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Article

Synthesis of zeolite Beta containing ultra-small CoO particles for ethylbenzene oxidation

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ARTICLE INFO

Article history:

Received 1 March 2017

Accepted 4 May 2017

Published 5 July 2017

Keywords:

Beta zeolite

Cobalt monoxide

Ultra-small CoO particle

Ethylbenzene oxidation

ABSTRACT

Zeolite Beta containing ultra-small CoO particles was synthesized from a one-step hydrothermal process. The synthesis route involves the pre-mixture of hydrofluoric acid with tetraethylammonium hydroxide (in a molar ratio of 1.3–1.5:1) before the addition of a silicon and cobalt source. Investigations by scanning electron microscopy, X-ray diffraction, UV-Vis spectroscopy, X-ray photoelectron spectroscopy, H₂-temperature-programmed reduction and transmission electron microscopy confirm the presence of ultra-small CoO particles in the zeolite Beta structure. The ultra-small CoO particles in zeolite Beta present high stability against both oxidation and reduction atmospheres at high temperatures. The catalytic performance of the CoO-containing zeolite Beta catalysts was compared with other Co-containing zeolites by evaluating ethylbenzene oxidation reactivity. The CoO-containing zeolite Beta exhibits high ethylbenzene conversion and high selectivity to acetophenone and 1-phenylethanol. The high activity of this catalyst system can be attributed to the high dispersion of the ultra-small CoO particles in the Beta structure.

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1. Introduction

Zeolites containing transition metals are well known for their excellent catalytic performance in oxidation/reduction reactions in addition to exerting shape selectivity to reactants, intermediates and products [1,2]. The three-dimensional microporous channel system of zeolites serves as the host to disperse metal or metal oxide particles, and the pore size of the channel/cavities can restrict the growth or sintering of the nanoparticles even at high reaction temperatures [3,4]. Cobalt

ion- or oxide-containing zeolites have drawn particular interest because of their wide applications in various hydrocarbon oxidation reactions, such as alkene selective oxidation to its terminal alcohol [5], cyclohexane to the corresponding alcohol and ketone [6], and Fischer-Tropsch reactions [7]. Conventionally, cobalt-containing zeolites are synthesized *via* hydrothermal synthesis, ion-exchange or impregnation; and the corresponding cobalt species exist as framework Co²⁺, ion-exchanged Co²⁺ or as extra-framework Co₃O₄ or Co metal particles, respectively. The coordination, chemical state and size of the cobalt species

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This work is supported by Strategic Priority Research Program of the Chinese Academy of Sciences (XDA07020300).

DOI: 10.1016/S1872-2067(17)62853-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 7, July 2017

in cobalt-containing zeolites exert great influence over the physical and chemical properties, and by extension, determine the applications of these zeolites in specific catalytic reactions. Thomas et al. [5] and Lin et al. [8] reported that aluminophosphate zeolites containing framework Co^{2+} , such as CoAPO-18 and CoAPO-5, are highly active in the selective oxidation of linear alkanes and cyclohexane. Tang et al. [9] demonstrated that Co^{2+} -exchanged FAU-type zeolites are highly efficient in styrene epoxidation. Tang et al. [10] reported that Co_3O_4 nanoparticles supported on X and Y zeolites exhibit high activity in Fischer-Tropsch reactions. Recently, cobalt monoxide (CoO) nanoparticles have gained increasing attention for their high activity in the areas of electrocatalysis [11] and photocatalysis [12]. However, there are few reports of the catalytic properties of CoO particles in oxidation reactions. According to Yang [13] and Li [14,15], Co_3O_4 is thermodynamically more stable than CoO, and CoO can spontaneously transform into Co_3O_4 even under low O_2 partial pressures. Therefore, with CoO easily converting to Co_3O_4 under O_2 atmospheres, the applications of CoO in catalytic oxidation reactions are hindered greatly.

