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Solvent effect on the formation of active free radicals from H_2O_2 catalyzed by Cr-substituted PKU-1 aluminoborate: Spectroscopic investigation and reaction mechanism



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proposed accordingly.

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ARTICLE INFO	A B S T R A C T
<i>Keywords:</i> Solvent effect Active radicals Molecule probe method Styrene epoxidation Reaction mechanism	The nature of a solvent plays an important role in selectively catalytic oxidations, influencing the catalytic activity and product selectivity. Most work attribute such roles to the polarity, acidity/basicity, or coordination ability of the solvent. Here, we systematically investigated the generated active free radicals in five different organic solvents during the catalytic oxidation of styrene by H_2O_2 . Cr-doped PKU-1 aluminoborate was selected as the heterogeneous catalyst in this system. The solvent effect was comprehensively understood along this perspective. Hydroxyl radicals (`OH) were preferred to be formed in CH ₃ CN and responsible for the formation of carbonyl compounds, while superoxide ion radicals (` O_2^-) were favored in DMF and beneficial to the epoxide production. The function of Cr^{3+} was correlated with the solvent effect and a tentative mechanism pathway was

1. Introduction

Liquid-phase selective oxidations towards value-added organic products become more and more important because of the high economic benefit and wide applications in chemical industry and our daily life [1,2]. A number of studies have demonstrated that the used solvents exert a significant influence on the catalytic activity and product distribution [3,4], even the same reaction carried out in different solvents may give completely different catalytic performances [5–7]. In general, the solvent functions as a medium to transfer the mass and heat during reactions, therefore the solvent property, such as dielectric constant, acidity and basicity, coordination ability, polarity and dynamic viscosity, will display an indispensable role in the process of the catalytic oxidations [8-10]. In addition, a synergistic effect between the co-solvents, or between the solvent and the hydrophilicity-hydrophobicity surface of catalysts, also influences the catalytic activity [11,12]. In most cases, solvents may interplay with the active sites on catalyst surfaces, thereby modify the reaction pathways and the product distribution. For example, Flaherty et al discovered the solvent molecules with a high nucleophilicity restrain the H₂O₂ activation to form reactive species through a strong competition with the involved active sites, and thus give a lower activity [4]. Despite these achievements, a comprehensive understanding to the solvent effect is so far mysterious because of the complexity in reaction synergy and the difficulty in observing the key intermediates directly.

In essence, the type and concentration of active free radicals generated determine the efficiency and pathways of catalytic reactions. With this regards, we investigated the solvent effect on the formation of free radicals during a particular organic oxidation. Selective oxidation of olefins to obtain epoxides, particularly for the epoxidation of styrene, have attracted great attentions during the past decades. As a commercially important reaction, the epoxidation of styrene can provide a useful organic intermediate-styrene oxide, which was commonly used as versatile chiral building blocks in organic synthesis. Various catalysts have been attempted in the epoxidation of styrene in previous studies, such as molecular sieve [13-17], nano-scaled materials [18-23], transition-metal complexes [24-27], metal-organic framework (MOF) [28,29], metal cluster [30-33], composite oxides [34,35]. Among these investigations, only a few reports focused on the solvents effect. For example, Corma et al discovered the dramatic differences in catalytic activity using different solvents during the olifins oxidation, and they believed this solvent effect may attribute to the poisoning of framework aluminium, i.e. Brönsted acid sites, by the basic solvent molecules [17]. Zahra et al. investigated the solvent effect on catalytic activity in the presence of manganese porphyrins catalyst, and they attributed the large differences between the product distributions to the stability and high valence manganese-oxo and Mn(III) porphyrins species in the protic and aprotic solvents [27].

