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Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

One-pot synthesis of primary amides on bifunctional Rh(OH)_x/TS-1@KCC-1 catalysts

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ABSTRACT

A new microporous/mesoporous composite with a core-shell structure, TS-1@KCC-1, was fabricated in a microemulsion system by coating flower-like mesoporous silica (KCC-1) on the crystal surface of TS-1 zeolite. The synthesis conditions and a possible formation mechanism were studied in detail for the TS-1@KCC-1 material. A suitable temperature and assembly time were found to be 373–393 K and 4 h, respectively. The shell thickness of TS-1@KCC-1 was conveniently tuned in the range 25–80 nm. Rh(OH)_x species were supported on TS-1@KCC-1, giving rise to a novel bifunctional tandem catalyst Rh(OH)_x/TS-1@KCC-1, which effectively catalyzed the one-pot synthesis of primary amides directly from aldehydes, ammonia, and hydrogen peroxide.

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1. Introduction

Porous core-shell materials have attracted much attention because of their potential application in catalysis [1–5], separation [6–8], drug/gene delivery [9–13], and biosensors [10,14,15]. These extensive studies of core-shell-structured materials stem from their bi- or multi-functional characteristics, which enable their optical, electronic, magnetic, and chemical properties to be assembled either in the cores or in the shells. Numerous functionalized core-shell materials have therefore been designed and synthesized [14,16–18]. To date, porous core-shell materials that were successfully fabricated include zeolite-shell-encapsulated zeolites [6] or solid cores [4,19–21], and mesoporous-shell-encapsulated zeolites [22–26] with solid [27–29] or mesoporous cores [30–33]. Bouizi et al. [6,7] fabricated a silicalite-1-encapsulated β-zeolite core-shell material

with different zeolite crystalline structures in the core and the shell; this type of material exhibited superior performance for butane, toluene, and 1,3,5-trimethylbenzene separation. Yang et al. [34] reported a core-shell material with H-ZSM-5 as the shell and Pd/silica as the core. This material, which integrated different functionalities in the core and shell, served as a tandem catalyst for direct synthesis of dimethyl ether from syngas. Mesoporous materials with large pore structure can avoid the diffusion limitations imposed by zeolites with relatively small pore dimensions (<1.5 nm) when used in reactions or separations involving bulky molecules or as carriers for metal nanoparticles [35–37]. There are a number of literature reports on core-shell materials with mesoporous shells [16,17]. Büchel et al. [28] first reported a material consisting of a mesoporous silica shell encapsulating a solid silica core, using tetraethyl orthosilicate (TEOS) and *n*-octadecyltrimethoxysilane as the

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silica source and the pore-forming agent, respectively. Using the same method, a novel type of porous material with a mesoporous silica or carbon shell and silicalite-1 core was readily synthesized [38]. This was the first report of microporous/mesoporous core-shell materials. Recently, a dual-mesoporous sphere with a core-shell structure was successfully synthesized using an amphiphilic block copolymer [polystyrene-*b*-poly(acrylic acid)] and cetyltrimethylammonium bromide (CTAB) as co-templates [33].

In 2010, Polshettiwar et al. [39] reported new flower-like mesoporous silica spheres (KCC-1) assembled from radial fibrous silica in a microemulsion solution. KCC-1, which has superior properties such as monodispersity, a high specific surface area, an open pore structure, and high thermal/hydrothermal and mechanical stability, has been used as a supporter to support various metal nanoparticles in catalytic reactions [40–42]. Conventionally, porous core-shell materials are synthesized in dilute aqueous solution. For instance, Deng et al. [27] fabricated a mesoporous silica shell-magnetic core material using CTAB as the shell template in a basic ethanol-water solution. Qian et al. [25] reported the synthesis of an SBA-15-encapsulated ZSM-5 core-shell material in a dilute solution of a strong acid. We prepared a three-dimensional interconnected worm-hole-like mesoporous silica coated on TS-1 zeolite in neutral or weakly acid ethanol-water solutions [23]. To date, there have been few reports dealing with the synthesis of porous core-shell materials in synthesis systems with relatively high solid/liquid ratios, especially microemulsion systems.