In the present work, we report the facile hydrothermal synthesis of a CoO-containing zeolite Beta from a homogenous emulsion comprising hydrofluoric acid, a silicate precursor and a cobalt salt under mild conditions at pH = 5–6. The synthesized products were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), UV-Vis spectroscopy, X-ray photoelectron spectroscopy (XPS), H_2 -temperature-programmed reduction (H_2 -TPR) and transmission electron microscopy (TEM), which demonstrate the presence of sub-nanoscale CoO particles within the framework of zeolite Beta. The synthesized CoO-containing zeolite Beta products show considerable activity in ethylbenzene oxidation reactions with 64.7% selectivity to acetophenone and 21.3% selectivity to 1-phenylethanol, which present significantly higher selectivity than previously reported cobalt-containing zeolites. The high activity of the CoO-containing zeolite Beta catalysts is ascribed to the well-isolated ultra-small CoO particles, which act as excellent surface oxygen carriers and donors.

2. Experimental

2.1. Zeolite synthesis

Zeolite Beta catalysts containing ultra-small CoO particles (Co-Beta-H) were synthesized as follows. 18.375 g of tetraethylammonium hydroxide solution (TEAOH; 40 wt%) was mixed with 10 g of deionized water and 3.25 g of hydrofluoric acid (HF). Thereafter, 0.291 g of cobalt(II) nitrate hexahydrate and 20.833 g of tetraethyl orthosilicate were added to the above solution. The mixture was stirred in a water bath at 60 °C until a concentrated emulsion formed having a molar composition of 0.5 TEAOH : 1 SiO_2 : x CoO : 0.65 HF : 5 H_2O , where x = 0.005, 0.01 or 0.02. The gel was transferred to a Teflon-lined stainless steel autoclave and heated at 140 °C for 3 d. The pink solid products were filtered, dried at 100 °C overnight before calcining at 550 °C for 5 h to remove the occluded TEAOH. The resultant materials were labelled according to the sol-gel Co/Si

ratios, as Co-Beta-H0 (Co/Si = 0.005), Co-Beta-H1 (Co/Si = 0.01) and Co-Beta-H2 (Co/Si = 0.02).

Siliceous zeolite Beta (Si-Beta) was synthesized as in the aforementioned procedure, except that no cobalt salt was added to the sol-gel.

Zeolite Beta containing ion-exchanged Co^{2+} (Co-Beta-E) was prepared following a modified ion-exchange method adopted by Armor's group [16]. 2.0 g zeolite Beta having a Si/Al ratio of 25 was stirred together with 25 mL 2 wt% cobalt(II) nitrate solution at 60 °C for 24 h. After the ion-exchange procedure, the mixture was filtered, and the recovered solids dried at 100 °C. The ion-exchange filtration process was repeated four times before recovering the final material by drying at 100 °C overnight.

Zeolite Beta containing impregnated Co_3O_4 (Co_3O_4 -Beta) was prepared by impregnating zeolite Beta with cobalt(II) nitrate solution. 2.0 g of Si-Beta zeolite was mixed with 1.25 mL 5 wt% cobalt(II) nitrate solution (roughly corresponding to a Co-Beta-M with the Co/Si molar ratio of 0.01) at room temperature. Thereafter, the mixture was dried at 100 °C for 6 h followed by calcination at 550 °C for 5 h before use.

Zeolite Beta containing surface CoO (CoO-Beta-M) was prepared by grinding 0.016 g of CoO with 2 g of calcined Si-Beta in a N_2 -atmosphere glovebox for 30 min. The mixed product was maintained under the inert atmosphere until needed.

Co-containing aluminophosphate zeolite, CoAPO-5, was prepared by modifying a previously reported method by Thomson et al. [17]. 0.291 g of cobalt(II) nitrate hexahydrate and 10.21 g of aluminum isopropoxide were added to 30 mL water, and stirred for 30 min to homogenize. Thereafter, 5.76 g of phosphoric acid, 8.10 g of trimethylamine and 50 mL water were added to the solution. The mixture was stirred in a water bath at 60 °C to yield a pink solution having a molar composition of Al_2O_3 : P_2O_5 : 0.01 CoO : 1.6 TEA : 20 H_2O . The gel was transferred to a Teflon-lined stainless steel autoclave and heated at 190 °C for 3 d. The blue solids, recovered by filtration, were dried at 100 °C overnight. CoAPO-5 samples were calcined at 550 °C for 5 h to remove the occluded trimethylamine.