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Although a great efforts have been made in literature, most of them paid close attention to the relationship between catalytic activity and surface characters of catalytic materials, no emphases has been paid to correlate the solvent effect and the so-produced active free radicals. In this study, selectively catalytic oxidation of styrene using H₂O₂ oxidant was employed as a model reaction. We interpret the solvent effects in terms of the involved free radicals released from H₂O₂ and catalyzed by Cr-doped PKU-1 aluminoborate with an octahedra-based framework [36-44]. The types and concentration evolution of the radicals have been evaluated in five different solvents in order to understand the product distributions and the proposed reaction pathways. In CH₃CN, the majority of products were carbonyl compounds (95% selectivity) as well as a few amount of epoxide. On the contrary, the selectivity to epoxide reached 53% in DMF. Molecule probe methods proved a direct relationship between the selectivity tendency and the involved free radicals, indicating that 'OH radicals were preferred to be formed in CH₃CN and responsible for the formation of carbonyl compounds, while O_2^{-} ion radicals were favoured in DMF and beneficial to the epoxide production. A tentative reaction mechanism was proposed to explain the reaction pathways of styrene epoxidation based on our results.

2. Experimental section

2.1. Catalysts preparation and characterizations

Cr-PKU-1 was synthesized using boric acid as the flux without using any organic template as described in previous report [44]. For simplicity, the as-synthesized samples were denoted as 0%, 5%, 10%, 15% and 20%Cr-PKU-1. Powder X-ray diffraction data were collected at room temperature on a PANalytical Empyrean powder diffractometer equipped with a PIXcel 1D detector under Cu Ka radiation $(\lambda = 1.5406 \text{ Å})$. In order to refine the cell parameters, Le Bail fitting was performed using the TOPAS software package. A field emission scanning electron microscopy (JEOL, JSM-7800F) was used to examine sample morphology by dispersing dry powder on double-sided conductive adhesive tape. X-ray photoelectron spectra (XPS) were acquired with UK Kratos Axis Ultra spectrometer with Al Ka X-ray source. Electron binding energies were calibrated against the C 1s emission at $E_{\rm b} = 284.6 \, {\rm eV}$ to correct the contact potential differences between the sample and the spectrometer. Combined thermogravimetric (TG) and differential scanning calorimeter (DSC) analyses were performed on a Mettler-Toledo TGA/DSC1 instrument at a heating rate of 10 K/min from room temperature to 1173 K.

2.2. Catalytic reaction

Styrene and other all organic solvents were purified by distillation method. In a standard run, 1 mmol styrene, 6 mL DMF, 30 mg 10%Cr-PKU-1 catalyst and 3 mmol H_2O_2 were mixed in a 10-mL single-neck round-bottom flask and then immersed into a silicon oil bath to be heated under stirring. After reacting at 343 K for 10 h, a small amount of mixture was extracted with a syringe to transfer into a centrifuge tube, then centrifuged to separate solid powder. Finally, the remaining transparent solution was analyzed qualitatively or quantitatively with gas chromatography-mass spectrometry (GC–MS) or gas chromatography (GC), respectively.

GC–MS was performed to identify the structure of produced organic compounds on an Agilent 7890 N gas chromatograph coupled with a capillary column (DB-5: length, 50 m; inner diameter, 0.25 mm; film thickness, 0.25 μ m) and mass spectrum system (Agilent 5975C). GC was used to determine the concentration of the substrates and products on a SHIMADZU gas chromatograph (GC2010 plus) equipped with a flame ionization detector (FID). A capillary column (DB-5: length, 50 m; inner diameter, 0.25 mm; film thickness, 0.25 μ m) was chosen to separate the mixed components at the following condition: 393 K for capillary column, 523 K for injector port, and 523 K for FID detector.