The porous core-shell materials used in catalytic reactions can be classified into three types [16]: (1) those with the catalytic active sites located in the core; (2) those with active sites in the porous shell; and (3) those with active sites in both the core and the shell. The first type has clear advantages for active sites such as metal nanoparticles sintering at high temperature and leaching to the solution phase are prevented [17]. Joo et al. [1] synthesized mesoporous-silica-encapsulated Pt nanoparticles and used the material as the catalyst in the CO oxidation reaction; the catalyst showed high thermal stability. For the second type, metal nanoparticles can be supported on the mesoporous shell, which can also avoid sintering at high temperature [43]. For the third type, different active sites can be assembled separately in the core and the shell to obtain multifunctional catalysts; these different active sites act independently, without mutual destruction, in one-pot tandem reactions [24,34,44]. For example, acidic and basic active sites can be assembled in the core and shell as a bifunctional heterogeneous catalyst to avoid them neutralizing each other [34,44].

Recently, Fujiwara et al. [45,46] reported $\text{Rh}(\text{OH})_x$ supported on Al_2O_3 as a heterogeneous catalyst for one-pot synthesis of primary amides from aldehydes and hydroxylamine salts. However, one of the reactants used in this one-pot reaction is the expensive and explosive sulfate or hydrochloride of hydroxylamine [47]. If hydroxylamine could be synthesized in situ in organic synthesis, greener and more atom-efficient reactions could be developed for synthesizing primary amides [47]. Ti-

tanosilicates such as TS-1 and Ti-MWW are effective catalysts for the ammoximation of ketones or aldehydes with ammonia and hydrogen peroxide to the corresponding oximes [48–50]; in situ formation of hydroxylamine in these reactions has been confirmed. An appropriate combination of titanosilicates and $\text{Rh}(\text{OH})_x$ could therefore be used to design a new tandem catalyst for producing primary amides directly from aldehydes, ammonia, and hydrogen peroxide. However, $\text{Rh}(\text{OH})_x$ species directly supported on Ti-MWW or TS-1 zeolites are easily leached from the zeolite surface [51] because the conversion of intermediate aldioximes to primary amides needs a high reaction temperature (393–433 K). Very recently, we reported that supporting $\text{Rh}(\text{OH})_x$ species on core-shell TS-1@KCC-1 gave a material with high hydrothermal stability [52].

In this study, we optimized the synthesis conditions for TS-1@KCC-1 materials in a microemulsion system, and supported $\text{Rh}(\text{OH})_x$ species with Lewis and Brønsted basic active sites on the core-shell material, to produce a catalyst for the rearrangement of aldehyde oximes to primary amides. The resultant bifunctional $\text{Rh}(\text{OH})_x/\text{TS-1@KCC-1}$ catalyst was used to synthesize primary amides directly from aldehydes, ammonia, and hydrogen peroxide through a one-pot ammoximation and rearrangement reaction.

2. Experimental

2.1. Material preparation

2.1.1. Preparation of TS-1@KCC-1

The core TS-1 zeolite ($\text{Si}/\text{Ti} = 40$) was synthesized according to a previously described method [53]. KCC-1 and the TS-1@KCC-1 shell were synthesized using a method similar to that in the literature [39]. A typical procedure for the synthesis of TS-1@KCC-1 was as follows. CTAB (1 g) and 0.6 g of urea were dissolved in 30 mL of deionized water, and then 30 mL of cyclohexane and 1.5 mL of *n*-pentanol were quickly added. The mixture was stirred to form a microemulsion solution, and then 0.5 g of calcined TS-1 powder was poured into the microemulsion. The mixture was stirred rapidly for 20 min and ultrasonicated for 1 h to ensure that the TS-1 particles were highly dispersed. Then 10 mmol of TEOS was added, and the mixture was stirred at room temperature for 3 h. Finally, the mixture was transferred to a Teflon-sealed autoclave equipped with a magnetic stirrer, and left at 393 K for 4 h. The products were collected and calcined at 823 K for 6 h to remove the template. The reaction time, temperature, and gel composition were changed to optimize the synthesis conditions and to investigate the possible formation mechanism. The shell thickness of TS-1@KCC-1 was controlled by changing the ratio of TEOS to TS-1 (mmol/g).

