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Catalytic aerobic oxidation of ethylbenzene over Co/SBA-15

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Co(II)O was highly dispersed in the mesopores of SBA-15 by alcoholic impregnation method and characterized by XRD, TEM, UV–VIS DRS, TPR, and XRF techniques. It was found that tetrahedral coordinated Co(II)O was stabilized by SBA-15 at low Co-loading. Co/SBA-15 showed much higher activity than $Co(OAc)_2$ or Co_3O_4 in the liquid-phase aerobic oxidation of ethylbenzene under solvent-free condition.

KEY WORDS: cobalt oxide; ethylbenzene; oxidation; SBA-15.

1. Introduction

Catalytic oxidation of hydrocarbons like cyclohexane, ethylbenzene, toluene, etc., provides routes to a wide range of important functionalized molecules including alcohols, ketones, epoxides, and carboxylic acids [1]. Homogeneous catalysis systems, always including lower oxidation state transition metals and acetic acid media, have been successfully applied in industrial oxidation processes. Moreover, promoters or additives were added to improve the activities. For example, bromide could promote the oxidation of *p*-xylene to terephthalic acid using Co/Mn catalyst system [2]. NHPI serving as a radical catalyst promoter, usually combined with Co(II) or Mn(II) salts, was found to effectively catalyze oxidation of various hydrocarbons in acetic acid [3–5]. Though addition of promoters or additives is very efficient for oxidation of hydrocarbons, it may cause more cost. Furthermore, these homogeneous systems still have several inherent disadvantages of the difficulties in separation of products and the disposal of toxic solids and liquid wastes.

One way to resolve these problems of homogeneous systems is to heterogenize transition metal complexes on porous supports. Nowotny *et al.* immobilized cobalt acetate complexes on carboxylate silica. However, the complexes tended to leach in reaction conditions [6]. Furthermore, various cobalt-containing molecular sieves have been employed. Thomas et al. had extensively studied iron, manganese, and cobalt substituted microporous aluminophosphate (AlPOs) molecular sieves, and found that oxidisable cobalt(II) in the framework was responsible for the activity [7, 8]. Recently, mesoporous siliceous materials have attracted considerable attention as promising new hydrocarbon oxidation carriers [9]. The use of very uniform mesoporous siliceous materials such as MCM-41, TUD-1, and SBA-15 as support has been recently explored. The large amount of Si–OH inside the mesopores should facilitate the introduction of precursors and the very high surface should allow the high dispersion. In case of Co/SiO_2 catalysts, the previous study indicated that high Co-loading in MCM-41 or SBA-15 facilitated the formation of bulk crystals of Co_3O_4 by direct hydrothermal treatment methods [10] or impregnation methods [11]. So it is necessary and useful to synthesize the oxidisable cobalt(II) species in mesoporous silica and study its catalytic performance in hydrocarbon oxidation.

In this paper, highly dispersed tetrahedral Co(II)O, not Co_3O_4, was found to be stabilized in the SBA-15 mesopores at low CoO-loading. The catalytic activity of Co/SBA-15 was tested. It showed high activity in the liquid oxidation of ethylbenzene by dioxygen without additives or solvents. Highly dispersed Co(II)O in tetrahedral state may be responsible for its high activity.

2. Experimental

2.1. Chemicals and catalyst preparation

The mesoporous silica SBA-15 sample (surface area of 800 m^2/g and mean pore size of 7 nm) was from Changchun Jilin University High-Tech, Co. Ltd. $Co(OAc)_2\cdot 4H_2O$ (99%) and ethanol (99.7%) were obtained from Tianjin Kermel Chemical Reagent Development Center. Acetophenone (AcPO, 99.9%) was purchased from Beijing Chemical Plant.

After the templates had been completely removed by calcination, 1.0 g SBA-15 was added into ethanol solutions of $Co(OAc)_2\ 4H_2O$ (0.005 M, 100 mL) and stirred

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overnight at 313 K. After filtered and dried by evaporation under reduced pressure, the sample was calcined in air at 773 K for 5 h. The resulting sample was denoted as Co/SBA-15.