2.3. Detection of free radicals

The revolved free radicals were determined by photoluminescence (PL) spectroscopy and UV-vis absorption spectra. For details, PL spectroscopy was used to detect 'OH radicals using terephthalic aicd (TA) as a probe molecule. In a typical run, a solution containing 1 mmol styrene, 6 mL solvent, 40 mg TA and 3 mmol H₂O₂ was mixed with 10%Cr-PKU-1 (30 mg) under stirring, then heated at 343 K for a specified interval of time. After a centrifugation to remove the powder from the suspension, the upper solution was taken 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. Superoxide ion (O_2) was determined by UV-vis absorption spectra using nitroblue tetrazolium (NBT) as a probe molecule. In a typical run, a solution containing1 mmol styrene, 5 mg NBT, 6 mL solvent and 3 mmol H₂O₂ was mixed with 30 mg 10%Cr-PKU-1 and heated at 343 K under stirring for a specified interval of time. The suspension was centrifuged to remove the solid powder and the upper clear liquid was measured on an UV-vis spectrometer (PUXI TU-1810, China).

3. Results and discussion

3.1. Characterizations of Cr-doped PKU-1 catalysts

The XRD patterns of the as-synthesized *x*%Cr-PKU-1 samples were shown in the right inset of Fig. 1 (x = 5, 10, 15 and 20) and give almost the same profile with the parent catalyst (0%Cr-PKU-1), hinting that Cr-incorporation does not change their host structures. In addition, the refined unit cell volumes give a linear dependence on the Cr-content. The expansion of unit cell volumes comply with the fact that Cr^{3+} ion has a larger radius (0.615 Å, coordination number (CN) = 6) than Al³⁺ (0.535 Å, CN = 6) [45]. The physicochemical properties of the as-synthesized Cr-PKU-1 catalysts have been characterized by many measurements, i.e. the morphology and homogeneity by SEM, the thermal behavior by TG-DSC analysis, the chemical compositions and valence states by XPS spectrum. Detailed discussions were provided in Supporting information (SI) from Figs. S1–S3.

3.2. Catalytic activity

In general, the oxidation of styrene has two reaction pathways, one is the epoxidation to styrene oxide (SO) and the other is the carbonylation to carbonyl compounds (CA), such as phenylacetaldehyde (PAC), benzaldehyde (BZA), benzoic acid (BA). As evidenced in some



Fig. 1. XRD patterns of Cr-PKU-1 samples with different Cr^{3+} content, and the corresponding reflection indices for 10%Cr-PKU-1were also labeled, as a representative.



Fig. 2. Styrene conversion and the selectivity to styrene oxide (S_{SO}) and carbonyl compounds (S_{CA}) using different solvents over 10%Cr-PKU-1. Reaction conditions: 1 mmol styrene, 30 mg catalyst, 6 mL solvent, 3 mmol H₂O₂, and heated at 343 K for 10 h.

references [8–10], reaction medium was a remarkable factor to influence catalytic styrene activity, both in homogeneous and heterogeneous systems. An appropriate solvent can effectively optimize the reaction route and greatly alter the product distribution. Herein, five solvents, including acetonitrile (CH₃CN), 1,4-dioxane, tetrahydrofuran (THF), acetone and dimethyl formamide (DMF) were chosen as reaction medium due to their good miscibility with reactants. As shown in Fig. 2, a completely different catalytic activity was obtained in these solvents. In detail, a slight enhancement from 39.2% (in THF) to 58.0% (in DMF) was observed in the styrene conversion, while the product distributions were quite different. When using DMF as solvent, styrene was oxidized simultaneously into both epoxide and carbonyl compounds (0.53/0.46 in molar ratio), however it preferred to generate much more carbonyl compounds in CH₃CN, i.e. the selectivity to carbonyl compounds (S_{CA}) reached ~ 95%.