2.1.2. Preparation of $\text{Rh}(\text{OH})_x/\text{TS-1@KCC-1}$

$\text{Rh}(\text{OH})_x/\text{TS-1@KCC-1}$ was synthesized according to the literature [45,46] but with slight modifications. The typical procedure was as follows. TS-1@KCC-1 (2.0 g) was added to 60 mL of RhCl_3 aqueous solution (6.5 mmol/L) at room temperature and stirred for 3 h. Then the pH value of the mixture was ad-

justed to 9–10 with an aqueous solution of tetramethylammonium hydroxide (1.0 mol/L), and the resulting mixture was stirred at room temperature for 24 h. The solid was collected by filtration, washed with deionized water to remove chlorine species, and vacuum dried at room temperature overnight. The shell thickness was conveniently changed by adjusting the amounts of TEOS and TS-1 particles.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were collected using a Rigaku Ultima IV X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15405$ nm) at 30 kV and 25 mA. The pore structure of the core-shell and related materials was analyzed by nitrogen adsorption-desorption at 77 K using a BELSORP-MAX instrument. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method in the relative pressure (p/p_0) range 0.05–0.25. The pore size distributions were calculated using the Horvath-Kawazoe method for micropores and the Barrett-Joyner-Halenda method for mesopores. The total pore volume was obtained at a relative pressure of $p/p_0 = 0.99$. The micropore volume and external surface area were obtained using the t -plot method.

Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 field-emission scanning electron microscope. Transmission electron microscopy (TEM) images were obtained using a Tecnai™ F30 transmission electron microscope. The amounts of Si, Ti, and Rh were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Thermo IRIS Intrepid II XSP atomic emission spectrometer. X-ray photoelectron spectra (XPS) were obtained using a Perkin-Elmer PHI 500C X-ray photoelectron spectrometer.

2.3. Catalytic reactions

One-pot synthesis of benzamide from benzaldehyde through direct ammoxidation and rearrangement was carried out as a model reaction. A typical procedure was as follows. $\text{Rh}(\text{OH})_x/\text{TS-1@KCC-1}$ (0.2 g) was added to a mixture of 1.5 mL of deionized water, 2.0 mmol of benzaldehyde, 2.5 mmol of hydrogen peroxide (5 wt%), and 2.5 mmol of ammonia (25 wt%) in a Teflon vessel with a magnetic stirring bar; the vessel was purged with N_2 and then sealed. The Teflon vessel was attached to an autoclave, and the autoclave was heated at 343 K for 1 h and subsequently heated at 433 K for 7 h. After the reaction was complete, the autoclave was cooled to room temperature, and 2 mL of ethanol was added to the tri-phase system to form one liquid phase and one solid phase (catalyst). The spent catalyst was separated by centrifugation and washed with ethanol, and dried in a vacuum prior to being recycled. The liquid phase was analyzed using a Shimadzu GC2014 gas chromatograph equipped with a flame ionization detector and a DM-WAX capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μm). $\text{Rh}(\text{OH})_x/\text{TS-1@KCC-1}$ was also used to synthesize other primary amides.