2.2. *Oxidation reaction and products analysis*

The typical catalytic oxidation of ethylbenzene was performed in a 50 ml stainless steel high-pressure reactor equipped with a magnetic stirrer. 50 mg Co/SBA-15 and 15 ml ethylbenzene (123 mmol) were added into the autoclave. After the given temperature reached, O_2 was pressurized (ca. 1.0 MPa) into the reactor and the pressure was kept constant by supplying dioxygen during the reaction.

The oxidation products were identified by Agilent 6890N GC/5973 MS detector and quantitated by Agilent 4890D GC equipped with FID detector. AcPO and 1-phenylethanol (PEA) were determined by the internal standard method using 1,2,4,5-tetramethylbenzene as the internal standard. Before GC measurement, the mixture was treated with excess Ph_3P for 1 h according to literatures [12–14]. 1-phenylethyl hydroperoxide (PEHP) and benzoic acid (BZA) were accurately quantified by titration using $Na_2S_2O_3$ and NaOH standard aqueous solution, respectively.

2.3. *Characterization of catalysts*

XRD patterns were recorded on a PANalytical X'Pert PRO instrument with Cu-Kα (Cu-Kα, $\lambda = 0.154$ nm, 40 kV, 40 mA) radiation in the range of 3–70°. Small-angle XRD were carried out using a Rigaku D/Max 3400 powder diffraction system using Cu-Kα radiation ($\lambda = 0.154$ nm, 40 kV, 50 mA) in the range of 0.6–5°.

UV–VIS DRS spectra was collected over a wavelength range from 800 to 200 nm on Jasco V-550 UV–VIS spectrophotometer equipped with a diffuse reflectance attachment.

Philips Magix X-ray fluorescence spectrometer was used to determine the cobalt content of Co/SBA-15. The ICP analysis was carried out using ICP atomic absorption spectroscopy (Leeman PLA-SPEC-II) to examine the concentration of cobalt in the filtrate.

The microstructures of SBA-15 and Co/SBA-15 were obtained from TEM measures (JEOL-JEM-2000EX).

TPR was carried out by feeding 5% H_2 in N_2 to 30 mg sample in a conventional flow reactor without oxidation treatment prior to measurements. The rate of H_2 consumption was determined by a thermal conductivity detector and recorded on an on-line personal computer.

3. Results and discussion

3.1. *The characterization of catalysts*

Figure 1 illustrates the X-ray diffractions within the range of 3–70° of calcined SBA-15 and Co/SBA-15. Only the diffuse peaks of noncrystalline silica have been observed and no characteristic peaks belong to cobalt oxides. It indicates that the crystallite size of cobalt oxides are below the lower limit for XRD detectability (5 nm), or an amorphous CoO is formed [11]. The inset shows the small-angle XRD pattern of Co/SBA-15. It displays three well-resolved peaks which are indexed to (100), (110), (200) reflections of the hexagonal space group *p6mm*. The hexagonal structure was maintained.

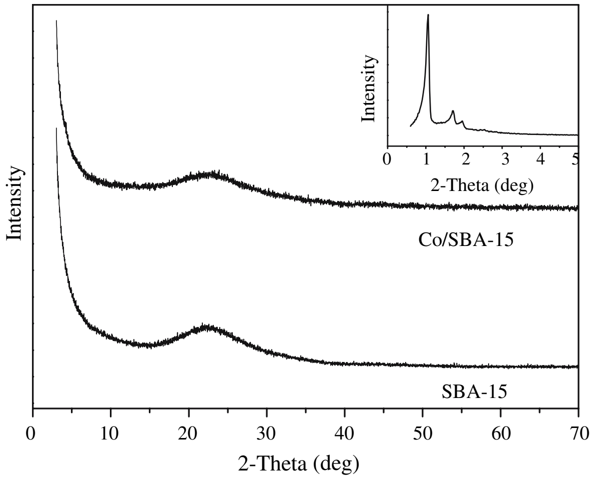

Figure 1. The XRD patterns of SBA-15 and Co/SBA-15. The inset is the small-angle XRD pattern for Co/SBA-15.

