



Hydrophobic Modification of Microenvironment of Highly Dispersed Co₃O₄ Nanoparticles for the Catalytic Selective Oxidation of Ethylbenzene

Li Zhao,^[a,b] Song Shi,^{*[a]} Meng Liu,^[a,b] Chen Chen,^[a,c] Guozhi Zhu,^[a,b] Jin Gao,^[a] and Jie Xu^{*[a]}

Abstract: Microenvironments in enzymes play crucial roles in controlling the activities of active centers. Here, hexagonal mesoporous silicas (HMS) with hydrophobic microenvironment was used to mimic the enzymes on the hydrocarbon oxidation with cobalt oxides incorporated as active sites. The variation of the structure and surface properties of the materials with phenyl group incorporation and the state of the supported cobalt oxides were carefully studied. It showed that cobalt oxides presented as Co₃O₄ distributed evenly among the support, and the catalytic microenvironment was modified by the neighboring phenyl groups to be hydrophobic. This novel catalyst showed enhancement in the adsorption of ethylbenzene and in turn promoted the catalytic conversion than the hydrophilic one. 55.1% conversion of ethylbenzene and 86.1% selectivity for acetophenone could be obtained at 393 K for 6 h under 1.0 MPa of O2 with free solvent. Hydrophobic microenvironment of pore surface was considered as an important factor for the better catalytic activity.

Introduction

Catalytic selective oxidation of hydrocarbons to oxygencontaining compounds such as ketone, alcohol, aldehyde and acid is an important industrial process, which supplies the essential fundamental chemicals to manufacture polyester, fibre, paint, etc. for our daily life.^[1] For its inert characteristic of C-H bond, the activation and catalytic selective conversion of hydrocarbons was considered as a challenging work in science.^[2] To solve this problem, learning from nature, i.e. the bio-mimic process is an efficient way. Enzymes is a kind of natural catalyst [3] and a lot of high efficient catalysts for hydrocarbon oxidation have been designed through mimicking the active center of metalloenzymes.^[4] Except for the active center, enzymes achieve high catalytic activities and selectivities by creating favorable microenvironments such as hydrophobic pockets around the active centers, which could have interactions with the substrates

L. Zhao, Dr. S. Shi, M. Liu, Dr. C. Chen, G. Zhu, Prof. Dr. J. Gao, [a] Prof. Dr. J. Xu State Key Laboratory of Catalysis **Dalian Institute of Chemical Physics** Chinese Academy of Sciences Dalian National Laboratory for Clean Energy Dalian 116023 (P.R. China) E-mail: shisong@dicp.ac.cn; xujie@dicp.ac.cn L. Zhao, M. Liu, G. Zhu [b] University of Chinese Academy of Sciences Beijing100049 (P.R. China) The present address of C. Chen is School of Materials Science & [c] Chemical Engineering, Ningbo University, Ningbo, Zhejiang, China.

Supporting information for this article is given via a link at the end of the document.

or products.^[5] With this inspiration, the microenvironment aspects such as distal hydrogen bond donors,^[6] hydrophobic binding cavities,^[7] and confined environments^[8] have been researched in the asymmetric synthesis,^[9] small molecule activation,^[10] hydrocarbon cracking,^[11] etc. While, during the selective oxidation of hydrocarbons, water is an unavoidable product. The competitive adsorption caused by the polar difference between weak polar hydrocarbons and strong polar products (including H₂O) could show obvious effect on the catalytic performance. With this special characteristic, it would be possible to design high efficient catalyst for the hydrocarbon oxidation by precisely controlling the hydrophobic microenvironment.

In our previous works, cobalt-silicon nanocomposites modified with oganic groups has shown good performance in the hydrocarbon oxidation.^[12] However, the state of cobalt was ambiguous and the reason for the promotion effect was unclear. Recently, mesoporous silicas have been applied to mimic the role of the scaffold in enzymes, and with supported metal complex as the active center.^[4b] With this model catalyst, the effect of the microenvironment and active center could be researched seperately.

Herein, in combination with our previous cobalt-silicon nanocomposite works, hexagonal mesoporous silicas (HMS) was used to mimic the enzymes' backbone and the highly dispersed Co_3O_4 nanoparticles was applied as active center. With the HMS skeleton modified with phenyl organic group, the hydrophilicity/hydrophobicity microenvironment of the active center could be changed. And with the increasement of the hydrophobicity of the micromentvironment, the catalytic performance on ethylbenzene oxidtion was promoted. Detailed research proved that the pore hydrophobic microenvironment enhanced the adsorption of ethylbenzene and in turn improved the catalytic activity.

Results and Discussion

Characterization of materials

First, the small-angle XRD patterns of HMS and Ph-HMS both exhibited a single diffraction peak corresponding to the (100) plane at 20 of 1-3 °, which was typical characteristic of HMS materials with thick framework wall (Figure 1A). And this single low-angle peak was considered to possess short-range hexagonal symmetry with uniform mesoporous diameter.^[13] Compared with the diffraction peak position in the pattern of HMS, a shift to higher angle for Ph-HMS appeared, manifesting that a lattice contraction occurred with the introduction of phenyl groups. At the same time, the diffraction peak intensity also decreased, manifesting that the ordered mesoporous structure was partly

FULL PAPER

destroyed for Ph-HMS. This situation usually happened during the preparation of organic-inorganic hybrid silica with higher content of organic groups.^[12b, 14] These demonstrated that the phenyl groups were successfully introduced into the materials.