3. Results and discussion

3.1. Material characterization

A flower-like mesoporous-silica-encapsulated TS-1 zeolite was synthesized in a microemulsion system using CTAB as a structure-directing agent and emulsifier and calcined TS-1 particles. When as-synthesized TS-1 was used, phase separation of KCC-1 occurred easily. Typical SEM and TEM images of pristine TS-1, pure KCC-1, and KCC-1-encapsulated TS-1 (TS-1@KCC-1) are shown in Fig. 1. The rectangular TS-1 core had a particle size of about 250 nm (Fig. 1(a)). The pure KCC-1 synthesized in the microemulsion system consisted of flower-like round spheres, with a particle size of approximately 300 nm (Fig. 1(b)). When the flower-like mesoporous silica KCC-1 was coated on the TS-1 surface, the particle size increased to 330–380 nm (Fig. 1(c)). The morphology of TS-1@KCC-1 was flower-like, similar to that of the pure KCC-1 material (Fig. 1(b)). TS-1@KCC-1 also exhibited an elliptical morphology resembling the TS-1 particles (Fig. 1(c)). Layered petaline silica was not only assembled on the TS-1 surface but also perpendicular to the core. The thickness of the layered petaline silica was about 8 nm (Fig. 1(c) and (d)), which was thicker than the pore walls of conventional mesoporous silica such as SBA-15 [54] and MCM-41 [55] (generally < 3 nm). This type of material was expected to have potential applications in high-temperature aqueous reactions. The TEM image of TS-1@KCC-1 (Fig. 1(d)) shows that the shell thickness of TS-1@KCC-1 was about 80 nm, which was consistent with the SEM image. We clearly observed that the petaline layered silica was perpendicular to the TS-1 core, and the thickness of the petaline layered silica was approximately 8 nm.

The powder XRD patterns of TS-1, KCC-1, and TS-1@KCC-1 are shown in Fig. 2. The pristine TS-1 showed MFI-structure-related diffraction peaks in the wide-angle region ($2\theta = 5^\circ$ – 35°), whereas in the small-angle region, no diffraction was observed (Fig. 2(1)). Pure KCC-1 spheres showed a diffraction peak at $2\theta = 1.0^\circ$ and a broad peak at $2\theta \approx 23^\circ$, proving that KCC-1 had a mesostructured amorphous structure (Fig. 2(2)). After KCC-1 was coated on TS-1, the TS-1@KCC-1 exhibited diffraction peaks from TS-1 and KCC-1 in both the small- and

Fig. 1. SEM images of TS-1 (a), KCC-1 (b), and TS-1@KCC-1 (c) and TEM image of TS-1@KCC-1 (d).

Fig. 2. XRD patterns of TS-1 (1), KCC-1 (2), and TS-1@KCC-1 (3).

wide-angle regions (Fig. 2(3)), but the intensity of these peaks was lower than that from TS-1 and KCC-1. Based on the XRD patterns, we deduced that TS-1@KCC-1 had a micro/mesoporous composite structure. N_2 adsorption-desorption analysis further proved that TS-1@KCC-1 had micropores (0.51 nm) and mesopores (3.0 nm), and the specific surface area and pore volume were 268 m^2/g and 0.354 cm^3/g , respectively [52]. These results verified that we successfully fabricated a new flower-like mesoporous-silica-encapsulated TS-1 micro/mesoporous composite core-shell material.

3.2. Synthesis conditions and possible formation mechanism

3.2.1. Effect of synthesis temperature

In the CTAB/cyclohexane/pentanol/urea/water micro-emulsion system for TS-1@KCC-1 synthesis, urea acts as a catalyst for the hydrolysis and condensation of TEOS. Urea decomposes at an appropriate temperature to release ammonia. The synthesis temperature was therefore critical for successfully obtaining a particular core-shell structure. SEM images of TS-1@KCC-1 synthesized at 333–413 K for 4 h are shown in Fig. 3. The flower-like mesoporous silica shell was not formed at 333 K (Fig. 3(a)). When the temperature was increased to 373 K, a beautiful flower-like core-shell material was con-

structed (Fig. 3(b)). This is because the urea decomposition temperature is about 353 K in aqueous solution. Urea therefore did not decompose to release ammonia, catalyzing the hydrolysis and condensation of TEOS to form a mesoporous silica shell below 353 K. When the temperature was further increased to 393 K, a well-structured mesoporous silica shell was also formed. However, at a higher temperature, 413 K, the shell became irregular. This could be attributed to the decomposition and hydrolysis and condensation of TEOS being too fast at high temperatures. The appropriate synthesis temperature was therefore between 373 and 393 K.