3.3. Detection of the involved active free radicals

In general, H₂O₂ decomposes into hydroxyl radicals ('OH) or superoxide ions (O_2) over some transition metal sites, subsequently the formed radicals will act as the critical species in redox reactions [46,47]. Molecular probe methods were usually applied to detect these generated active species, in which NBT is a widely used superoxide ion indicator for the formation of purple formazan with the absorbance at $\lambda = 560 \text{ nm}$ [48,49], and TA is used to react with 'OH radicals to form a highly fluorescent compound, 2-hydroxyterephthalic acid (TAOH) [50,51]. Herein this work, the styrene epoxide tends to be produced in DMF, while carbonyl compounds are easily formed in CH₃CN. Fig. 3 gives the corresponding spectra obtained by molecular probe methods in different solvents. Interestingly, the highest concentration of 'O₂ion was demonstrated in DMF, while the highest concentration of 'OH radicals was detected in CH₂CN. Both results are consistent with the observed catalytic selectivity in DMF and CH₃CN (see Fig. 2). As two key intermediates from the H₂O₂ decomposition, 'O₂⁻ ions and 'OH radicals will inevitably compete with each other to react with reactants, and their concentration fluctuation will play an important role on the product selectivity. Different with DMF, other four solvents do not exhibit any obvious preference in the production of O_2^- ions. They all have a weak capacity to initiate and maintain a low concentration of O_2^{-} ions in the reaction solution, therefore, the epoxide selectivity has been greatly restrained. Indeed, the solvent effect in a specific catalytic reaction is commonly complex, the generation of free radicals sometimes was influenced by the solvation process, and the solvation potential energy of products or active intermediates will determine the product distributions. Therefore, the further elucidation of this point needs more efforts in future studies.

As shown in Fig. 4, Cr-PKU-1 effectively activated H₂O₂ to form O_2^- and OH radicals in DMF, because the peak intensity, reflecting the concentration evolution of free radicals, became stronger and stronger along with the reaction time in the presence of the catalyst, while the peak intensity were quite weak without using Cr-PKU-1. This experiment demonstrates that Cr³⁺ species in the catalyst play an indispensable role in the pre-activation of H₂O₂. Cr-PKU-1 can promote H_2O_2 to decompose into both O_2^- ions and OH radicals when DMF was selected as reaction medium. For comparison, our previous work proved that Cr-PKU-1 in CH₃CN catalyzed the quick formation of active OH radicals from H_2O_2 , however strongly suppressed the generation of superoxide O_2^- ions [44]. Such a solvent effect can also be further clarified with the following experiments. In the mixed solvents of CH_3CN and DMF, the concentration of generated O_2^- ion radicals was greatly enhanced with decreasing $V(CH_3CN)/V(DMF)$ from 6:0 to 0:6 (see Fig. 5a), on the other hand, such an evolution of volume ratio restrained the formation of 'OH radicals as shown in Fig. 5b.

In previous sections, it is proved that CH₃CN is favorable for the production of carbonyl compounds (95% selectivity), but DMF solvent gradually weakens the tendency for carbonylation production and is growing to benefit epoxidation pathway. The most essential reason is that 'OH radicals as the critical active species can be largely produced in CH₃CN and responsible for the carbonylation, while 'O₂⁻ ion radicals tend to be formed in DMF and are responsible for the epoxiadation. To reinforce this statement, we purposely added radical quenchers to monitor the catalytic selectivity changing tendency as indicated in Fig. 6. A two-stage experiments for 3 batches were performed. In batch 1, the reaction system was kept at $343 \,\mathrm{K}$ for $4 \,\mathrm{h}$ in the first stage and another 6 h in the second stage with no quencher added during the reaction. For the second reaction stage, the selectivity to epoxide and carbonyl compounds were ~56.6% and 43.6%, respectively. Differently in **batch 2**, the quenching reagent for inhibiting O_2^- radical ions, benzoquinone (BQ), was added in the second stage, and the selectivity to epoxide and carbonyl compounds during the last 6 h time interval were determined to be $\sim 20.3\%$ and 78.8%, respectively. Apparently, the epoxide product was greatly inhibited due to the addition of BQ, in contrast, the selectivity to carbonyl compounds was largely strengthened. In batch 3, when t-butanol, a hydroxyl radical quencher, was added into the reaction system in the second stage, the selectivity of obtained carbonyl compounds were enormously reduced from 52.8% (in the first stage) to 23.1% (in the second stage), in the meantime, the selectivity of epoxide was promoted from 46.7% to 75.9%. In summary, the above quenching experiments strongly support the statement that the hydroxyl radical is responsible for the formation the carbonyl compounds, while the superoxide ion radicals are the key species to promote the epoxidation.