Moreover, through N₂ adsorption-desorption isotherm measurements (Figure S1a, S1c, S2a, S2c and Table 1), HMS exhibited a type IV isotherm with H1 hysteresis as defined by IUPAC for mesoporous materials.^[15] The isotherm exhibited the sharp inflection characteristic of capillary condensation with the uniform mesopores. However, with the introduction of phenyl group, the relative pressure range of P/P_0 of the hysteresis loops of Ph-HMs broaden and the two branches remained nearly horizontal and parallel over a wide range of P/P₀, which exhibited H4 type, indicating a decrease of mesoporosity caused by phenyl loading. Wahab and co-workers observed a similar phenomenon for hybrid periodic mesoporous organosilica materials.^[16] Table 1 lists the detailed structural parameters of the materials, it could found that, HMS and Ph-HMS both had high surface area and well-distributed pore size, and also big pore volume, which would be good candidates for catalysis application. Further, with phenyl modified Ph-HMS, the properties of pore diameter and pore volume were decreased, these verified that the phenyl was successfully introduced into the inner pore and the pore environment was changed.

Further, the FT-IR spectra of HMS and Ph-HMS are shown in Figure 2A. The absorption bands at around 1100, 800, and 470 cm⁻¹ were corresponding to Si-O-Si asymmetric stretching vibrations, symmetric stretching vibrations and bending vibrations, respectively. Typical bands associated with the formation of a condensed siloxane network were present in both cases. For the spectra of the Ph-HMS, typical bands associated with aromatic C=C ring stretching at around 1437 and 1600 cm⁻¹, monosubstituted benzene out-of-plane bending vibration at around 698 and 740 cm⁻¹ could be observed.^[12a] These results further confirmed the presence of phenyl groups in Ph-HMS. Moreover, phenyl immobilizations caused the monotonic blue shift of the band at around 470 cm⁻¹ assigned to Si-O bending vibration to



Figure 1. A) Small-angle XRD patterns of (a) HMS and (b) Ph-HMS; B) Smallangle XRD patterns of (a) 5Co/HMS, mCo/Ph-HMS (m= (b) 1.5, (c) 3, (d) 5 and (e) 7); C) XRD patterns of (a) 5Co/HMS, mCo/Ph-HMS (m= (b) 1.5, (c) 3, (d) 5 and (e) 7), (f) Co₃O₄



Figure 2. A) FT-IR spectra of (a) HMS and (b) Ph-HMS; B) FT-IR spectra of (a) 5Co/HMS, mCo/Ph-HMS (m= (b) 1.5, (c) 3, (d) 5 and (e) 7), (f) Co₃O₄.

higher wave numbers. This may be caused by the partial substitution of Si-O with Si-Ph, and the bending vibration of Si-O was affected by the neighboring phenyl groups. Therefore, these results can be considered as supplementary proof of the successful immobilization of phenyl groups in Ph-HMS.

The presence of phenyl organic group was also detected by ²⁹Si MAS-NMR characterization (Figure 3). For the unmodified HMS, obvious resonances characteristics of the silica network $[Q^n = Si(OSi)_n(OH)_{4-n}, n = 2-4]$ were observed, among which Q^4 $[Q^4 = Si(OSi)_4]$ and $Q^3 [Q^3 = Si(OSi)_3(OH)]$ species were the main components, showing characteristic peaks at around -110 and -102 ppm, respectively. In addition to the Q⁴ and Q³ signals, resonances characterizing of the organosiloxane network T³ [T³=PhSi(OSi)₃] was observed for the Ph-HMS material at around -78 ppm. The appearance of T³ organosilane signal was the



[a] Co content determined by ICP-OES. [b] Surface area calculated from nitrogen adsorption isotherms at 77 K using BET equation. [c] Average pore width calculated from nitrogen adsorption isotherms at 77 K using DFT methods. [d] Total pore volume calculated from nitrogen adsorption isotherms at 77 K at P/P₀ = 0.99. [e] Determined by sessile water contact angle measurements.

Table 1. The physical properties of the samples.

C03O4

content

(wt%)^[a]

7.14

2.07

4.18

7.18

9.94

7.30

SBET

83

811

842

1399

1374

1318

1315

1312

(m²/g)^[b]

Doore

(nm)^[c]

17.3

5.7

5.7

3.4

3.2

3.5

3.5

3.5

Vpore

0.40

2.33

2.48

1.66

1.86

1.84

1.54

1.98

13

19

18

148

147

147

138

138

(mL/g)[d]

7Co/Ph-HMS

FULL PAPER



Figure 3. ²⁹Si MAS NMR of (a) HMS and (b) Ph-HMS.

characteristic of fully crosslinked organosiloxane species,^[17] demonstrating the successful introduction of the phenyl organic groups, which is crucial for increasing the hydrophobic property of the material surface to change the pore environment. Really, sessile water contact angles were measured and the results showed that HMS had a low water contact angle with 19°, which was apparently hydrophilic. While Ph-HMS had a much higher water contact angle with 148° with hydrophobic property (Figure S3), indicating the phenyl modification can change the hydrophilic/hydrophobic property.