3.2.2. Effect of synthesis time

The effect of synthesis time was investigated between 0.5 and 12 h at 393 K. When the synthesis time was less than 1 h, e.g., 0.5 h, the KCC-1 shell was not formed because the reaction time was too short (Fig. 4(a)). When the synthesis time was prolonged to 1–12 h (Fig. 4(b)–(d)), and a flower-like shell of mesoporous silica KCC-1 was readily formed. However, coverage was incomplete at 1 h (Fig. 4(b)), as some of the silica source was not assembled on the surface of TS-1. The SEM image of TS-1@KCC-1 synthesized at 393 K for 4 h shows a perfect flower-like TS-1@KCC-1 material. A suitable synthesis time at 393 K was therefore 4 h.

3.2.3. Shell thickness tuning

The shell thickness of KCC-1-encapsulated TS-1 was conveniently controlled by adjusting the relative amounts of TEOS and TS-1. We fixed the amount of TEOS and changed the added amount of TS-1 zeolite. The particle size of TS-1@KCC-1 increased from 300 to 500 nm with decreasing amount of TS-1 (Fig. 5), and the shell thickness changed from 25 to 100 nm (Fig. 6). The SEM and TEM images were consistent with each other. However, when the ratio of TEOS to TS-1 was below 10 mmol TEOS/g TS-1 (Fig. 5(a) and Fig. 6(a)), some TS-1 particles were not encapsulated by KCC-1 silica. When the ratio was increased to 10 mmol/g (Fig. 5(b) and Fig. 6(b)), the TS-1 particles were well covered with a layer of KCC-1 shell. Phase separation of pure KCC-1 spheres was not observed, even when the ratio was increased to 20 mmol/g (Fig. 5(c)). However,

Fig. 3. SEM images of TS-1@KCC-1 synthesized at 333 K (a), 373 K (b), 393 K (c), and 413 K (d) for 4 h.

Fig. 4. SEM images of TS-1@KCC-1 synthesized at 393 K for 0.5 h (a), 1.0 h (b), 4.0 h (c), and 12 h (d).

Fig. 5. SEM images of TS-1@KCC-1 with different shell thicknesses synthesized at TEOS/TS-1 ratios of 5 (a), 10 (b), 20 (c), and 25 mmol/g (d).

Fig. 6. TEM images of TS-1@KCC-1 with different shell thicknesses synthesized at TEOS/TS-1 ratios of 5 (a), 10 (b), 20 (c), and 25 mmol/g (d).

when the ratio was further increased to 25 mmol/g, phase separation of KCC-1 spheres occurred, as indicated by the arrows in Fig. 5(d). A suitable TEOS to TS-1 ratio was therefore between 10 and 20 mmol/g. It should be noted that the ratio of the solid to the liquid phase in our synthesis system was less than 120 mL of solution per gram of solid (TS-1 zeolite), which was far below that in the conventional synthesis of porous core-shell materials. Conventional porous core-shell materials are usually synthesized in extremely dilute solutions (above 200 mL of solution per gram of solid core).

From these results, we can conclude that the appropriate synthesis conditions for TS-1@KCC-1 are 373–393 K for more than 4 h, and a suitable ratio of TEOS to TS-1 is 10–20 mmol/g. Under these appropriate synthesis conditions, perfect flower-like core-shell materials were successfully prepared.

Fig. 7. SEM images of TS-1@KCC-1 synthesized using synthesis systems with different compositions. (a) Without cyclohexane; (b) Without pentanol; (c) Without cyclohexane and pentanol; (d) With ammonia but without urea.