3.4. Reaction mechanism

In literature, it was pointed out that styrene can be oxidized into carbonyl compounds through two catalytic pathways, one is to oxidize sidechain alkyl of benzene to give benzaldehyde or other carbonyl compounds; the other is to form styrene oxide firstly, then the formed epoxide will suffer a nucleophilic attack to produce benzaldehyde [15,52]. Nevertheless, it was surprising that the second pathway, i.e. the epoxide-to-benzaldehyde transformation, proceeds in a very limited degree. In other words, most benzaldehyde was achieved through the breaking of C=C double-bond in the side chain of benzene. The above abnormal results were further clarified as follows. Under the same reaction conditions, styrene oxide, benzaldehyde and phenylacetaldehyde were used separately as starting reactant to react with H₂O₂ in order to determine the actual reaction pathway for styrene oxidation. The quantitative results of the obtained products were determined with GC 7a). It clearly shows that both benzaldehyde and (Fig.



Fig. 3. Concentration variety of formed O_2^- ion radicals and 'OH radicals in different solvents monitored by (a) UV–vis absorption spectrum of the produced formazan and (b) fluorescent spectrum of the produced TAOH. Operational condition: TA (40 mg) or NBT (5 mg), styrene (1 mmol), H₂O₂ (3 mmol), solvent (6 mL) and 10%Cr-PKU-1 (30 mg).



Fig. 4. Concentration evolution along the reaction time for O_2^- ion radicals (a) and OH radicals (b) with and without 10%Cr-PKU-1 catalyst. Operating conditions: TA (40 mg) or NBT (5 mg), styrene (1 mmol), H₂O₂ (3 mmol), DMF solvent (6 mL) and solid catalyst (30 mg).



Fig. 5. Concentration variety of so-formed O_2^- and OH radicals in different volume ratios *V/V* (CH₃CN/DMF) monitored by (a) UV-vis spectrum of the produced formazan and (b) fluorescent spectrum of the produced TAOH. Operating conditions: TA (40 mg) or NBT (5 mg), styrene (1 mmol), H₂O₂ (3 mmol), solvent (6 mL), 10%Cr-PKU-1 (30 mg) and heated at 343 K for 6 h.

phenylacetaldehyde have high conversions than styrene oxide, the very small conversion for styrene oxide in DMF (2.0%) and in CH₃CN (1%) indicate that it may be a thermodynamically stable product in both solvents, probably combining with DMF or CH₃CN molecules to form a strong solvation product and is difficult to be activated in the catalytic

active sites, therefore the epoxide-to-benzaldehyde transformation needs a higher activation energy and is unfavorable under the performed conditions. Based on the above discussion, the actual oxidation process for styrene oxidation were presented in Fig. 7b.

The evolution of styrene conversion and the selectivity with



Fig. 6. A proof evidenced by adding BQ and *t*-butanol quencher to determine the formed O_2^- ions and OH active free radicals. The conversion and selectivity shown in the second stage are determined only with the amounts changes in these 6 h time interval. Reaction conditions: 1 mmol styrene, 30 mg catalyst, 2 mg BQ or 0.1 mL *t*-butanol quencher, 6 mL DMF, H₂O₂ oxidant, and heated for 10 h.



Fig. 7. The experimental schemes designed to search for the actual reaction pathway (a) and two reaction pathway proposed (b) for styrene oxidation using Cr-PKU-1 catalyst in both DMF and CH_3CN solvent. Reaction conditions: 1 mmol reaction substrate, 30 mg 10%Cr-PKU-1 catalyst, 6 mL DMF or CH_3CN , 3 mmol H_2O_2 , and heated at 343 K for 10 h.