2.2. Characterization

SEM was performed using a JSM 7800F field emission scanning electron microscope operating at 1 kV. N_2 isotherms were measured using a Micromeritics ASAP 2420 apparatus at –196 °C. Inductively coupled plasma (ICP) analysis was performed using a PerkinElmer Optima 7300DV instrument. Powder XRD data was acquired from a PANalytical X'Pert Pro diffractometer equipped with a Pixel detector using $\text{Cu } K_{\alpha 1}$ radiation (λ = 0.15406 nm) operated at 40 mA and 40 kV with a scanning speed of 5°/min. Diffuse reflectance ultraviolet-visible (DRUV-Vis) spectra were obtained using an Hitachi U-3900H spectrophotometer equipped with a BaSO_4 integrating sphere. XPS measurements were performed in an ultra-high vacuum multipurpose surface analysis system (ESCALAB 250Xi) using a conventional X-ray source (XR-50, Specs, Al- K_{α} , 1486.6 eV) in a “constant analyzer energy” mode. The binding energies were referenced to the C 1s line at 284.6 eV from adventitious car-

bon. ^{29}Si solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) measurements were acquired using an Agilent DD2-500 MHz spectrometer at room temperature. H_2 -TPR experiments were performed using a Micromeritics AutoChemII 2920 in a 10% H_2 /90% Ar atmosphere (50 mL/min); the temperature was increased from 40 to 900 °C at a 10 °C/min heating rate. TEM investigations were conducted using a JEM-2100 EX field emission electron microscope.

2.3. Catalytic activity evaluation

Ethylbenzene oxidation reactions were evaluated in a 50 mL Teflon-lined autoclave reactor containing a magnetic stirrer bar. Typically, 10 mL of ethylbenzene and 50 mg of catalyst were placed in the reactor. The reactor was then sealed and heated to the reaction temperature. The batch reactor was continuously charged with an O_2 atmosphere at a constant pressure of 1.0 MPa after reaching 120 °C for 6 h. Reaction products were identified by gas chromatography (GC, Agilent 6890N GC/5973 MS detector) and quantified with an internal standard (1,4-dichlorobenzene) using an Agilent 6890D GC equipped with an Innovex capillary column (50 m $\times$ 0.32 mm $\times$ 0.4 μm). Triphenylphosphine (1 mol/L in THF) was added to one of the samples to reduce the peroxide product to the alcohol.

3. Results and discussion

Fig. 1 shows that the crystals of Si-Beta and Co-Beta-H zeolites have truncated bipyramidal morphologies that are typical of zeolite Beta [18]. Particle size distribution is in the range of 40–60 μm . Compared with Si-Beta crystals, Co-Beta-H crystals have more surface fractures and holes, which become more prominent with increasing sol-gel Co/Si ratios. As a mineralizing agent, HF slows down the crystallization kinetics of the zeolites, leading to the formation of a crystalline product [19]. In the presence of a cobalt salt in the synthesis medium, the coordination reactions between cobalt cations with HF would consume a considerable amount of HF [20], reducing the available amount of HF for zeolite crystallization. It is likely that insufficient stoichiometric amount of HF in the synthesis medium is responsible for the loss of crystallinity of the Co-Beta-H zeolites. N_2 adsorption/desorption measurements show that

Fig. 1. SEM images of Si-Beta and Co-Beta-H zeolites.

the specific surface areas and microporous volumes of the Co-Beta-H zeolites are 480–520 cm^2/g and 0.19–0.20 cm^3/g , respectively, which is similar to the Si-Beta zeolite textural properties [21].