As shown in Figure 2, the UV–VIS spectra of Co/SBA-15 sample displays three absorption peaks (525 nm, 590 nm, and 640 nm), which can be unambiguously assigned to the$^4A_2(F) \rightarrow {}^4T_1(P)$ transition of Co(II) ions in tetrahedral environments as identified in previous study [15–17]. The tripartition of the peak is due to spin-orbit coupling. The blue color of Co/SBA-15 is also a fingerprint of tetrahedral Co(II)O_4 sites. In addition, the

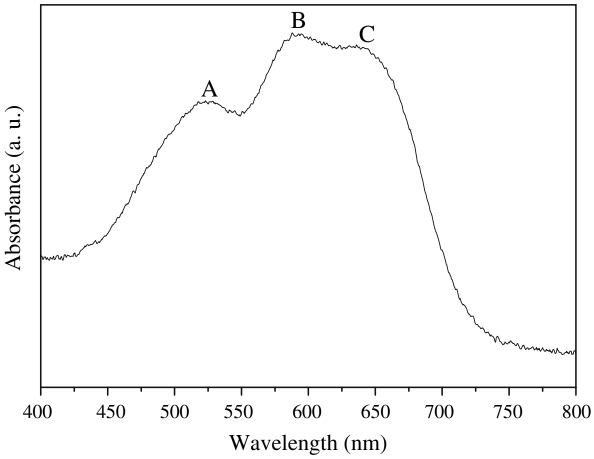

Figure 2. UV–VIS spectrum of the Co/SBA-15 calcined in air at 773 K. The bands centred at 525, 590, and 640 nm are typical for Co(II) ions in tetrahedral coordination.

absence of peaks at around 480 and 506 nm indicates the absence of Co(II) in an octahedral environment [18], and the absence of a peak at 410 nm indicates the absence of Co(III) [19]. As we known $Co(OAc)_2$ can convert to Co_3O_4 after calcination at 773 K in air, but it converted to CoO after impregnation on SBA-15 in our work. This phenomenon may be explained in terms of *interfacial coordination chemistry*. When the pH of impregnation solution was higher than the isoelectric point of silica (pH 1–2.2), negative-charged SiO^- groups are present on the surface. In the impregnation process, the pH of $Co(OAc)_2$/ethanol was around 6, indicating SiO^- species was on the silica surface. The long time stirring, subsequently filtrating, and gently washing permit the sufficient reaction between Co^{2+} and SiO^- groups and prevent excessive Co^{2+} from adsorpting on the surface. Thus, at low CoO-loading (1.6%, determined by XRF), CoO may be formed in tetrahedral coordination state inside the walls and inner surface of SBA-15. The abundant silanol and the walls of SBA-15 may stabilize low loading CoO in tetrahedral coordination, instead of Co_3O_4. The similar UV–VIS spectrum was observed in Co/MCM-41 synthesized by surface grafting methods [15]. They proved that the tetrahedral Co(II) was bonded to the surface of MCM-41.

Figure 3 illustrates H_2–TPR for the prepared Co/SBA-15 sample compared with the pattern of Co_3O_4. For Co_3O_4 sample, two main reduction peaks close to each other with temperature maxima at about 740 K and 850 K are observed. The first peak is assigned to the reduction of Co_3O_4 to CoO, and the second one to the subsequent reduction of CoO to Co^0 [20]. In case of Co/SBA-15, only a narrow reduction peak centered at ca. 870 K is observed. It suggests that cobalt is in divalent state and an interaction is existed between CoO and silica surface.

Morphology as well as structural ordering of Co/SBA-15 was analyzed by electron microscopy studies and is shown in Figure 4. The micrographs taken with the beam direction perpendicular to the pores (Figure 4A) evidences that the well-ordered hexagonal arrangement of the SBA-15 frameworks is maintained after CoO is introduced. On the other hand, taken with the beam direction parallel to the pore direction (Figure 4B), the hexagonally ordered pore structure can clearly be observed in the micrographs, and no CoO particles have been found on the outside surfaces of sample, indicating that CoO is highly dispersed. It is also consistent with the XRD spectra.