The adsorption isotherms of water and ethylbenzene on HMS and Ph-HMS were measured using the IGA at 298 K, respectively (Figure 4). For the isotherms of water on HMS and Ph-HMS (Figure 4A), which could both be characterized as type III, exhibiting gradually increasing with the pressures.^[15a, 18] While the phenyl modified Ph-HMS showed a much lower adsorption amount at the low pressure and at high pressure mostly exhibited physical condensation. In addition, HMS always exhibited higher adsorption amounts than Ph-HMS over the range of test pressure, which indicates higher water adsorption capacity. The results showed that water sorption capacity on HMS is 2.35 times to that of Ph-HMS. The reason would be, on the one hand, HMS had a bigger pore volume (Table 1), 2.33 mL/g for HMS and 1.66 mL/g for Ph-HMS, which is 1.40 times as large as Ph-HMS; on the other hand, HMS was hydrophilic with much stronger interaction with water relative to Ph-HMS (Figure S3). Combining with the curves of the adsorption amount of water on HMS and Ph-HMS at different time (Figure S4), we can see that the adsorption amount of water on HMS was higher than that of Ph-HMS over the range of time, deducing the adsorption rate of water on HMS was higher than that of Ph-HMS. As a result, water was much easier adsorbed on HMS than Ph-HMS. Meanwhile, the corresponding isotherms of ethylbenzene on HMS and Ph-HMS were also characterized (Figure 4B). The adsorption amounts of both were increased with the pressure. However, the adsorption amount of ethylbenzene on Ph-HMS was increased faster than on HMS at the low pressure and reached approximately to pseudoequilibrium quickly, while the adsorption amount of ethylbenzene on HMS was increased steadily. Finally, the adsorption amounts



Figure 4. A) The adsorption isotherms of water on (a) HMS and (b) Ph-HMS; B) The adsorption isotherms of ethylbenzene on (a) HMS and (b) Ph-HMS.

of ethylbenzene on HMS was higher than Ph-HMS because of the high pore volume of HMS. Furthermore, compared with the curves of the adsorption amount of ethylbenzene on HMS and Ph-HMS at different time (Figure S5), the adsorption rate of ethylbenzene on Ph-HMS was higher than HMS, which suggested that ethylbenzene was more easily and more quickly to be adsorbed on Ph-HMS. In conclusion, HMS was easier to adsorb water than Ph-HMS, while the Ph-HMS was easier to adsorb ethylbenzene relative to HMS, which verified the hydrophobic and lipophilic property of Ph-HMS. As a consequence, Ph-HMS could be used as a support to investigate the effect of the hydrophobic pore environment for the catalytic reactions and might have a higher catalytic activity.

More than above, HMS and Ph-HMS introduced with cobalt oxides were firstly tested by small angle XRD (Figure 1B). The patterns showed that 5Co/HMS and the different Co content of Co/Ph-HMS all owned a kind of short-range symmetry of mesoporous structure with the diffraction peaks at 20 of 1-3 °, suggesting the ordered mesoporous structure of the materials were maintained after the introduction of cobalt oxides. Inevitably, with the increasing of Co content, partial destroy of the mesoporous structure appeared and caused the diffraction peak of Co/Ph-HMS in the small-angle region slightly decreased. Yet, through N₂ adsorption-desorption measurement results (Table 1), it could found that, these materials still remained a high specific surface area and big pore size after the cobalt oxides species being immobilized, almost the same with the corresponding supports HMS and Ph-HMS, which were advantageous factors for good catalytic performance.

Through TG-DSC analysis of the as-synthesized 5Co/Ph-HMS (Figure S6), it could be acknowledged that after the weight loss of crystal water with a small amount of adsorbed water and residual ethylene glycol before 530 K, the decomposition temperature of $Co(NO_3)_2$ being supported on Ph-HMS gradually occurred at about 573 K and the dissociation of Si-Ph was above 623 K.^[12a, 19] Here, the calcinations temperature was set as 603 K to assure the full decomposition of $Co(NO_3)_2$ to cobalt oxides and avoid the cleavage of Si-Ph at the same time. Cobalt contents were determined by ICP-OES, and the results with Co_3O_4 loadings are listed in Table 1. The real cobalt contents in different

FULL PAPER

samples were almost the same with the theoretical calculation in the initial precursor.

The crystalline phase of the cobalt oxides was determined by the wide angle XRD measurements (Figure 1C). In the patterns of all the samples, typical diffraction peak of amorphous SiO₂ emerged at 2 θ of 22 °. In addition, with the increasing of the cobalt content, the diffraction peaks located at around 37 °, 45 °, 59 ° and 65 ° gradually appeared, corresponding to (311), (400), (511) and (440) diffractions of Co₃O₄ (ICDD-JCPDS: 00-042-1467), revealing the formation of compound probably as Co₃O₄ form. While weak diffraction intensity and broad diffraction peaks suggested that cobalt oxides owned small nanoparticles and presented as a high dispersion state on the materials.^[20]

The TEM images showed that Co/HMS and Co/Ph-HMS possessed the typical wormhole structure of HMS material assembled from long alkyl chain neutral amine as templates (Figure 5). From the low resolution of the TEM graphs, cobalt nanoparticles could not be seen clearly, which might be existed with too small size and the weak contrast difference between the support SiO₂ and Co₃O₄ nanoparticles, consistent with the results of weak and broad diffraction peaks of XRD. While from the HR-TEM micrographs, we can see the randomly oriented lattice fringes, including (222), (311) and (400), further verified the cobalt oxides presented as Co₃O₄. And the particle size was about 2-3 nm, which was easily to locate in the pore of the silicas.