Cobalt-containing materials are usually featured by their characteristic colors that can provide important information about the valences and the coordination states of the cobalt species. Fig. 2 displays images of synthesized cobalt-containing zeolites before and after calcination at 550 °C. The color of the as-synthesized CoAPO-5 is vivid blue, which turns pale blue after calcination. The vivid blue and the pale blue colors are attributable to tetrahedrally coordinated Co^{2+} and Co^{3+} in CoAPO-5, respectively [22]. The Co-Beta-E zeolite maintains a pinkish/red color before and after calcination. This pinkish/red color results from stable Co^{2+} ions occupying specific exchange sites of zeolite Beta even when subjected to high temperatures [23]. The Co_3O_4 -Beta zeolite has a pink color that is similar to that of Co-Beta-E, however, after calcination the color of Co_3O_4 -Beta turns black. The initial pink color can be ascribed to Co^{2+} species that exist in the form of $\text{Co}(\text{NO}_3)_2$ or $\text{Co}(\text{OH})_2$, however, during calcination the Co^{2+} species readily transforms to Co_3O_4 , giving rise to the black color of the corresponding zeolites [24,25]. The CoO-Beta-M zeolite presents a dark brown color that later converts to black after calcination. The dark

Fig. 2. Images of as-synthesized (top) and calcined (bottom) cobalt-containing zeolites.

brown color is typical of bulky CoO ; during calcination, CoO transforms to Co_3O_4 that results in the black color of the CoO -Beta-M zeolite. Regarding Co -Beta-H zeolites, a pinkish/violet color is observed in the as-synthesized zeolites, whereas after calcination the color turns pale violet. Each material implies the presence of a distinct cobalt species: from framework Co^{2+} in CoAPO-5 , the ion-exchanged Co^{2+} in Co -Beta-E, the bulky Co_3O_4 in Co_3O_4 -Beta and bulky CoO in CoO -Beta-M.

Fig. 3 displays the XRD patterns of calcined samples of Co -Beta-H0, Co -Beta-H1 and Co -Beta-H2. The XRD patterns of all Co -Beta-H zeolites exhibit characteristic diffraction peaks of phase pure zeolite Beta and contain no additional peaks ascribed to impurities. The diffraction peak intensity slightly decreases from Co -Beta-H0 to Co -Beta-H2, indicating a reduction in zeolite crystallinity as a function of increased cobalt in the sol-gel. The high diffraction intensity of Co -Beta-H0, Co -Beta-H1 and Co -Beta-H2 indicates the high crystallinity of these zeolites. The absence of characteristic diffraction peaks ascribed to CoO or Co_3O_4 in the Co -Beta-H samples confirms that no bulky CoO or Co_3O_4 particles are formed in Co -Beta-H zeolites.

UV-Vis spectroscopy has been widely employed to study the valence and coordination environment of cobalt species in cobalt-containing zeolites [26,27]. Fig. 4 shows the UV-Vis spectra of Si -Beta and Co -Beta-H zeolites. In comparison with Si -Beta, Co -Beta-H zeolites show an additional band in the ultraviolet region at 238 nm, and a broad band in the visible region at 490–540 nm. The band at 238 nm can be ascribed to the charge transfer of O^{2-} - Co^{2+} , suggesting the existence of Co^{2+} [22]. The broad band at 490–540 nm can be attributed to octahedral Co^{2+} , which indicates the presence of extra-framework Co^{2+} species in Co -Beta-H zeolites [22,23]. The intensities of these bands increase as a function of increasing Co/Si ratio in the zeolite Beta materials.

^{29}Si MAS NMR spectra can provide important information regarding the local environment around Si heteroatoms in zeolites [28]. Fig. 5 shows the ^{29}Si MAS NMR spectra of Si -Beta and Co -Beta-H zeolites. For Si -Beta and Co -Beta-H zeolites, three

Fig. 3. XRD patterns of calcined Co -Beta-H zeolites as a function of Co/Si ratio.

