-1 would lead to a better catalytic efficiency due to the quicker decomposi-



**Fig. 9.** Recyclability of 10%Cr-PKU-1 catalyst for CHOL dehydrogenation evidenced by XRD pattern after 5 runs and the catalytic performances for each run. Because the powdered catalyst unavoidably has a small loss after each run, the amounts of reactants and solvent will be reduced accordingly in the identical proportion with above operations.



**Fig. 10.** O<sub>2</sub> bubbling rate monitored by catalytic decomposition of H<sub>2</sub>O<sub>2</sub> over the Cr-PKU-1 catalysts (a) and the consumed amount of KMnO<sub>4</sub> (b), respectively. Reaction conditions: 20 mg Cr-PKU-1 catalyst, 1.5 mL H<sub>2</sub>O<sub>2</sub>, 2.5 mL CH<sub>3</sub>CN, and heated at 313 K for 4 h.

tion of  $H_2O_2$  into active intermediate. In this sense, it is understandable about the positive correlation between the reaction rate of CHOL and Cr content in Cr-PKU-1, while excessive chromium sites are detrimental to CYC selectivity, as is previously shown in Fig. 7.

#### 3.3.2. Detection of the involved critical radicals

 $H_2O_2$  is popularly believed to decompose into hydroxyl radicals ('OH) and/or superoxide ions (' $O_2^-$ ), which thereafter act as critical species in redox reactions [48,49]. In the following, it is important to figure out the real active intermediate species when  $H_2O_2$  was activated by Cr-PKU-1.

First, the so-called terephthalic acid (TA) fluorescent method was performed to *in-situ* monitor the formation of •OH radicals [50]. In detail, the hydroxyl radicals can be trapped by TA to form a highly fluorescent compound, 2-hydroxyterephthalic acid (TAOH), whose maximum fluorescence emission is centered about at 440 nm and the emission intensity is proportional to the amount of the produced TAOH in the liquid phase [51]. If without any catalyst, the PL was too weak to be detected, which means the amount of •OH radicals produced under the catalyst-free conditions was negligible. Once 10%Cr-PKU-1 was added, a broad absorption band centered at 440 nm was observed and the intensity gradually grew with time increasing from 1 to 4 h (see Fig. 11a).

On the other hand, NBT is a widely used superoxide ion indicator for the formation of purple formazan with the absorbance at  $\lambda = 560$  nm [52,53]. Here, NBT was used as the probe molecule to *in-situ* detect another possible reactive species 'O<sub>2</sub>'. The blank experiment was performed without adding any catalyst, and the concentration of formazan also has a continuous increase (see Fig. 11b); however, when 10%Cr-PKU-1 is added into the test solution, the concentration of formazan was far below the ones generated in the blank experiment.

It is quite interesting to observe the opposite tendency of the concentration variation of OH and  $O_2^-$  radicals. In other words, Cr sites catalyzed the quick formation of active OH radicals from  $H_2O_2$ , however strongly suppressed the generation of superoxide  $O_2^-$  ions. Therefore, we reasonably considered OH radicals as the critical active species to catalyze the dehydrogenation of *sec*-alcohols. It is also very important that Cr-PKU-1 suppressed the generation of superoxide  $O_2^-$  ions, which will eliminate the possible side reactions caused by  $O_2^-$ .

As evidenced in Figs. 7 and 8, the type or concentration of incorporated transition-metals played a vital role on the conversion rate and the selectivity. First, a high concentration of  $Cr^{3+}$  leads to a

high conversion rate. It is a convincing proof to confirm the enhanced production of 'OH radicals by Cr-PKU-1 catalysts. In order to further demonstrate this structure-activity relationship, we also employed fluorescence molecular probe to monitor the formation of OH radicals in the presence of different type of M-PKU-1 catalysts. Fig. 12 gives the amount of 'OH radicals resulted from the catalytic decomposition of H<sub>2</sub>O<sub>2</sub> by Cr-PKU-1 or Fe-PKU-1 catalyst, and shows 'OH generation rate was greatly dominated by the type and amount of active metal sites. Cr<sup>3+</sup> ions efficiently promote the formation of 'OH radicals, while iron ions exhibit a poor capacity to catalytically convert H<sub>2</sub>O<sub>2</sub> into OH radicals. This result explains why Cr-PKU-1 catalysts have much better catalytic activity than Fe-PKU-1 catalysts. Fig. 12 also indicates that the fluorescence intensity of TAOH has a rapid increase along with increase in the amounts of incorporated amounts transition metal. That is to say, a higher concentration of Cr<sup>3+</sup> ions will have a stronger capacity to accelerate the generation of OH radicals, thus can greatly improve the catalytic conversion of CHOL.