The coordination geometries of cobalt species supported on HMS and Ph-HMS were carefully studied by UV-Vis DRS method (Figure 6). A broad absorption band around 700 nm was attributed to Co (II) in tetrahedral environments and the absorption band emerging at 420 nm was attributed to Co (III), which were similar with the spectrum of Co_3O_4 (Figure 6f).^[20a, 21] These results indicated that the cobalt oxides supported on HMS or Ph-HMS presented as Co₃O₄ phase. This was consistent with the characterization results of wide angle XRD and TEM. At the same time, it can be deduced that the presence of phenyl groups did not change the crystal phase of cobalt oxides because that the coordination geometries of cobalt species were same for Co/HMS and Co/Ph-HMS. Moreover, two intense bands in the UV region centered at 212 and 262 nm exhibited characteristic vibration structure for all the samples with Ph-HMS as support (Figures 7be), which were assigned to π - π * transitions of benzene ring.^[12b] It can be taken as a strong evidence for the presence of phenyl groups in these materials.

The FT-IR spectra of the samples are shown in Figure 2B. For Co/HMS and Co/Ph-HMS, like the supports HMS and Ph-HMS, typical bands associated with formation of a condensed siloxane network were present in all cases (Si-O-Si bands around 1100, 800, and 470 cm⁻¹). For the spectra of all the Co/Ph-HMS, typical bands associated with aromatic C=C ring stretching (weak peaks around 1437 and 1600 cm⁻¹), mono-substituted benzene bending vibration (around 698 and 740 cm⁻¹) could be observed. These results further confirmed the presence of phenyl groups in Co/Ph-HMS. The introduction of hydrophobic phenyl groups on the surface of these Co/Ph- HMS materials might change their pore environment of surface hydrophilicity/hydrophobicity. Actually, through the sessile water contact angle measurement (Table 1), it could be observed that phenyl-containing materials all owned a high water contact angle between 138-147 °, which



Figure 5. TEM images of (a, a') 5Co/HMS, mCo/Ph-HMS (m= (b, b') 1.5, (c, c') 3, (d, d') 5 and (e, e') 7) and (f, f) 5Co/Ph-HMS after reaction.

FULL PAPER



Table 2. Catalytic oxidation of ethylbenzene over the catalysts^[a]. $\bigcap_{1} \longrightarrow \bigcap_{2}^{H} + \bigcap_{3}^{H} + \bigcap_{4}^{H} + \bigcap_{5}^{H} + \bigcap_{6}^{H} + \bigcap_{6}^{$

Catalysts	Conv. (%)	Products distribution (%)					TOF
		2	3	4	5	6	(h ⁻¹) ^[b]
Co ₃ O ₄	21.6	56.8	28.2	1.7	3.4	9.9	14
5Co/HMS	40.8	80.9	15.1	0.5	3.3	0.2	376
1.5Co/Ph-HMS	47.8	82.4	11.6	0.9	4.7	0.4	1519
3Co/Ph-HMS	49.2	76.9	15.2	1.0	6.6	0.3	774
5Co/Ph-HMS	55.1	86.1	7.0	0.6	5.9	0.4	505
7Co/Ph-HMS	54.4	77.7	12.4	0.5	4.8	4.6	360

Figure 6. UV-Vis DRS of (a) 5Co/HMS, mCo/Ph-HMS (m= (b) 1.5, (c) 3, (d) 5 and (e) 7), and (f) Co_3O_4 .

[a] Reaction conditions: 10 mL of ethylbenzene, 50 mg of catalyst, 1.0 MPa of O₂, 6 h, 393 K. [b] TOF numbers were calculated based on the total molar quantity of Co_3O_4 .^[22]

was far bigger than that of Co/HMS (18 °) (Figure S3), demonstrating the materials changed from hydrophilic to hydrophobic with the phenyl group introduced. Otherwise, the increasing of cobalt content did not change the surface hydrophobicity apparently. In the distribution test, it could be observed that 5Co/HMS showed hydrophilicity and it distributed in the water phase, while 5Co/Ph-HMS distributed in the organicphase of ethylbenzene for its hydrophobicity (Figure S7). In addition, in the FT-IR spectra of Co/Ph-HMS, the absorption bands at around 580 and 660 cm⁻¹ were similar with that of Co-O vibration of Co₃O₄, which further indicated that the cobalt oxides presented as Co₃O₄, consistent with UV-Vis DRS and XRD characterization results.

Catalytic performances

Selective oxidation of ethylbenzene was chosen as a model reaction to study the improvement of supported cobalt oxides catalysts and the pore environment effect of surface hydrophilicity/hydrophobicity on the catalytic performance. The oxidation products were mainly including acetophenone (2), 1phenethyl alcohol (3), benzaldehyde (4), benzoic acid (5) and phenylethylhydroperoxide (6). Through the temperature test on 5Co/Ph-HMS catalyst, 393 K was selected as the best reaction temperature (Figure S8). The catalytic reactions were all operated at 393 K with O₂ as oxidant in the absence of any solvent and additives, and the results are listed in Table 2. Pure Co₃O₄ was taken as a referenced catalyst, which gave a 21.6% conversion of ethylbenzene under the present conditions. Compared with the pure Co₃O₄, the supported hydrophilic catalyst of 5Co/HMS showed a higher catalytic activity with 40.8% conversion of ethylbenzene. This result manifested that the catalytic active species supported on a porous material could show a better catalytic performance. Among the different supported hydrophobic catalysts of mCo/Ph-HMS, 5Co/Ph-HMS showed a best catalytic activity. The conversion of ethylbenzene reached 55.1%, which were higher than that with the hydrophilic catalyst of 5Co/HMS. The pore environment of surface hydrophobicity might be the main reason for this catalytic activity enhancement. It can be explained: for the catalytic selective oxidation of ethylbenzene, water is the inevitable by-product accompanying the formation of the oxygenated products, and the polarity is very different for ethylbenzene and water molecules, with the molecular dipole moment of 0.59 and 1.85 D, respectively.^[23] With the dispersion test (Figure S7), the weak polar of ethylbenzene and strong polar of water had quite different adsorption effect on the catalysts. On the hydrophobic microenvironment modified catalyst, the weak polar ethylbenzene molecule was more inclined to be adsorbed, while the strong polar molecule such as water molecule was more inclined to be adsorbed on the hydrophilic catalyst. In addition, with the IGA measurements in Figure 4 and the adsorption amount of ethylbenzene and water versus time in Figures S4 and S5, we can deduce that ethylbenzene was easier and faster adsorbed on the sample with hydrophobic microenvironment, reflected by the higher adsorption amount of ethylbenzene on Ph-HMS at the same time, while water was easier and faster adsorbed on the sample with hydrophilicity (Figure S4, S5). As a result, for hydrophilic sample who preferred to adsorb water than hydrophobic one, the active center was occupied by water. While for the hydrophobic microenvironment catalyst, ethylbenzene was easier and faster to be adsorbed which lead to the inhibition of water to occupy the active site than the hydrophilic sample. Thus the hydrophobic on microenvironment modified catalyst promoted the adsorption of ethylbenzene and in turn improved the catalytic activity.