Fig. 4. UV-vis spectra of Si -Beta and Co -Beta-H zeolites.

partially overlapped resonance bands are present between -110 and -116 ppm, corresponding to $\text{Si}-(\text{OSi})_4$ species. The different chemical shifts of the three resonance bands arise from tetrahedral Si atoms located at different crystallographic sites of zeolite Beta [29]. The presence of $\text{Si}-(\text{OSi})_4$ species indicate that Co -Beta-H zeolites have a defect-free structure, similar to Si -Beta, and contain no siloxy ($\text{Si}-\text{O}^-$) or silanol ($\text{Si}-\text{OH}$) groups that can serve as the exchange sites for Co^{2+} [23], therefore the Co^{2+} of Co -Beta-H are not likely to exist as the ion-exchange form in the zeolite structure. Additionally, the ^{29}Si MAS NMR spectra of Co -Beta-H are similar to those of Si -Beta, indicating that the cobalt species in Co -Beta-H zeolite have negligible interactions with the $\text{Si}-\text{O}-\text{Si}$ environment. Therefore, the Co^{2+} species of Co -Beta-H zeolites are likely to exist as extra-framework species rather than framework-substituted heteroatoms.

XPS is a reliable method for the detailed investigation of cobalt species. Fig. 6 shows the XPS spectra of Co_3O_4 -Beta, CoO -Beta-M and Co -Beta-H1 zeolites. For all Co -Beta-H samples, intense doublet bands are present at 798.0 and 781.7 eV in the $\text{Co } 2p$ region, and an intense satellite accompanies each

Fig. 5. ^{29}Si MAS NMR resonance spectra of Si -Beta and Co -Beta-H zeolites.

Fig. 6. XPS profiles of calcined (a) Co_3O_4 -Beta, (b) CoO -Beta-M and (c) Co -Beta-H1 zeolite.

of the doublets at higher energies. The XPS spectrum of CoO -Beta-M also exhibits a doublet band with approximate binding energies close to those of Co -Beta-H, suggesting a close relationship between CoO in Co -Beta and the Co^{2+} species in Co -Beta-H. The binding energies of the doublets of Co -Beta-H and CoO -Beta-M can be attributed to the $\text{Co } 2p_{1/2}$ (798.0 eV) and $2p_{3/2}$ (781.7 eV) photoelectrons of extra-framework CoO species [13,30]. Conversely, the XPS spectra of Co_3O_4 -Beta-M exhibits a doublet band at 795.3 and 779.9 eV, and the presence of a pair of weak satellites at higher binding energies; such doublet bands and satellite pairs are characteristic of Co_3O_4 [15].

The existence of CoO in Co -Beta-H is further evidenced by analyzing the XPS satellites. The intense satellite pairs result from the charge-transfer band structure characteristics of late 3d transition metal monoxides [15]. When other cobalt compounds, such as Co_3O_4 , replace CoO , the satellites remarkably diminish [31]. Furthermore, Carson et al. [15] discovered that the intensity ratio of the $\text{Co } 2p_{1/2}$ satellite to its main peak is ~ 0.9 for CoO , and ~ 0.3 for Co_3O_4 . For Co -Beta-H, this ratio is 0.92, in good agreement with that for CoO .

The oxidation/reduction properties of Co -Beta-H zeolites were investigated by H_2 -TPR. As Fig. 7 shows, for Co -Beta-E the

Fig. 7. H_2 -TPR spectra of several synthesized Co-containing zeolites.

reduction band is beyond 900 °C. Co -Beta-H displays a major reduction band at 740 °C and a minor band at 850 °C. A reduction band is observed at 260 °C for Co_3O_4 -Beta. Two reduction bands are present in CoO -Beta-M at 303 °C and 332 °C, while for CoAPO-5 , a broad reduction band is centered at approximately 860 °C. The reduction temperature of cobalt-containing zeolites is related to the valence, coordination state and the location of the cobalt species. The relatively low reduction temperatures of Co_3O_4 -Beta and CoO -Beta-M are consistent with the easy reduction of both bulky Co_3O_4 and CoO particles to cobalt metal. The high reduction temperatures of Co -Beta-E and CoAPO-5 result from the stable Co^{2+} exchange site and tetrahedral framework Co^{2+} , respectively. The double-band profile of Co -Beta-H is similar to that of CoO -Beta-M, which further suggests the presence of CoO in Co -Beta-H. Nevertheless, the high reduction temperature of Co -Beta-H indicates that the CoO particles in Co -Beta-H are relatively stable, and are significantly more difficult to reduce than the corresponding bulky CoO particles in CoO -Beta-M. Furthermore, as the Co/Si ratio increases in Co -Beta-H, the minor band becomes more prominent with respect to the major band.