Accordingly, we believe Cr-PKU-1 holds a great potential because it has a controllable capability of  $H_2O_2$  activation, and 'OH is the exclusive product. In our study, the model reaction was the dehydrogenation of *sec*-alcohols, and the compatible concentration of  $Cr^{3+}$  was estimated to be 10 % to achieve both high conversion rate and selectivity (>99 %). Apparently, the allowed-concentration of  $Cr^{3+}$  in the octahedral-based framework of PKU-1 is much higher than the case of TS-1. Although the further increase of the  $Cr^{3+}$  concentration of CYC, the Cr-PKU-1 catalyst with high concentration might provide a great potential in other catalytic oxidation systems.

#### 3.3.3. Discussions about induction period

The catalytic CHOL dehydrogenation was largely dominated by the concentrations of hydroxyl group radicals, and a critical concentration seemed required to push forward this dehydrogenation reaction. Table 1 gives the time dependence of CHOL conversion and CYC selectivity over the Cr-PKU-1 with different Cr contents. A pre-activation stage for CHOL dehydrogenation was needed, and the higher the chromium content, the shorter the activation time. For instance, in the presence of 6%Cr-PKU-1 catalyst, CHOL conversion was negligible within 3 h; for 10%Cr-PKU-1 catalyst, the induction period was shortened to about 1 h, and CHOL conversion only reached 4 % after 2 h; if 20%Cr-PKU-1 was chosen, the induction period of about 1 h was still required, but the CHOL conversion could reach up to 25 % after 2 h. In the meantime, the



**Fig. 11.** Formation of  $\cdot$ OH radicals and  $\cdot$ O<sub>2</sub><sup>-</sup> radicals ion monitored by molecular probe method: (a)  $\cdot$ OH radicals evidenced by the production of the fluorescent TAOH and (b)  $\cdot$ O<sub>2</sub><sup>-</sup> ion evidenced by UV-vis absorption spectrum of the production of formazan. Operational condition: TA or NBT (3 mmol), CHOL (20 mmol), H<sub>2</sub>O<sub>2</sub> (40 mmol) and CH<sub>3</sub>CN (20 mL). The blue and red lines represent the time-dependent spectra measured with and without 10%Cr-PKU-1 catalyst, respectively.



**Fig. 12.** Formation of •OH radicals catalyzed by Cr-PKU-1 or Fe-PKU-1 with different transition metal contents evidenced by the production of the fluorescent TAOH after 2 h reaction time. Operational condition: TA (3 mmol), CHOL (20 mmol), H<sub>2</sub>O<sub>2</sub> (40 mmol) and CH<sub>3</sub>CN (20 mL).

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ïme dependence of CHOL conversion and CYC selectivity over the Cr-PKU-1 with different Cr contents.	

Time (h)	6% Cr-PKU-1		10% Cr-PKU-1		20% Cr-PKU-1	
	Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)
1	<1	99	<1	99	<1	99
2	<1	99	4	99	25	82
3	<1	99	8	99	40	79
4	4	99	17	99	47	77
5	6	99	21	99	48	76
6	11	99	27	99	50	75
7	15	99	40	99	54	74
8	18	99	46	99	58	73

Reaction conditions: 20 mmol CHOL, 40 mg catalyst, 20 mL CH<sub>3</sub>CN, 2 equivalent H<sub>2</sub>O<sub>2</sub> oxidant, and refluxed at 354 K.

instantaneous reaction rate also decayed very rapidly because of the quick transformation of oxidant  $H_2O_2$  into active OH radicals catalyzed by the higher-chromium catalyst. In other words, the observation of induction period suggests that CHOL dehydrogenation reaction will be activated, only when the concentration of OH radicals reaches the minimum threshold.