Fig. 8. Evolution of catalytic activity and selectivity with reaction time using DMF and CH₃CN as reaction solvent. Reaction conditions: 1 mmol styrene, 30 mg 10%Cr-PKU-1 catalyst, 6 mL DMF (a) or CH₃CN (b), 3 mmol H₂O₂ and heated at 343 K.

reaction time also gives a powerful evidence on the above-proposed pathways. As the representatives, two solvents, DMF and CH₃CN were selected as reaction medium, and the samples have been collected at the time interval of 1, 2, 4, 6, 8 and 10 h, then were further analyzed quantitatively using GC. The obtained results shows that, with prolonging reaction time, styrene conversion is rapidly increasing, however the product selectivity exhibits an opposite tendency in DMF and CH₃CN solvents. As shown in Fig. 8a, when using DMF as reaction medium, the selectivity to epoxide product (S_{SO}) gives a slow increase from 45.9 to 53.3% during 1 h and 10 h, while the ones of BZA has a very dramatic decrease from 54 to 28.1%, which was mainly oxidized into BA product. The above results means, completely different with BZA, SO should be a thermodynamically stable substance in DMF solvent, the formed solvation product or other analogues has a lower potential energy, thus results into a higher activation energy and can afford to the nucleophilic attack of the active radicals. On the contrary, it is interesting that, when selecting CH₃CN as reaction solvent, the selectivity to SO and BZA show an opposite tendency. The epoxidation product distributes a weak preference, and S_{SO} has a great decline from 21.6 to 5.12%; while the S_{BZA} turns favorable, increasing from 62.5 to 87.5%, accompanying with the drop of SBA from 15.8% to 7.05%. This phenomenon largely distributes from the fact that SO is neither easy to be produced nor degraded with a ring-open reaction in CH₃CN solvent. At the same time, BZA seems to be an end product in CH₃CN solvent, it is relatively stable and difficult to be oxidized into BA products, therefore results into an obvious achievement in the overall selectivity to BZA, as indicated in Fig. 8b.

In order to demonstrate the structure-activity relationship shown in the catalytic oxidation of styrene, we further employed fluorescence and UV-vis molecule probes to monitor the formation of 'OH radicals and 'O2 ion radicals in the presence of Cr-PKU-1 catalysts with different \overline{Cr}^{3+} concentrations. Fig. 9 gives the concentration dependency of the formed O_2^- ions radical and OH radicals from the catalytic decomposition of H₂O₂ by Cr-PKU-1 catalyst. It clearly exhibits the generation rate of both 'OH and 'O₂⁻ were greatly influenced by the amount of active Cr³⁺ sites. When Cr-free catalyst (0%Cr-PKU-1) was used, the peak intensity were very weak, hinting the poor catalytic capacity. With the increase of Cr content, the formation of 'OH radicals was greatly promoted (Fig. 9b). On the other hand, a raising-first-thenfalling curve was obtained to convert H_2O_2 into O_2^- radicals (Fig. 9a), the maximum concentration was achieved over 10%Cr-PKU-1 catalyst. That is to say, the excessive Cr^{3+} active sites are detrimental to the formation of O_2^- radicals, and O_2^- radicals are very reactive at the higher Cr³⁺ concentration, and they are inclined to be quickly decomposed into the more stable O₂.

The above concentration fluctuation phenomenon was also accordant with our former catalytic results, it shows the Cr^{3+} -incorporated concentration obviously played a vital role on the styrene conversion and the product selectivity. As shown in Entry 3–6 in Table 1, the higher concentration of Cr^{3+} will lead to the higher conversion, changing greatly from 25.9% to 67.9% with increasing Crcontent from 5% to 20%. However, as for the product distributions, the selectivity to both epoxide and carbonyl compounds has the opposite variety tendency. The total amount of carbonyl compounds is



Fig. 9. Concentration variety of formed O_2^- ions radical and OH radicals in the different Cr^{3+} concentration in Cr-PKU-1 catalysts monitored by (a) UV-vis absorption spectrum of the produced formazan and (b) fluorescent spectrum of the produced TAOH. Operational condition: TA (40 mg) or NBT (5 mg), styrene (1 mmol), H₂O₂ (3 mmol), DMF solvent (6 mL), Cr-PKU-1 (30 mg) and heated at 343 K for 6 h.