Fig. 8 displays TEM images of CoO -Beta-M and Co -Beta-H zeolites. For all samples, a well-defined zeolite lattice is observed indicating high zeolite crystallinity. Additionally, the TEM image of CoO -Beta-M shows the presence of CoO particles ranging from 10–40 nm. However, no CoO particles are observed from the TEM images of Co -Beta-H zeolites. Energy-dispersive X-ray spectroscopy (EDS) measurements (Fig. 8 insets) confirm the presence of a considerable amount of Co in

Fig. 8. TEM images of CoO-Beta-M and Co-Beta-H zeolites.

Co-Beta-H zeolites, suggesting that CoO may exist as sub-nanoscale particles in Co-Beta-H zeolites that are below the nanoscale resolution limit of the TEM. This suggestion is supported by the TEM images of Co-Beta-H samples after EDS treatment, wherein nanoscale CoO particles can be observed from the collapsed lattices of Co-Beta-H zeolites. An explanation for the lack of visible CoO particles prior to EDS treatment, and the emergence of CoO nanoscale particles after EDS, is rationalized as follows: prior to EDS treatment, the CoO particles are confined within the Beta structure as sub-nanoscale particles; during EDS treatment the particle bombardment by the electron beam compromises zeolite framework integrity and releases the ultra-small CoO particles; thereafter, the CoO particles agglomerate into larger particles to reduce surface energy, which results in the observation of nanoscale CoO particles, as observed in the TEM images of the EDS-treated Co-Beta-H samples.

XRD, UV-Vis and XPS suggest that the cobalt species of Co-Beta-H exists as CoO particles, with TEM observations providing indirect evidence of the presence of small CoO particles, the particle size of CoO is likely to be <1 nm. Previous research shows that the formation of ultra-small metal or metal oxide particles within zeolites can result from chemical bonding (ion-exchange or framework substitution) with the zeolite framework [9,28] or spatial confinement in the channels or cages [7,32]. The analysis of ^{29}Si NMR spectra shows that CoO is weakly bound to the siliceous framework of zeolite Beta. Therefore, we speculate that the small CoO particles are encapsulated in the confined spaces of the [4³5⁴] or [4⁶] cages [33], in Beta during zeolite crystallization.

The easy conversion of CoO to Co_3O_4 under normal conditions results in conventional synthesis procedures of CoO nanoparticles to often include special treatment during synthesis

or post synthetically to avoid the unexpected formation of Co_3O_4 [12]. However, in our experiments, zeolite Beta materials containing ultra-small CoO particles are successfully obtained without the need for special treatment; additionally, the CoO particles in Co-Beta-H can withstand oxidation atmospheres at 550 °C and reduction atmospheres at 700 °C without transformation into other cobalt oxides.

Co_3O_4 -supported porous materials have exhibited high activity in the selective oxidation of many hydrocarbons, such as cyclohexene, tetralin and ethylbenzene [34,35]. In our experiment, the catalytic properties of two types of CoO-containing zeolites, Co-Beta-H1 and CoO-Beta-M, were investigated in the solvent-free oxidation of ethylbenzene and compared with Co-Beta-E, Co_3O_4 -Beta and CoAPO-5. The main products from the reactions are acetophenone (ACPO), 1-phenylethanol (PEA) and 1-phenyl-ethylhydroperoxide (PEHP). Ethylbenzene conversion and product distribution are listed in Table 1.