#### 3.3.4. Redox couples evaluated by electrochemical measurement

As discussed above,  $Cr^{3+}$  ions were proved to play a key role in the catalytic transformation of  $H_2O_2$  into active radicals, therefore the identification of  $Cr^{3+}$  functioned in this process was much attractive. In some transition-metal-catalyzed organic reactions with using  $H_2O_2$  as oxidant, the higher-valence-state transition metal ion was generally discovered to be reduced to a lower one. For example,  $Fe^{2+}$  species were commonly identified in the Fenton or Fenton-like reaction system ( $Fe^{3+}-H_2O_2$  system), among which, a  $Fe^{3+}-Fe^{2+}-Fe^{3+}$  cycle was established accompanied with the generation of  $\cdot$ OH radicals according to the so-called Fenton-like mechanism [54–56]. Similarly, some kind of chromium-containing ion couple (probably the coupled  $Cr^{3+}/Cr^{2+}$ ) is highly possible to be involved in the  $Cr^{3+}-H_2O_2$  reaction system, which was hereinafter identified by cyclic voltammetry (CV) measurement.

Cyclic voltammetry is in fact an useful technique in characterizing the local environment in the case of transition-metal-bearing porous solids. For example, Cartro-Martins et al. applied the CV measurements to prove that only the  $Ti^{4+}$  ions in the framework underwent electron-transfer processes, not the extra-framework  $Ti^{4+}$  ions [57,58]. Venkatathri and his co-workers investigated several vanadium-containing molecular sieves and found that two distinct sets of redox couples were present in the CV curves, which were speculated to be  $V^{5+}/V^{4+}$  in two different coordination environments, namely a distorted tetrahedral and a square pyramidal symmetry [59–62]. Borges et al. studied the electrochemical properties of a cobalt-substituted aluminophosphate (CoIST-2) and provided a clear evidence for the presence of at least two types of Co<sup>2+</sup> species [63].

The CV curves in Fig. 13 exhibit a single oxidation and reduction process for all Cr-PKU-1 samples (10%, 30% and 50%), and their relative peak potentials ( $E_{1/2}$ ) located at ~-0.48 V vs Ag/AgCl reference electrode, in which  $E_{1/2}$  is the average value of the oxidation potentials (around -0.64 V) and reduction ones (around -0.32 V). The peak separation and similar current intensity ratio indicate that the redox process is quasi-reversible and reproducible for Cr species within the PKU-1 framework. Since the CV peaks are the indications of the valence alternation of Cr ions, it is as expected that the relevant current intensities become more and more significant with the increase in Cr concentration. For comparison, no such redox behavior is observed in the chromium-free PKU-1 sample at the same experimental conditions (see the inset of Fig. 13).

As previously indicated by XPS analyzes (Fig. S10, SI), chromium species in the Cr-PKU-1 are proved to be  $Cr^{3+}$ . Accordingly, these paired anodic and cathodic peaks are supposed to result from the reversible reaction between  $Cr^{3+}$  and another type of Cr couple, reasonably  $Cr^{2+}$  ions, based on the related standard redox potentials. As shown in Fig. 13, the observed  $E_{1/2}$  is about -0.48 V (vs Ag/AgCl), and is reasonably close to the one of the



Fig. 13. Cyclic voltammetry curves of Cr-PKU-1 samples with different Cr contents.

coupled  $Cr^{3+}/Cr^{2+}$  (-0.63 V vs Ag/AgCl). The shift toward a more negative potential should attribute to the difference in coordination modes between solid and solvated environments [64]. There was no detectable redox peak when scanning from 0 to 1 V. Thus, from another perspective, the absence of higher  $E_{1/2}$  implied that the redox circulation for coupled  $Cr^{3+}/Cr^{6+}$  or  $Cr^{3+}/Cr^{5+}$  was unlikely to proceed [65].

Some researchers suggested that an extremely stable framework is often unfavorable to configuration transitions of active metal cations, and the resistance against redox process seems to highly depend on the porous structure and the resultant framework with strong stress, which often results in a local distortion or even a lower structural asymmetry [66,67]. In fact, the crystal structure of Cr-PKU-1 possesses three independent metal sites in the space group of *R*3, and one of them is located in a quite distorted octahedral environment [28]. From the structural point of view, the distorted  $AlO_6/CrO_6$  octahedra seem to afford the static stress in the main framework, for this particular reason,  $Cr^{3+}$  ions are reasonably speculated to easily undergo a catalytic circulation for a given redox reaction. In the next step, the real functionality of  $Cr^{3+}$  and the mechanism are validated by catalytic oxidative dehydrogenation of *sec*-alcohol shown in the following sections.