3.2.4. Possible formation mechanism

Inorganic porous core-shell materials are usually synthesized in aqueous solution, and there are few reports of the synthesis of inorganic porous core-shell materials in microemulsion systems. Examples of core-shell materials fabricated in microemulsion systems are polymer-shell-encapsulated solid cores, such as $\text{Fe}_3\text{O}_4/\text{PS}$ [56] and SiO_2/PS [57]. The components of the microemulsion synthesis system were investigated to clarify the possible formation mechanism of TS-1@KCC-1. When there was no organic solvent (cyclohexane) in the synthesis system, conventional mesoporous-silica-encapsulated TS-1 core-shell materials were obtained by templating with CTAB as the pore-directing agent (Fig. 7(a)). When the cosurfactant (*n*-pentanol) or the organic solvent and cosurfactant were absent, the core-shell materials were not formed (Fig. 7(b) and (c)). Finally, when urea was replaced by ammonia, phase separation of floccules and TS-1 occurred (Fig. 7(d)). Therefore, all the components constituting the microemulsion system are necessary for the successful fabrication of flower-like mesoporous silica on the TS-1 zeolite.

It is well known that in basic solution, the TS-1 zeolite surface is negatively charged, whereas the surfactant CTAB micelle is positively charged. In our synthesis system, CTAB works as both an emulsifier and a mesopore-directing agent. A possible formation mechanism for TS-1@KCC-1 is shown in Fig. 8. In a high-temperature solution, the urea could slowly release ammonia into the emulsion system to form a basic environment. First, the CTAB micelles adsorb on the surface of the TS-1 zeolite by electrostatic interaction, and then a silica or TEOS oligomer is assembled by CTAB micelles, forming the special flower-like mesoporous-silica-coated core-shell material.

3.3. Catalytic performance

TS-1@KCC-1 was used as a supporter to support $\text{Rh}(\text{OH})_x$ species, combining Ti and Rh active sites and leading to a bifunctional catalyst, $\text{Rh}(\text{OH})_x/\text{TS-1@KCC-1}$. The amount of Rh

Fig. 8. Possible formation mechanism of TS-1@KCC-1.

species on Rh(OH)_x/TS-1@KCC-1 was 1.6% (mass fraction), determined by ICP-AES analysis [52]. The specific surface area and pore volume of Rh(OH)_x/TS-1@KCC-1 were 211 m²/g and 0.303 cm³/g, respectively, a little lower than those of the parent TS-1@KCC-1 [52]. The XRD pattern of Rh(OH)_x/TS-1@KCC-1 was similar to that of the parent TS-1@KCC-1, and no signals arising from Rh and rhodium oxides were observed. Large particles of Rh and rhodium oxides were not observed in the TEM images of Rh(OH)_x/TS-1@KCC-1 [52]. The Rh(OH)_x species were therefore highly dispersed on the TS-1@KCC-1 support. The XPS spectrum of Rh(OH)_x/TS-1@KCC-1 showed the binding energy of Rh 3d_{5/2} and Rh 3d_{3/2} at 309.0 and 313.7 eV, respectively, indicating that the oxidation state of the Rh species is +3 [52].

Rh(OH)_x/TS-1@KCC-1 was used as a tandem catalyst in the one-pot direct synthesis of primary amides from aldehydes, ammonia, and hydrogen peroxide. First, the TS-1 core catalyzed the oxidation of ammonia by hydrogen peroxide to synthesize a hydroxylamine intermediate in situ; this intermediate then reacted with an aldehyde via non-catalytic oximation to produce an aldoxime. The aldoxime is then transformed into a primary amide, catalyzed by the Rh(OH)_x species on TS-1@KCC-1. The whole process is shown in Scheme 1.