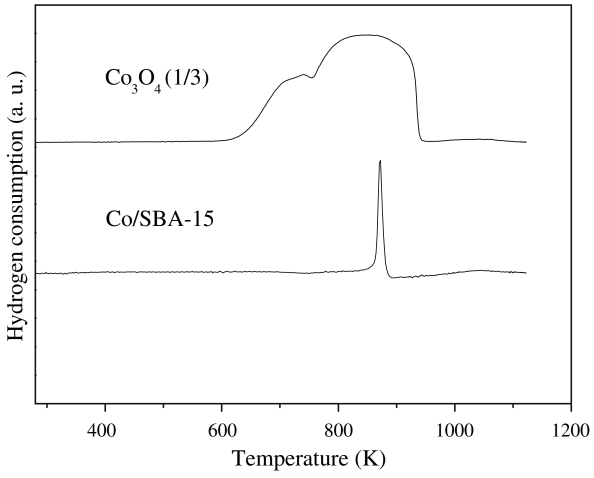

Figure 3. H_2-TPR of Co/SBA-15 sample compared with the pattern for Co_3O_4.

3.2. *Performances of the catalyst*

Ethylbenzene was oxidized by molecular oxygen to AcPO, PEA, PEHP, and BZA. The reaction results are listed in Table 1. In the absence of catalysts, only 4.5% of ethylbenzene was directly oxygenated as a result of autoxidation at 393 K for 6 h. With $Co(OAc)_2$ or Co_3O_4, the conversion of ethylbenzene was 9.2% and 7.1%, respectively. At the same conditions, over Co/SBA-15, conversion of ethylbenzene was 37.3%. The selectivity for PEHP was dramatically decreased to 1.9%, which was far lower than that with $Co(OAc)_2$ or Co_3O_4. The catalytic performances of Co/SBA-15 were also investigated at elevated temperature. It can be seen that elevating the operation temperature from 393 K to 413 K significantly increased the conversion of ethylbenzene. But the conversion increased slightly at 423 K. The phenomenon that PEHP was produced as main product without catalysts, and then drastically decomposed by Co/SBA-15 strongly implied that tetrahedral cobalt(II) played an important role in decomposing PEHP. The decomposition of PEHP can contribute to the further oxidation of ethylbenzene, and thus the conversion was increased.

As illustrated in Table 1, the conversion of ethylbenzene increased rapidly in the initial 3 h at 423 K, and then slowed down. When reaction time was up to 9 h, the conversion of ethylbenzene increased to 70.1%. In the whole reaction process, the selectivity for PEHP was lower than 0.2%. At the same time, the selectivity for AcPO increased with time. The results suggested PEHP was efficiently decomposed to secondary products, such as PEA or AcPO. The selectivity to AcPO was increased with the reaction proceeding, suggesting part of PEA further converted to AcPO. Moreover, the selectivity to BZA increased slightly with the reaction proceeding. In another experiment, AcPO was used as substrate. After the reaction was run at 423 K under 1.0 MPa O_2 for 6 h, only trace BZA was detected. It suggested that AcPO was difficult to convert to BZA, and most of BZA was formed in the β-scission of RO.

To examine the heterogeneity of the reaction, the catalyst was removed from the reaction by hot-filtration and the reaction was continued with the filtrate without catalyst (Figure 5). It was observed that after Co/SBA-15

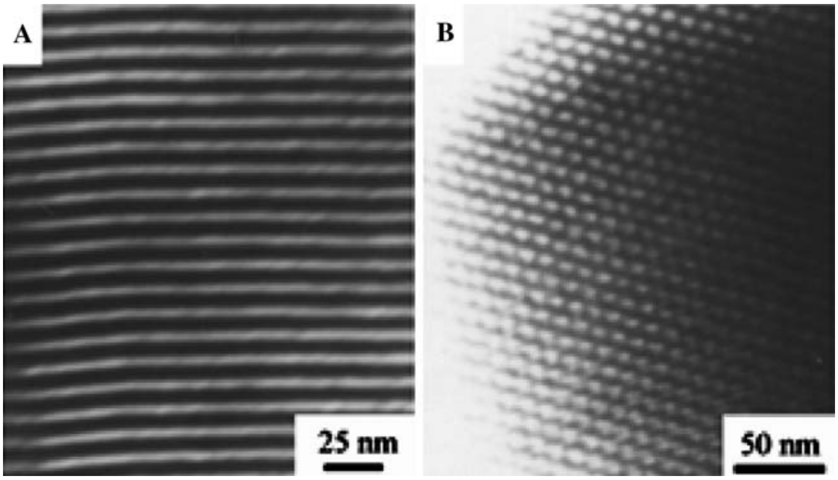

Figure 4. TEM images of Co/SBA-15 taken with the beam direction perpendicular (A) and parallel (B) to the *c* axis.