Compared with the previous reported catalytic system for the solvent-free oxidation of ethylbenzene under oxygen in the references (Table S1), $^{[20a,\ 24]}$ most of which belong to the

FULL PAPER

hydrophilic catalyst, the present hydrophobic microenvironment modified 5Co/Ph-HMS catalyst showed predominance.

The Co content of the solution was only 3.5 ppm after reaction, suggesting trace Co was lost in the reaction. In addition, the conversion of ethylbenzene with homogeneous catalyst with similar Co content of cobalt acetate was only 9.2 % under the same condition,^[20a] which indicated that cobalt aqueous made little contribution to the reaction and supported Co₃O₄ was the actual active composition. Besides, the FT-IR spectrum and UV-Vis DRS of 5Co/Ph-HMS after the reaction were shown in Figure S9 and Figure S10. From the FT-IR spectrum we can see the mono-substituted benzene out-of-plane bending vibration peaks at around 698 and 740 cm⁻¹, suggesting the phenyl group was remained during the reaction. At the same time, UV-Vis DRS of 5Co/Ph-HMS after the reaction showed two intense bands exhibited in the UV region centered at 212 and 262 nm, which were assigned to π - π ^{*} transitions of benzene ring. It can be taken as a strong evidence for the presence of phenyl groups in the catalyst, which was consistent with the result of FT-IR. In addition, TEM characterization showed that cobalt oxide after the reaction was still highly dispersed and kept the Co₃O₄ structure (Figure 5(f, f')), in agreement with the result of UV-Vis DRS, of which a broad absorption band around 700 nm was attributed to Co ($\rm II$) in tetrahedral environments and the absorption band emerging at 420 nm was attributed to Co (III). All these indicated the active centers were relatively stable during the reaction process.

The effect of reaction time on the conversion of ethylbenzene is shown in Figure 7. At the first 1 h, the conversion of ethylbenzene was both very low, 7.8% and 11.9% with 5Co/Ph-HMS and 5Co/HMS, respectively. With time going on, the conversion of ethylbenzene increased uniformly and then remained stable over 5Co/HMS, while with 5Co/Ph-HMS, the conversion of ethylbenzene increased steeply at the initial 1-2 h, from 7.8% to 34.5% and then increased linearly till to reach steady. Compared with non-phenyl modified 5Co/HMS catalyst, the initial reaction of ethylbenzene was relatively faster with phenyl modified 5Co/Ph-HMS catalyst. The reason may be that phenyl modified catalyst had hydrophobic and lipophilic properties, it can adsorb and accumulate substrate ethylbenzene, which is a weak polar molecular, more quickly than non-phenyl catalyst, thus had a higher concentration of substrate and a faster conversion. As



Figure 7. Influence of reaction time on catalytic performances at 393 K over (a) 5Co/ HMS and (b) 5Co/Ph-HMS.

the reaction time increased, the two catalysts both had the ability to accumulate high concentration of ethylbenzene, the conversion of ethylbenzene would both increase smoothly. This was consistent with the IGA measurement results of the adsorption amount of ethylbenzene on Ph-HMS and HMS at different time (Figure S5). And the adsorption rate of ethylbenzene on Ph-HMS was higher than that of HMS at the initial period, which was reflected by the higher adsorption amount at the same time. Thus it was quickly to reach adsorption pseudo -equilibrium on Ph-HMS, which could promote phenyl modified catalyst have higher concentration of ethylbenzene at the initial period and then have higher conversion increasing from 1 h to 2 h in the initial reaction period. We also got a suitable reaction time of 6 h to make a sufficient conversion of ethylbenzene.

Conclusions

Hexagonal hydrophobic mesoporous with silicas microenvironment to mimic the enzymes was realized to achieve high efficiency catalyst for the liquid phase oxidation of ethylbenzene with oxygen. Carefully characterizations revealed that phenyl groups were successfully introduced into the frameworks of HMS through co-condensation method and had made a difference on the structure properties compared with nonmodification material, providing a hydrophobic pore environment around the cobalt oxide nanoparticles, of which dispersed evenly on the support presented as Co₃O₄. As a result, phenyl hydrophobic modification made the catalyst showed enhancement in the adsorption of ethylbenzene and in turn promoted the catalytic conversion than non-phenyl modification one. This research makes us believe that carefully tune the hydrophobicity of catalytic microenvironment will open a new avenue for heterogeneous catalysis.