Rh(OH)_x/TS-1@KCC-1 was used to catalyze benzaldehyde ammoximation and rearrangement with ammonia and hydrogen peroxide to synthesize benzamide, as a model reaction. The catalyst showed superior reusability compared with Rh(OH)_x directly supported on TS-1 and superior hydrothermal stability compared with Rh(OH)_x supported on conventional porous core-shell materials such as TS-1@MS-P123 and TS-1@MS-CTAB [52].

The tandem reaction can be divided into two steps according to the reaction temperature. The first step is the ammoximation of the aldehyde by ammonia and hydrogen peroxide catalyzed by the core TS-1 at low temperature (343 K). This step is rapid. The reaction temperature of the second step (transformation of the aldoxime to an amide catalyzed by Rh(OH)_x species) needs to be relatively high (>393 K). For in-

stance, when the reaction was carried out at 343 K for 1 h, the conversion of benzaldehyde was 72%, and the selectivity for benzaldoxime and benzamide was 82.0% and 17.0%, respectively. This means that a large portion of the benzaldoxime intermediate was not effectively converted to benzamide (Fig. 9). However, when the temperature was further increased to 433 K in the second step, the selectivity for benzamide increased, and the selectivity for benzaldoxime decreased with increasing reaction time. The selectivity for benzamide reached 94.7% after further reaction at 433 K for 7 h, whereas the selectivity for benzaldoxime decreased to 1.4%. Surprisingly, the conversion of benzaldehyde and selectivity for the by-product, benzonitrile, did not change with reaction time. Thus, to obtain high amide selectivity, the temperature of the second step should be adjusted to a relatively high temperature.

Compared with Rh(OH)_x/TS-1, i.e., Rh(OH)_x species supported directly on TS-1, Rh(OH)_x/TS-1@KCC-1 had the advantage of reusability in the one-pot synthesis of benzaldoxime. After reuse five times, the benzaldoxime selectivity was maintained at over 80% on Rh(OH)_x/TS-1@KCC-1 but decreased to below 20% on Rh(OH)_x/TS-1 [51]. This implies that KCC-1 stabilizes the Rh(OH)_x species, probably through the confining effects of its mesopores.

We found that the shell thickness of KCC-1 influenced the catalytic performance of Rh(OH)_x/TS-1@KCC-1 in the one-pot synthesis of benzaldoxime. A series of Rh(OH)_x/TS-1@KCC-1

Fig. 9. Changes in conversion and selectivity with reaction time in benzaldehyde ammoximation and rearrangement (beginning at the second temperature step).

Scheme 1. One-pot synthesis of primary amide catalyzed by Rh(OH)_x/TS-1@KCC-1.

Table 1Catalytic activity of Rh(OH)_x/TS-1@KCC-1 with different shell thickness synthesized at different TEOS/TS-1 ratios.

TEOS/TS-1 ratio (mmol/g)	Shell thickness (nm)	TS-1 content ^a (wt%)	Rh content ^b (wt%)	Aldehyde conversion (%)	Selectivity (%)	
					Amide	Oxime
5	25	76.9	1.72	89.7	94.3	1.8
10	50	62.5	1.74	83.5	94.5	1.7
20	80	45.5	1.63	72.1	94.9	1.4
25	100	40.0	1.65	65.3	93.1	1.5

Reaction conditions: catalyst 0.2 g, H₂O 1.5 mL, benzaldehyde 2 mmol, NH₃·H₂O 2.5 mmol, H₂O₂ 2.5 mmol, at 343 K for 1 h and then at 433 K for 7 h.^aTheory content according the relative amount of TS-1 and KCC-1 (SiO₂).^bDetermined by the ICP analysis.**Table 2**Catalytic performance of Rh(OH)_x/TS-1@KCC-1 in one-pot synthesis of primary amides.