As Table 1 shows, ethylbenzene is not converted over Co-Beta-E, which is consistent with the reported inactivity of Co^{2+} ion-exchanged zeolites in ethylbenzene oxidation [35]. Ethylbenzene conversion is 6.1% over CoAPO-5, 8.1% over Co_3O_4 -Beta, and 5.9% over CoO-Beta-M. In the reaction atmosphere, CoO particles in CoO-Beta-M would quickly transform to Co_3O_4 , which is the most likely reason for similar ethylbenzene conversions over Co-Beta-M and CoO-Beta-M. Conversely, ethylbenzene conversion over Co-Beta-H1 reaches 15.9%, almost double that of CoAPO-5 and Co-Beta-M.

Additionally, further increasing the reaction temperature to 150 °C and 160 °C results in enhanced ethylbenzene conversion over Co-Beta-H1 to 31.4% and 34.6%, respectively. However, when Co-Beta-H2 is employed in the reaction at 150 °C and 160 °C, ethylbenzene conversion is remarkably lower than that of Co-Beta-H1. The selectivity to ACPO in the presence of

Table 1

Ethylbenzene oxidation over various Co-containing zeolites.

Catalyst	Temperature (°C)	Conversion (%)	Product distribution (%)		
			ACPO	PEA	PEHP
Co-Beta-E	120	—	—	—	—
Co ₃ O ₄ -Beta	120	8.1	54.6	24.7	17.8
CoO-Beta-M	120	5.9	45.9	36.0	14.5
CoAPO-5	120	6.1	32.3	34.8	30.5
Co-Beta-H1	120	15.9	64.7	21.3	12.8
Co-Beta-H1	150	31.4	71.1	24.7	0.8
Co-Beta-H2	150	24.6	60.6	29.0	8.0
Co-Beta-H1	160	34.6	72.9	20.6	0.2
Co-Beta-H2	160	24.8	63.9	32.4	0

Co-Beta-H2 is higher than the corresponding Co-Beta-H1 zeolites, while the selectivity to PEA is higher over Co-Beta-H2 than that of Co-Beta-H1. The decreased activity and ACPO selectivity of Co-Beta-H2 is thought to relate to the low crystallinity of the zeolite (as shown by Brunauer-Emmett-Teller (BET) data and SEM observations) so that the CoO particles occluded within the zeolite channels or cages remain unreactive toward ethylbenzene molecules.

The above results demonstrate that ethylbenzene conversion is facilitated by the presence of ultra-small CoO particles. At higher temperatures, selectivity to ACPO rises significantly from 64.7% to 72.9%, whereas, the selectivity to PEA remains constant and the selectivity to undesirable PEHP dramatically drops from 12.8% to 0.2%. The high activity and product selectivity makes Co-Beta-H a promising catalyst for ethylbenzene oxidation and other carbohydrate oxidations.

As proposed by Hermans et al. [36], hydrocarbon oxidation

is a radical substitution-type reaction. In the absence of any catalyst, such reactions would form peroxide as the major product. When metal oxides, such as Co₃O₄ or MnO₂, are present in the oxidation medium, these metal oxides can catalyze the decomposition of the peroxides yielding ketones or alcohols as the main products [35]. Although catalytic performance studies of the CoO-containing materials are still at preliminary stages, the high activity of Co-Beta-H suggests that the ultra-small CoO particles act as oxygen carriers and donors that facilitate the radical substitution reactions, and effectively promote peroxide decomposition, producing ketones and alcohols as the minor products [30]. Additionally, a recent report discovered that Co₃O₄ particles supported on hydrophobic SiO₂ display significantly higher activity for the selective oxidation of cyclohexene, cyclohexene and ethylbenzene when compared with Co₃O₄ particles on hydrophilic SiO₂ [34]. For Co-Beta-H, the defect-free, pure-silica framework of the zeolite Beta material acts as a highly hydrophobic host for CoO particles, which may be crucial to the high activity of Co-Beta-H zeolites in the oxidation of ethylbenzene.

4. Conclusions

Zeolite Beta catalysts containing ultra-small CoO particles were synthesized from a homogenous emulsion comprising hydrofluoric acid, a silicate precursor and a cobalt salt under slightly acidic conditions. Characterization of the materials by SEM, XRD, UV-vis, XPS, H₂-TPR and TEM confirm the presence of sub-nanoscale CoO particles in the zeolite structure. This promising material possesses high thermal stability and is an efficient catalyst for the oxidation of ethylbenzene.