Experimental Section

Material preparation

Tetraethyl orthosilicate (TEOS, 98%), cobalt nitrate ($Co(NO_3)_2$ - $6H_2O$, 99%), and ethylene glycol ((CH_2OH)₂, 99%) were obtained from Tianjin Kermel Chemical Reagent Development Center, China. Phenyltriethoxysilane (PTES, 98%) and hexadecylamine (HDA, 90%) were purchased from Aladdin, China. Deionized water used in all experiments was obtained from a Milli-Q system (Millipore). Other reagents were used as received.

Phenyl modified hexagonal mesoporous silicas (Ph-HMS) was synthesized based on the previous report by a modified method.^[13] A typical material was synthesized from the gels with the following total molar composition: 0.85 TEOS: 0.15 PTES: 0.27 HDA: 10.78 C₂H₅OH: 60.89 H₂O. The template was removed from the as-synthesized material by NH₄NO₃/ethanol extraction. A pure siliceous HMS was synthesized as above method without PTES.

Co/Ph-HMS and Co/HMS were prepared by quantitative impregnation method with Ph-HMS and HMS as support and $Co(NO_3)_2$ - $6H_2O$ as metal precursor in ethanol solution. Typically, 0.3 g support was pre-treated with 20.5 g ethylene glycol for 1 h at room temperature and then filtrated, dried at oven under 120 °C. Next, appropriate amount of $Co(NO_3)_2$ - $6H_2O$ was added into 5 mL ethanol solution and stirred homogeneously, then the

VIANUSCII

じい

FULL PAPER

support was added and stirred overnight under 40 °C. The solution was evaported and then dried under 80 °C. The as-synthesized catalysts were calcined at 603 K for 10 min in muffle furnace. The obtained catalysts were denoted as mCo/Ph-HMS and mCo/HMS (m is the initial mass fraction of cobalt in the catalysts). Co_3O_4 was achieved by the calcination of $Co(NO_3)_2$ -6H₂O.

Characterization methods

The X-ray powder diffraction (XRD) patterns were obtained using Rigaku D/Max-2500/PC powder diffraction system with Cu K radiation (λ =0.15406 nm) between 5 and 80 ° by 5 °/min (40 KV, 200 mA) and smallangle XRD between 0.5 and 10 ° by 2 °/min (40 KV, 30 mA), respectively. Fourier transform infrared (FT-IR) spectra were collected in KBr media between 4000 and 400 cm⁻¹ on a Bruker Tensor 27. The specific surface area and pore volume was determined by N₂ adsorption-desorption at 77 K on a Quantachrome Autosorb-1 instrument, the samples were degassed for 12 h before determination. Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) were collected on a Jasco V550 spectrophotometer equipped with a diffuse reflectance attachment. The microstructures of the materials were examined by transmission electron microscopy (TEM) on a FEI Tecnai G2 F30 S-Twin electron microscope. Thermogravimetric analysis (TGA) measurements were carried out under air flow on a NETZSCHSTA 409 PC instrument. Nuclear magnetic resonance spectra of ²⁹Si with magic-angle spinning (²⁹Si MAS- NMR) were obtained on a Bruker DRX-400 spectrometer. Water (ultrapure Millipore) and ethylbenzene (purity > 99.7%) adsorption isotherms at 298 K were measured on an Intelligent Gravimetric Analyser (IGA-Hiden Ltd.). The samples were outgassed in 393 K under high vacuum (10⁻⁷ mbar) before determination, while proper outgassing was ensured by monitoring the samples weight changes during heating. For measurements, the system was allowed to wait until the weight changes lower than 0.01 mg in 60 s We each set point. also measured the surface hydrophilicity/hydrophobicity of these materials by depositing as a film on a glass substrate using the contact angle measuring system JC 2000 A. The amount of water droplet was 5 µL.

Catalytic selective oxidation of ethylbenzene

Catalytic reactions were performed on a 60 mL autoclave reactor with a Teflon insert inside. Here, 10 mL of ethylbenzene and 50 mg of catalyst were added into the reactor at the absence of any solvent. When heated to the desire temperature, the reactor was charged with 1 MPa of O2 under magnetic stirring and kept constant by feeding O2 during the reaction. The products were quantitated by Agilent 6890N GC equipped with an Agilent HP-INNOWAX column (30.0 m×320 µm×0.25 µm) and flame ionization detector. After the quantitative decomposition of phenylethylhydroperoxide to 1-phenethyl alcohol by adding triphenylphosphine to the reaction mixture, phenylethylhydroperoxide was calculated based on the difference value of 1-phenethyl alcohol between the sample with triphenylphosphine and without triphenylphosphine, 1-phenethyl alcohol was calculated based on the sample without triphenylphosphine, acetophenone, benzaldehyde, and benzoic acid were calculated based on the sample with triphenylphosphine. The conversion of ethylbenzene was calculated based on the yield of products. They were all determined by an internal standard method using p-dichlorobenzene as the internal standard.