Table 1
Oxidation of ethylbenzene over Co/SBA-15[a]

Catalysts	Reaction temperature (K)	Run time (h)	Conversion (mol %)	Products distribution [b](mol %)			
				AcPO	PEA	PEHP	BZA
–	393	6	4.5	21.4	0	78.6	0
$Co(OAc)_2$	393	6	9.2	27.5	12.9	59.6	0
Co_3O_4	393	6	7.1	43.7	9.5	46.9	0
Co/SBA-15	393	6	37.3	74.3	19.0	1.9	4.8
Co/SBA-15	403	6	50.3	78.3	10.8	0.9	10.0
Co/SBA-15	413	6	60.9	81.4	6.4	0.4	11.8
Co/SBA-15	423	6	64.5	82.8	6.8	0.0	10.4
Co/SBA-15	423	0.5	19.2	59.4	34.4	0.2	6.0
Co/SBA-15	423	1	26.3	64.5	28.6	0.1	6.8
Co/SBA-15	423	2	40.2	72.5	20.0	0	7.5
Co/SBA-15	423	3	47.1	75.4	16.1	0	8.5
Co/SBA-15	423	9	70.1	83.7	4.1	0.1	12.1

[a] Reaction condition: 50 mg Co/SBA-15, or equal molar Co, 15 ml ethylbenzene, 1.0 MPa O_2.

removal (1 h) the conversion of ethylbenzene slowed down significantly, and the selectivity for PEHP was increased. Without catalyst, the generated PEHP was thermally decomposed partly. The further radical chain oxidation was induced and slowly came to an end. The results clearly proved that the reaction was a heterogeneous process [21–23]. The filtrate was analyzed by ICP mass spectrometry, and only 0.2 ppm of cobalt was detected. The contribution of the leached cobalt was neglectable because the amount of dissolved cobalt was much lower than that in the homogeneous catalysis. Therefore, it may be concluded that tetrahedral cobalt(II) in Co/SBA-15 is responsible for the catalytic activity in the oxidation of ethylbenzene.

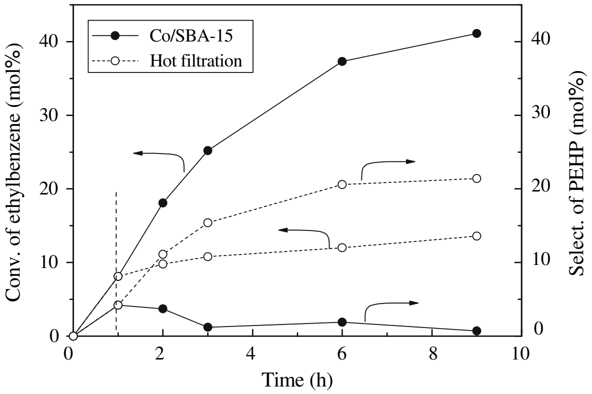

Figure 5. Conversion of ethylbenzene and selectivity of PEHP in reaction solution with Co/SBA-15 (up to 1 h) and after Co/SBA-15 removal (1–9 h). (●) Co/SBA-15; (○) Hot filtration. Reaction condition: 50 mg Co/SBA-15, 15 ml ethylbenzene, 393 K, 1.0 MPa O_2.

4. Conclusion

The Co/SBA-15 catalyst has been synthesized by alcoholic impregnation method. Only tetrahedral cobalt(II) was highly dispersed inside the SBA-15 mesopores. It is an efficient catalyst for the oxidation of ethylbenzene by molecular oxygen in the absence of solvents and additives. It also exhibits high efficiency in decomposing PEHP. The results suggest that SBA-15 is an excellent catalytic support. Application of the

Co/SBA-15 catalyst to other hydrocarbon oxidation reactions is now in progress.

Acknowledgments

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