Graphical Abstract

Chin. J. Catal., 2017, 38: 1207–1215 doi: 10.1016/S1872-2067(17)62853-5

Synthesis of zeolite Beta containing ultra-small CoO particles for ethylbenzene oxidation

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Beta zeolite containing ultra-small CoO clusters was synthesized from a one-step hydrothermal process. The CoO-containing Beta zeolite exhibits high activity and selectivity in ethylbenzene oxidation.

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含超微氧化亚钴颗粒Beta分子筛的合成及其催化乙苯氧化性能

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摘要: 杂原子分子筛是指在硅铝分子筛或磷铝酸盐分子筛中含有骨架内或骨架外某种原子或其化合物的分子筛。这些杂原子可以是某些主族元素(如硼、锆、镓)或有变价特性的过渡金属元素(如钛、铁、钴、镍)等。将杂原子或其化合物通过浸渍、离子交换、水热晶化等方式引入沸石分子筛骨架中形成杂原子分子筛, 往往可以改变沸石分子筛的骨架结构和理化性能, 并赋予沸石分子筛新的催化反应性能。自1983年钛硅分子筛TS-1被发现能够高效催化烯烃环氧化以来, 许多杂原子分子筛因其在催化烷烃类及芳烃类氧化、醛酮选择氧化及烯烃类环氧化等领域表现出的优良性能得到了广泛关注。目前, 合成含不同杂原子的分子筛已成为分子筛材料开发的一个重要内容。分子筛的微孔孔道结构赋予了被引入其中作为催化中心的杂原子对反应物/产物分子独特的择形选择性; 同时, 分子筛骨架与杂原子之间往往存在化学键或空间限域作用, 使得杂原子在高温高压等反应条件下依然保持高度的分散性, 避免由于团聚导致活性降低。

钴离子及含钴化合物在烷烃及芳烃类催化氧化反应中表现出很好的活性, 能够利用分子氧实现对高碳烷烃及烷基苯的催化氧化。将钴离子及其化合物引入具有合适孔道结构的分子筛, 可以提高催化反应的选择性。目前将对含钴分子筛的

合成研究主要有后处理法及直接水热法。后处理法包括负载法及离子交换法,用于制备含有钴物种的硅铝分子筛;而直接水热法主要用于制备含有骨架钴的磷酸铝分子筛。目前为止,使用水热法合成含钴的分子筛材料的合成及其催化应用至今鲜有研究报导。这主要是由于传统的分子筛合成体系的高碱性环境会导致钴盐的沉淀,导致其无法被引入分子筛。

我们通过优化合成条件,利用含氟体系直接水热法将钴引入Beta分子筛,得到含超微氧化亚钴团簇的Beta沸石分子筛。通过扫描电子显微镜、X射线粉末衍射、紫外-可见漫反射光谱、X射线光电子能谱、透射电子显微镜及H₂程序升温还原等表征手段对合成样品的物理化学性质进行了研究,并与使用浸渍、离子交换得到的含钴Beta沸石及水热合成得到的含钴AlPO-5分子筛的相关性质进行了对比。合成得到的含钴分子筛材料中,钴物种以亚纳米尺度的氧化亚钴颗粒形式存在。我们使用分子氧作为氧源,考察了该含超微氧化亚钴的Beta沸石作为催化剂催化乙苯氧化反应的活性。与浸渍、离子交换制得钴硅分子筛及含有骨架钴的磷酸铝分子筛材料相比,含超微氧化亚钴的Beta分子筛表现出更高的催化活性及对苯乙酮/醛的选择性。

关键词: Beta分子筛; 氧化亚钴; 超微氧化亚钴颗粒; 乙苯氧化

收稿日期: 2017-03-01. 接受日期: 2017-05-04. 出版日期: 2017-07-05.

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基金来源: 中国科学院重点战略研究项目(XDA07020300).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).