Entry	Reactant	Product	Temperature (K)	Conversion (%)	Selectivity (%)
1			433	72.1	94.9
2			433	74.0	82.0
3			433	73.9	82.0
4			433	86.4	86.7
5			393	79.7	64.1
6			433	52.4	85.2
7			433	50.0	85.0

Reaction conditions: catalyst 0.2 g, H₂O 1.5 mL, aldehyde 2 mmol, NH₃·H₂O 2.5 mmol, H₂O₂ 2.5 mmol, 343 K for 1 h and further at 433 or 393 K for 7 h.

catalysts with different shell thickness (25–100 nm) was prepared by varying the ratio of TEOS to TS-1; the data are shown in Table 1. With increasing shell thickness, the relative amount of TS-1 and the aldehyde conversion both decreased simultaneously at comparable Rh loadings (1.63%–1.74%).

Using a bifunctional catalyst, i.e., Rh(OH)_x/TS-1@KCC-1 synthesized at a TEOS/TS-1 ratio of 20 mmol/g, various structurally diverse aldehydes, including aromatic, aliphatic, and heterocyclic aldehydes, were directly converted to the corresponding primary amides with ammonia and hydrogen peroxide in one-pot tandem reactions. The catalytic results are summarized in Table 2. The conversions of benzaldehydes and the selectivity for the corresponding benzamides were above 70% and 80%, respectively (Table 2, entries 1–4). An aliphatic aldehyde (isovaleraldehyde, Table 2, entry 5) was also converted to the corresponding aliphatic amide with high conversion (79.7%), although the selectivity (64.1%) was relatively low. For the heterocyclic aldehydes containing sulfur and nitrogen (Table 2, entries 6 and 7), the selectivity for the corresponding amides reached about 85% although the reaction activity was quite low (about 50.0%). Rh(OH)_x/TS-1@KCC-1 was therefore an efficient bifunctional tandem catalyst for the one-pot synthesis of primary amides directly from aldehydes with ammonia and hydrogen peroxide.

4. Conclusions

We successfully synthesized a novel core-shell material (TS-1@KCC-1) with a flower-like mesoporous silica shell and a TS-1 zeolite as the core in a microemulsion system. The fibrous petal-like silica was assembled perpendicularly on the surface of the TS-1 zeolite. TS-1@KCC-1 can be fabricated in a wide range of temperatures (373–393 K) and reaction time (at 393 K for more than 1 h). The shell thickness of TS-1@KCC-1 can be conveniently tuned by changing the amount of core material. As a result of the superior hydrothermal and mechanical stability of the KCC-1 shell, TS-1@KCC-1 is a good supporter for supporting Rh(OH)_x species, leading to a tandem catalyst for the one-pot direct synthesis of primary amides from aldehydes with ammonia and hydrogen peroxide.

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Graphical Abstract

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One-pot synthesis of primary amides on bifunctional Rh(OH)_x/TS-1@KCC-1 catalysts

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A novel bifunctional tandem catalyst for the one-pot synthesis of primary amides directly from aldehydes, ammonia, and hydrogen peroxide was synthesized.

Rh(OH)_x/TS-1@KCC-1双功能催化剂上一锅反应合成伯酰胺

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摘要: 在微乳液体系中成功地将花瓣状介孔氧化硅微球(KCC-1)包覆在钛硅分子筛TS-1表面, 得到了一种新型微孔/介孔复合核壳结构材料TS-1@KCC-1. 详细考察了TS-1@KCC-1的合成条件及可能的形成机理. 适宜的合成温度及时间分别为373–393 K和4 h. 壳层厚度可方便地通过改变硅源正硅酸乙酯和TS-1的比例在25–80 nm间进行调控. 以TS-1@KCC-1为载体负载Rh(OH)_x后即得到双功能催化材料Rh(OH)_x/TS-1@KCC-1, 该材料同时具有Ti和Rh(OH)_x活性中心, 可以高效催化醛、氨水和过氧化氢经一锅串联反应直接制备得到伯酰胺.

关键词: TS-1分子筛; 核壳材料; KCC-1; 伯酰胺; 串联催化剂

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