Table 1		
Summarized results for styrene oxidation	with H_2O_2 oxidant	over Cr-PKU-1 catalyst. ^a

Entry	Temp. (K)	Catalyst	H ₂ O ₂ equiv.	Conv. (%)	S _{SO} (%)	S _{CA} (%)			TOF^{b} (h ⁻¹)	
						S _{BZA}	S _{BA}	S _{PAC}	S _{sum} ^c	
1	343	blank	3	0.41	6.20	90.6	2.10	_	92.7	0.001
2	343	0%Cr-PKU-1	3	6.41	28.2	67.8	2.60	0.38	70.8	0.024
3	343	5% Cr-PKU-1	3	25.9	57.9	24.5	13.8	2.30	40.6	0.207
4	343	10% Cr-PKU-1	3	58.0	53.3	28.1	15.1	2.90	46.1	0.427
5	343	15% Cr-PKU-1	3	62.6	45.7	34.1	16.8	3.05	54.0	0.395
6	343	20% Cr-PKU-1	3	67.9	41.5	37.0	18.5	2.50	58.0	0.389
7	323	10% Cr-PKU-1	3	12.5	29.5	60.1	7.58	0.62	68.3	0.051
8	333	10% Cr-PKU-1	3	25.8	44.2	41.3	11.5	1.85	54.6	0.158
9	353	10% Cr-PKU-1	3	66.2	42.3	35.9	17.5	3.07	56.5	0.387
10	363	10% Cr-PKU-1	3	79.3	31.4	44.9	19.7	2.75	67.4	0.344
11	343	10% Cr-PKU-1	0.5	15.2	60.1	26.4	10.3	2.07	38.8	0.126
12	343	10% Cr-PKU-1	1	31.5	57.5	26.9	11.5	2.42	40.8	0.250
13	343	10% Cr-PKU-1	2	43.8	55.6	27.8	12.6	2.58	43.0	0.336
14	343	10% Cr-PKU-1	4	65.2	48.7	30.4	17.1	2.70	50.2	0.439
15	343	10% Cr-PKU-1	5	68.5	44.1	33.5	19.3	1.85	54.6	0.417

^a Reaction conditions: 1 mmol styrene, 30 mg catalyst, 6 mL DMF, H₂O₂ oxidant, and heated for 10 h.

^b Turnover frequency (TOF) is calculated with the division of the moles of styrene oxide by the moles of used catalyst and reaction time.

 c S_{sum} refers to total selectivity of carbonyl compounds and is calculated by the addition of S_{BZA}, S_{BA} and S_{PAC}.

proportional to Cr^{3+} concentration probably due to the rising concentration of generated 'OH radicals from H₂O₂, among which, the amounts of benzaldehyde and benzoic acid were also becoming larger with the increase of Cr concentration. On the other hand, the amounts of styrene oxide gradually decreased, and its selectivity reduced from 57.9% to 41.5%.