Acknowledgements

This work was supported by National Natural Science Foundation of China (Grant no. 21790331 and 21603218), the Strategic Priority Research Program of Chinese Academy of Sciences (XDA21030400 and XDB17020300). **Keywords:** hydrophobic microenvironment • adsorption • catalytic oxidation • Co₃O₄ • hexagonal mesoporous silicas

- a) F. Recupero, C. Punta, *Chem. Rev.* 2007, *107*, 3800-3842.; b) P.
 Zhang, Y. Gong, H. Li, Z. Chen, Y. Wang, *Nat. Commun.* 2013, *4*, 1593;
 c) L. Y. Margolis, *Adv. Catal.* 1963, *14*, 429-501; d) Y. Ishii, S. Sakaguchi,
 T. Iwahama, *Adv. Synth. Catal.* 2001, *343*, 393-427.
- [2] a) D. Balcells, E. Clot, O. Eisenstein, *Chem. Rev.* 2010, *110*, 749-823; b)
 M. W. Smith, D. A. Berry, D. Shekhawat, D. J. Haynes, J. J. Spivey, *Fuel* 2010, *89*, 1193-1201; c) E. Roduner, W. Kaim, B. Sarkar, V. B. Urlacher, J. Pleiss, R. Glaeser, W.-D. Einicke, G. A. Sprenger, U. Beifuss, E. Klemm, C. Liebner, H. Hieronymus, S.-F. Hsu, B. Plietker, S. Laschat, *Chemcatchem* 2013, *5*, 82-112; d) D. Munz, T. Strassner, *Inorg. Chem.* 2015, *54*, 5043-5052; e) R. Burch, M. J. Hayes, *J. Mol. Catal. A-Chem.* 1995, *100*, 13-33.
- a) K. M. Koeller, C. H. Wong, *Nature* 2001, *409*, 232-240; b) F. Hollmann,
 I. W. C. E. Arends, K. Buehler, A. Schallmey, B. Bühler, *Green Chem.* 2011, *13*, 226-265; c) R. Fasan, *ACS Catalysis* 2012, *2*, 647-666.
- [4] a) B. E. R. Snyder, M. L. Bols, R. A. Schoonheydt, B. F. Sels, E. I. Solomon, *Chem. Rev.* 2018, *118*, 2718-2768; b) C.-C. Liu, T.-S. Lin, S. I. Chan, C.-Y. Mou, *J. Catal.* 2015, *322*, 139-151; c) C. Zhang, P. Srivastava, K. Ellis-Guardiola, J. C. Lewis, *Tetrahedron* 2014, *70*, 4245-4249; d) S. I. Chan, S. S. F. Yu, *Acc. Chem. Res.* 2008, *41*, 969-979.
- [5] a) C. U. Kim, W. Lew, M. A. Williams, H. T. Liu, L. J. Zhang, S. Swaminathan, N. Bischofberger, M. S. Chen, D. B. Mendel, C. Y. Tai, W. G. Laver, R. C. Stevens, *J. Am. Chem. Soc.* **1997**, *119*, 681-690; b) J. Gao, H. Wang, L. Wang, J. Wang, D. Kong, Z. Yang, *J. Am. Chem. Soc.* **2009**, *131*, 11286-11287.
- [6] a) A. S. Borovik, Acc. Chem. Res. 2005, 38, 54-61; b) M. X. Tan, L. Gu,
 N. Li, J. Y. Ying, Y. Zhang, Green Chem. 2013, 15, 1127-1132; c) C. L.
 Lockhart, M. A. Conger, D. S. Pittman, M. D. Liptak, J. Biol. Inorg. Chem.
 2015, 20, 757-770.
- [7] a) D. J. Xiao, J. Oktawiec, P. J. Milner, J. R. Long, *J. Am. Chem. Soc.* **2016**, *138*, 14371-14379; b) C. E. Song, S. J. Park, I. S. Hwang, M. J. Jung, S. Y. Shim, H. Y. Bae, J. Y. Jung, *Nat. Commun.* **2019**, *10*, 851.
- [8] a) D. Fiedler, D. H. Leung, R. G. Bergman, K. N. Raymond, *Acc. Chem. Res.* 2005, *38*, 351-360; b) D. Deng, X. Chen, L. Yu, X. Wu, Q. Liu, Y. Liu, H. Yang, H. Tian, Y. Hu, P. Du, R. Si, J. Wang, X. Cui, H. Li, J. Xiao, T. Xu, J. Deng, F. Yang, P. N. Duchesne, P. Zhang, J. Zhou, L. Sun, J. Li, X. Pan, X. Bao, *Sci. Adv.* 2015, *1*, e1500462; c) X. Cui, H. Li, Y. Wang, Y. Hu, L. Hua, H. Li, X. Han, Q. Liu, F. Yang, L. He, X. Chen, Q. Li, J. Xiao, D. Deng, X. Bao, *Chem* 2018, *4*, 1902-1910.
- [9] W. Gong, D. D. Chu, H. Jiang, X. Chen, Y. Cui, Y. Liu, Nat. Commun. 2019, 10, 600.
- [10] C. Costentin, M. Robert, J.-M. Saveant, Chem. Soc. Rev. 2013, 42, 2423-2436.
- [11] A. Primo, H. Garcia, Chem. Soc. Rev. 2014, 43, 7548-7561.
- [12] a) C. Chen, S. Shi, M. Wang, H. Ma, L. Zhou, J. Xu, *J. Mater. Chem. A* 2014, *2*, 8126-8134; b) C. Chen, J. Xu, Q. Zhang, H. Ma, H. Miao, L. Zhou, *J. Phys. Chem. C* 2009, *113*, 2855-2860; c) C. Chen, J. Xu, Q. Zhang, Y. Ma, L. Zhou, M. Wang, *Chem. Commun.* 2011, *47*, 1336-1338; d) Q. Zhang, C. Chen, M. Wang, J. Cai, J. Xu, C. Xia, *Nanoscale Res. Lett.* 2011, *6*, 586.
- [13] P. T. Tanev, T. J. Pinnavaia, *Science* **1995**, *267*, 865-867.
- [14] a) T. Yokoi, H. Yoshitake, T. Tatsumi, *J. Mater. Chem.* 2004, *14*, 951-957; b) D. Owens, A. J. Han, L. Y. Sun, Y. B. Mao, *Int. J. Hydrogen Energy* 2015, *40*, 2736-2741.
- [15] a) K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem.* **1985**, *57*, 603-619;
 b) M. Thommes, *Chem. Ing. Tech.* **2010**, *82*, 1059-1073.
- [16] M. A. Wahab, Kim, II, C. S. Ha, *Microporous Mesoporous Mater.* 2004, 69, 19-27.
- [17] S. Shi, C. Chen, M. Wang, J. Ma, H. Ma, J. Xu, Chem. Commun. 2014, 50, 9079-9082.
- a) E. C. Vermisoglou, V. Georgakilas, E. Kouvelos, G. Pilatos, K. Viras,
 G. Romanos, N. K. Kanellopoulos, *Microporous Mesoporous Mater.*