#### 3.3.5. Reaction mechanism

Based on above observations as well as those in previous studies [68–70], a possible reaction mechanism is proposed in Fig. 14. First, the sixfold coordination  $Cr^{3+}$  (1) easily reacts with  $H_2O_2$  to form  $Cr^{2+}$ —OOH (2) accompanied with the production of H<sup>+</sup>. Then, 2 undergoes a hemolytic cleavage of its O-OH bond to generate  $Cr^{2+}$ —O' (3) and 'OH radicals. Next, 3 can capture a hydrogen atom from organic substrate CHOL to form  $Cr^{2+}$ —OH (4), along with the formation of  $C_6H_{11}O'$  (5). Finally, 4 reacts with H<sup>+</sup> back to 1 and simultaneously generates a water molecule; Meanwhile, 5 combine with ·OH radicals (which was generated in the previous step) to generate CYC and  $H_2O$ .

#### 3.4. Reaction pathways under the over-oxidative conditions

#### 3.4.1. Reaction pathway for over-oxidation of CHOL

As described in previous sections, CYC selectivity was dependent on reaction conditions, especially the amount of  $H_2O_2$  or  $Cr^{3+}$  atom % in the Cr-PKU-1 catalyst. For instance, when the equivalent amount of  $H_2O_2$ /CHOL was raised from 2 to 3, the CYC



Fig. 14. The proposed reaction mechanism for catalytic dehydrogenation over Cr-PKU-1 catalyst.

selectivity would decrease about 50% because of the overoxidation (see Fig. 6), and consequently a large amount of byproducts such as dicarboxylic acids were generated. Interestingly, the identification of these emerging intermediates could provide solid evidences to recognize the degradation pathways of CHOL. In the present case, most intermediates were identified using GC–MS measurement, whose molecular structure was included in Fig. S10, SI. For clarify, the degradation of CHOL can be reasonably classified into 3 continuous routes: Route I (Fig. 15a), II and III (Fig. 15b).

In route I, CHOL was degraded successively into some smaller organic molecules through multistep oxidative reactions, such as catalytic dehydrogenation, Baeyer-Villiger oxidation and oxidative ring-opening reaction. In detail, CHOL was first oxidized to CYC through a dehydrogenation process. In an over-oxidative environment, the so-called Baeyer-Villiger oxidation will occur, and a cyclic lactone called  $\varepsilon$ -carprolactone was subsequently produced. In this way, these over-oxidative procedures would continue to consecutively produce other intermediates, such as adipic acid and  $\delta$ -valerolactone. Formic acid molecules, however, were produced as aliphatic dicarboxylic acids are transformed into cyclic lactone.

The oxidation process in routes II and III contains two same reactions: dehydrogenation and hydroxylation reactions, the only difference between these two routes is the sequence of these two reactions (Fig. 15b). For example in Route II, CHOL is initially oxidized into *o*, *m*, or *p*-cyclohexanediol, respectively, through a hydroxylation reaction, subsequently the dehydrogenation process to corresponding 2, 3, or 4-hydroxycyclohexanone occurs. While in Route III, the hydroxycyclohexanone can be produced in the sequence of dehydrogenation and hydroxylation reactions. Eventually, two competitive reactions, i.e. dehydrogenation or dehydration steps, are followed by the production of cyclohexanedione or cyclohexenone.

#### 3.4.2. Discussion about the selectivity for each pathway

As might be expected, these parallel over-oxidation routes are not equivalent and will be largely influenced by different reaction conditions. Probably the concentration of intermediates will give a hint about the most favorable route. As already proved, both the Cr<sup>3+</sup> concentration and the oxidant equivalence have an important influence on the CYC selectivity. Rationally, three batches with different catalytic conditions were performed, and the concentrations (selectivity) of main intermediates were also determined using GC or HPLC.