In our previous work, Cr³⁺ active sites were proved to be an efficient stimulus for activation of H2O2 into 'OH radicals in the CH3CN [44], whereas the formation of O_2^- were inhibited in the meantime. A Cr³⁺-Cr²⁺-Cr³⁺ circle was discovered with cyclic voltammetry analysis during the oxidation reaction, and a tentative mechanism was proposed to demonstrate the functions of Cr³⁺ sites based on the obtained results. We believe the oxidative transformation from styrene to carbonyl compounds in CH₃CN medium will also comply with the similar catalytic mechanism. Therefore, in the following, we intend to elucidate the reaction mechanism for styrene epoxidation using DMF solvent over Cr-PKU-1. As far, the mechanism of catalytic epoxidation of styrene with H₂O₂ using active transition metal is not completely understood, therefore the proposed mechanism based on our finding as well as the previously-reported evidences is tentative. As shown in Scheme 1, DMF molecule has a good coordination ability and firstly coordinates to Cr^{3+} to form a transition metal complexes DMF-Cr (III) – OH (⁽¹⁾), which has been evidenced in FTIR and UV–vis spectrum [17,53]. After combining with H₂O₂, metal complexes ^① will transfer into superoxo-type of complex H⁺-DMF-Cr(II)-OO' (2) and undergoes an oxidative addition to the C=C double-bond in the side chain to give an intermediate 3, accompanying with a valence transition of $Cr^{3+} \rightarrow Cr^{2+}$ in the meantime [44]. Thereafter, a cyclic peroxide radical (5) is formed through a migration insertion of the intermediate (3), and simultaneously metal complexes ① is regenerated through the transition state ④. In the end, the obtained cyclic peroxide radical ⑤ can further react with another styrene molecule to give styrene oxide.

Emphatically, 1n the previous studies [52,54,55], some authors have reported that cyclic peroxide radicals ③ can undergo a thermal decomposition to form benzaldehyde or formaldehyde. However, it does not seem to be the case in our current catalytic system. It is well known that epoxide will also suffer a nucleophilic attack to undergo a ring-open catalytic process in a stronger oxidation environmental system, the active intermediates, such as cyclic peroxide radical ③, were believed to be formed and can further perform a thermal decomposition [15,52]. In our case, although a large amount of carbonyl compounds have been produced, they were mostly likely to come from the first pathway, i.e. the oxidation of sidechain alkyl of benzene, based on our experimental fact that epoxide was unable to undergo a deeper decomposition to form benzaldehyde, whether using DMF or CH₃CN solvent. In this sense, we exclude the possibility of thermal decomposition of cyclic peroxide radicals \textcircled into benzaldehyde and other products, although the further elucidation of this point is still needed in future studies. Therefore, it also needs to denote that a few amount of `OH radicals will be inevitable to be formed in DMF, therefore resulting in the formation of carbonyl compounds, such as benzaldehyde and benzoic acid. Nevertheless, as for CH₃CN solvent, the majority of H₂O₂ can be catalytically decomposed into `OH radicals and a trace amount of superoxide ion radicals were produced, therefore it was not surprising to observe the much higher selectivity to carbonyl compounds in CH₃CN.

4. Conclusions

Catalytic oxidation of styrene was performed using H₂O₂ as oxidant and Cr-PKU-1 aluminoborate as catalyst in five different solvents, including CH₃CN, DMF, THF, acetone and 1,4-dioxane, to achieve a comprehensive understanding to the solvent effect in terms of the generated active free radicals. Under the employed reaction conditions, the isolated Cr³⁺ sites in Cr-PKU-1 were proved to function as catalytic sites to activate rapidly H₂O₂ to release two different active free radicals, 'OH radicals and 'O $_2^-$ ions radicals. The molecule probe methods including fluorescence and UV-vis absorption spectra indicated Cr³⁺ catalytic sites promoted the activation of H₂O₂ into [']OH radicals exclusively and restrained the formation of 'O2- ion radicals in CH3CN, while the opposite tendency was observed in DMF. Furthermore, catalytic results showed that an enormous difference in product selectivity occurred in these different solvents. Carbonyl compounds were preferred to be formed probably due to the strong carbonylation effect of hydroxyl radicals in CH₃CN, but the styrene oxide was favorably produced in DMF solvent because of the obvious tendency towards the epoxidation with the help of superoxide ion radicals.

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Scheme 1. The tentative reaction mechanism for styrene epoxidation using DMF solvent and H₂O₂ oxidant over Cr-PKU-1 catalyst.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2019.117283.

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