FULL PAPER

2007, 99, 98-105; b) L. Cossarutto, T. Zimny, J. Kaczmarczyk, T. Siemieniewska, J. Bimer, J. V. Weber, *Carbon* 2001, *39*, 2339-2346.

- [19] a) X. Lv, J.-F. Chen, Y. Tan, Y. Zhang, *Catal. Commun.* 2012, *20*, 6-11;
 b) M. J. Tiernan, E. A. Fesenko, P. A. Barnes, G. M. B. Parkes, M. Ronane, *Thermochim. Acta* 2001, *379*, 163-175; c) M. Wang, C. Chen, Q. Zhang, Z. Du, Z. Zhang, J. Gao, J. Xu, *J. Chem. Technol. Biotechnol.* 2010, *85*, 283-287.
- [20] a) H. Ma, J. Xu, C. Chen, Q. Zhang, J. Ning, H. Miao, L. Zhou, X. Li, *Catal. Lett.* **2007**, *113*, 104-108; b) M. Stoyanova, I. Slavova, S. Christoskova, V. Ivanova, *Appl. Catal. A: Gen.* **2014**, *476*, 121-132.
- a) P. Visuvamithiran, B. Sundaravel, M. Palanichamy, V. Murugesan, J. Nanosci. Nanotechnol. 2013, 13, 2528-2537; b) M. S. Hamdy, A. Ramanathan, T. Maschmeyer, U. Hanefeld, J. C. Jansen, Chem. Eur. J. 2006, 12, 1782-1789.
- [22] a) H. C. Hu, I. E. Wachs, *J. Phys. Chem.* **1995**, *99*, 10911-10922; b) L.
 E. Briand, A. M. Hirt, I. E. Wachs, *J. Catal.* **2001**, *202*, 268-278; c) K. An,
 S. Alayoglu, N. Musselwhite, S. Plamthottam, G. Melaet, A. E. Lindeman,
 G. A. Somorjai, *J. Am. Chem. Soc.* **2013**, *135*, 16689-16696.
- [23] a) W. J. Hehre, J. A. Pople, L. Random, J. Am. Chem. Soc. 1972, 94, 1496-1504; b) S. A. Clough, Y. Beers, G. P. Klein, L. S. Rothman, J. Chem. Phys. 1973, 59, 2254-2259.
- [24] a) C. Yang, L. Fu, R. Zhu, Z. Liu, *Phys. Chem. Chem. Phys.* 2016, *18*, 4635-4642; b) V. Choudhary, J. Indurkar, V. Narkhede, R. Jha, *J. Catal.* 2004, *227*, 257-261; c) W.-F. Xu, W.-J. Chen, D.-C. Li, B.-H. Cheng, H. Jiang, *Ind. Eng. Chem. Res.* 2019, *58*, 3969-3977; d) Y. Chen, S. Zhao, Z. Liu, *Phys. Chem. Chem. Phys.* 2015, *17*, 14012-14020; e) J. Gao, X. Tong, X. Li, H. Miao, J. Xu, *J. Chem. Technol. Biotechnol.* 2007, *82*, 620-625; f) S. Jie, C. Yang, Y. Chen, Z. Liu, *Mol. Catal.* 2018, *458*, 1-8; g) S. Jie, X. Lin, Z. Chao, Z. Liu, *Mater. Chem. Phys.* 2018, *214*, 239-246; h) S. K. Jana, P. Wu, T. Tatsumi, *J. Catal.* 2006, *240*, 268-274; i) S. Jana, Y. Kubota, T. Tatsumi, *J. Catal.* 2007, *247*, 214-222.

FULL PAPER

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Hexagonal mesoporous silicas with hydrophobic microenvironment modified by phenyl group was used to mimic the enzymes with Co_3O_4 incorporated as active sites, the pore hydrophobic environment had an enhancement in the adsorption of ethylbenzene and in turn improved the catalytic selective oxidation activity than the hydrophilic one.



Li Zhao, Song Shi,* Meng Liu, Chen Chen, Guozhi Zhu, Jin Gao, and Jie Xu*

Page No. – Page No.

Hydrophobic Modification of Microenvironment of Highly Dispersed Co₃O₄ Nanoparticles for the Catalytic Selective Oxidation of Ethylbenzene