As shown in Table 2, the selectivity to main intermediates was determined, and especially the summed selectivity for each route was emphasized. First in Batch 1, when the high chromium catalyst (30%Cr-PKU-1) was used, CHOL conversion was enhanced from 46 % to 62 %, however, the CYC selectivity was dramatically reduced from 99 % to 46 % compared to the 10%Cr-PKU-1 model



**Fig. 15.** The supposed reaction pathway for over-oxidation of CHOL, the main product and by-products of CHOL (1) oxidation is listed as below: CYC (2); ε-carprolactone (3); adipic acid (4); δ-valerolactone (5); glutaric acid (6); γ-butyolactone (7); *o*, *m* or *p*-cyclohexanediol (8); 2, 3 or 4-hydroxycyclohexanone (9); 2-cyclohexen-1-one (10) and *p*-cyclohexanedion (11).

#### Table 2

The beleening of bound by produced energed in the proposed reaction of entropy and the anterent reaction conditions,	The selectivity	of some by	y-products	emerged in th	e propose	d reaction rout	tes for the c	ver-oxidation	of CHOL	under the	different r	eaction cond	litions.
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Compounds No.		Batch 1 (62 %) <sup>a</sup> Selectivity (%)	Batch 2 (80 %) <sup>b</sup> Selectivity (%)	Batch 3 (70 %) <sup>c</sup> Selectivity (%)
	2	46	38	43
Route I	3	Trace	Trace	Trace
	4	12	18	17
	5	0.1	0.9	0.2
	6	14	11	9
	7	0.2	0.2	0.6
	Sum	26.3	30.1	26.8
Route II and III	8	8	10	10
	9	14	18	18
	10	0.6	0.6	0.6
	11	1.0	2.0	1.0
	Sum	23.6	30.6	29.6

Reaction conditions for each batch:

<sup>a</sup> 20 mmol CHOL, 40 mg 30%Cr-PKU-1 catalyst, 20 mL CH<sub>3</sub>CN, 2 equivalent H<sub>2</sub>O<sub>2</sub>, refluxed at 354 K for 8 h.

<sup>b</sup> 20 mmol CHOL, 40 mg 10%Cr-PKU-1 catalyst, 20 mL CH<sub>3</sub>CN, 4.5 equivalent H<sub>2</sub>O<sub>2</sub>, refluxed at 354 K for 12 h.

<sup>c</sup> 20 mmol CHOL, 40 mg 30%Cr-PKU-1 catalyst, 20 mL CH<sub>3</sub>CN, 2.5 equivalent H<sub>2</sub>O<sub>2</sub>, refluxed at 354 K for 12 h. The value in parentheses is the CHOL conversion for each batch.

catalyst (see Fig. 7). The over-oxidation selectivity through Route I and II and III is 26.3 % and 23.6 %, respectively. In general, a higher  $Cr^{3+}$  concentration in Cr-PKU-1 did not show a significant preference to boost either Routes I or II and III, which seems to be really equivalent.

In Batch 2, a higher equivalent  $H_2O_2$  ( $H_2O_2/CYOL = 4.5$ ) was added into the reaction system. The results indicate that CHOL conversion further increased from 46 % to 80 %, in the meantime, the CYC selectivity declined to an even smaller value of 38% comparing to the optimized ratio of  $H_2O_2/CYOL = 2$ . The overall selectivity to either Route I or II and III exhibited a further increase (30.1 and 30.6 %, respectively) compared to Batch 1. That is to say, the competition between Routes I and II and III was well matched and not dominated by any of the above two factors ( $Cr^{3+}$  concentration or equivalence of  $H_2O_2$ ).

In Batch 3,  $H_2O_2$  (in the equivalence of 2.5) was added with a slow rate and in a successive manner, which has been proved to affect the selectivity of main products [8,71]. In the current case, the CHOL conversion and CYC selectivity were 70% and 43%, respectively, but the previously competitive Routes I and II and III became somewhat selective. In other words, the selectivity to Route I substantially unchanged comparing to Batch 1, while the ones toward Routes II and III elevated from 23.6% to 29.6%. This is a hint that the successive adding of  $H_2O_2$  provided a sustainable but a low concentration of  $\cdot$ OH radicals, and a low but instantaneous concentration of active species is beneficial to hydroxylation reactions involved in Routes II and III, while a higher one is in favor of oxidative degradation involved in Route I.

On the whole, an excessive concentration of  $Cr^{3+}$  in the Cr-PKU-1 catalyst definitely leads to over-oxidative conditions for deep-oxidized by-products through two completely different pathways, which was only probably controlled by the instantaneous concentration of oxidative species in solution. The particularity of Cr-PKU-1 is to catalyze the selective decomposition of H<sub>2</sub>O<sub>2</sub> into 'OH and interestingly in a controllable rate. For the sake of a high selectivity from *sec*-alcohols to ketones, the most efficient catalyst is 10%Cr-PKU-1 under the performed conditions, while the further improvement to develop possible bi-catalyst systems is proposed.

# 4. Conclusions

As a novel octahedral-based redox molecular sieve, M-PKU-1 (M=Cr or Fe) has been facilely synthesized by the boric acid reflux method. X-ray Diffraction Rietveld refinement method has evidenced that transition metals have been successfully

incorporated into the framework sites, and the linear expansions of cell unit volume indicate M-PKU-1 have a higher upper limit for doping transition metal cations (50 atom % for Cr<sup>3+</sup>). XPS, cyclic voltammetry and crystal structure analyzes suggested Cr<sup>3+</sup> ions were much likely to locate in a highly-distorted octahedral environment and thereby can easily and quickly forward the redox circles when the oxidative reaction happened.

Under the performed conditions, Cr-PKU-1 samples show much superior catalytic performance to Fe-incorporated ones (99% selectivity and ~15 times higher in TOF for 10 atom % substitution). The isolated Cr sites are proved to function as active sites and be responsible to activate rapidly H<sub>2</sub>O<sub>2</sub> to release the active OH radical. The fluorescence probe method indicates the presence of Cr<sup>3+</sup> in the framework of PKU-1 promotes the activation of H<sub>2</sub>O<sub>2</sub> into OH radicals exclusively and prohibits the formation of  $O_2^$ ions in the meantime, and the amount of OH radicals was greatly dominated by the type and amount of active metal sites. A lowlevel Cr in PKU-1 (6%Cr-PKU-1) tends to provide lower concentration of OH radical and thus results into a long reduction period; on the contrary, an excessive amount of Cr active centers (20%Cr-PKU-1) will bring an over-high concentration of 'OH (at least ten times, compared to 6%Cr-PKU-1 catalyst) and thus greatly shorten induction period, thereafter however produce a variety of by-products such as adipic acid or hydroxycyclohexanone. A hypothetical mechanism was also proposed to demonstrate the functions of Cr catalytic sites, in which a Cr<sup>3+</sup>-Cr<sup>2+</sup>-Cr<sup>3+</sup> circle was involved and very different with the Cr<sup>3+</sup>-Cr<sup>3+</sup> circle presented in the tetrahedral-based redox molecular sieves. The stepwise byproducts were analyzed by GC-MS and HPLC to demonstrate the probable reaction route under over-oxidation conditions, and three parallel pathways containing dehydrogenation, hydroxylation, Baeyer-Villiger oxidation or ring-opening reactions, were speculated to clarify the progressive oxidation of CHOL under the overoxidation environment. Although this study is a preliminary study on the controllable and selective activation of H<sub>2</sub>O<sub>2</sub> catalyzed by Cr-PKU-1, and considering their significant capacity to accommodate desired metals with high level, M-PKU-1 catalysts really holds high potentials, for example, on catalyzing other redox reactions, probably with additional loading of cocatalysts.

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# **Appendix A. Supplementary material**

In supporting information, the supplementary materials in Figs. S1-S10 have been provided: UV-Vis absorption spectra of Cr<sub>2</sub>O<sub>3</sub> and Cr-PKU-1 with different Cr content (Fig. S1); Powder XRD patterns of Fe-PKU-1 with different Fe content (Fig. S2); The dependence of unit cell volumes for Fe-PKU-1 samples on the different concentration of Fe atoms (Fig. S3); Powder XRD patterns of Fe-5%Cr-PKU-1 with different Fe content (Fig. S4), The dependence of unit cell volumes for Fe-5%Cr-PKU-1 samples on the different concentration of Fe atoms (Fig. S5), SEM images and EDS analysis of 20%Cr-PKU-1 sample (Fig. S6), In-situ high temperature XRD patterns for 10%Cr-PKU-1 sample (Fig. S7), TG-DSC analysis of 10%Cr-PKU-1 sample (Fig. S8), XPS survey spectrum of Cr-PKU-1 (Fig. S9) and the emerging intermediates determined by GC-MS measurement (Fig. S10). This material is available free of charge via the Internet at http://www.elsevier.com. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2017.05.007.

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