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One-pot synthesis of benzamide over a robust tandem catalyst based on center radially fibrous silica encapsulated TS-1†

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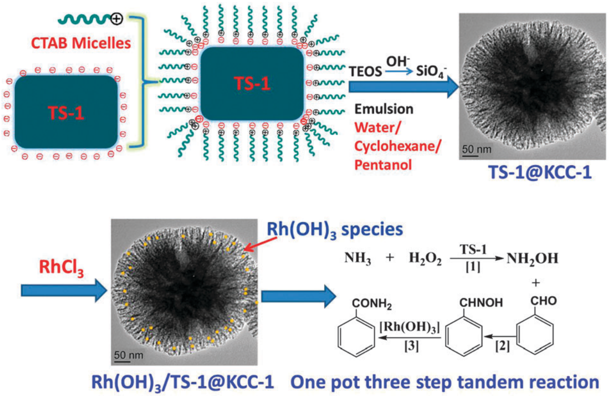
A center radially fibrous silica encapsulated TS-1 zeolite (TS-1@KCC-1) has been synthesized in a microemulsion system for the first time. Supporting the $Rh(OH)_3$ species, this novel core–shell structured material serves as a robust bifunctional catalyst for one-pot synthesis of benzamide from benzaldehyde, ammonia and hydrogen peroxide, in which the aldehyde ammoximation and oxime rearrangement occur in a tandem way.

One-pot tandem or cascade reactions have received intensive research interests in green and sustainable chemistry owing to their advantages in terms of atom economic efficiency, easy separation of products and intermediates as well as process intensification.[1–6] Recently, Mizuno *et al.*[7] reported that $Rh(OH)_3$ supported on Al_2O_3 could catalyse the rearrangement of aldehyde oximes to amides as well as one-pot synthesis of amides from aldehydes and hydroxylamine derivatives. This may open up the possibility of developing new chemical processes for producing primary amides, the important intermediates widely used in organic synthesis, and in detergents and lubricants production.[8] Nevertheless, as one of the reactants, expensive and explosive sulphate or hydrochloride hydroxylamine is used in the above-mentioned one-pot reaction.[9] If hydroxylamine could be *in situ* formed in organic synthesis, more greener and atom-efficient reactions are expected to be developed for synthesizing primary amides.[10] Titanosilicates are effective catalysts for the ammoximation of ketones or aldehydes with ammonia and hydrogen peroxide to corresponding oximes, in which *in situ* formation of a hydroxylamine intermediate has been confirmed.[11,12] Thus, an appropriate combination of titanosilicates and $Rh(OH)_3$ may lead to suitable tandem catalysts of choice.

Porous core–shell materials are known as good supports for dispersing and stabilizing metal nanoparticles or other coordinate compounds useful for catalytic reactions.[13,14] Some examples have been reported on the combination of inorganic oxides (*e.g.* Fe_3O_4[15]) or zeolites (TS-1[16] and ZSM-5[17]) cores with MCM-41, SBA-15 or worm-hole like mesoporous silica shells.[15–18] Recently, Polshettiwar *et al.* developed fibrous silica nanospheres (KCC-1) with open pore structures and extremely high thermal, hydrothermal and mechanical stabilities.[19] KCC-1 can be used as a versatile support for noble metal nanoparticles in liquid-phase catalytic reactions.[20–22]

We communicate here the design and synthesis of a new core–shell material with TS-1 zeolite as core and fibrous silica KCC-1 as shell, the first example of constructing the inorganic porous core–shell materials on the zeolite surface in a microemulsion system at high solid to liquid ratios. TS-1@KCC-1 thus prepared was further employed as the support for the $Rh(OH)_3$ species. The resultant bifunctional $Rh(OH)_3$/TS-1@KCC-1 catalyst was applied to directly synthesize primary amides from aldehyde, NH_3 and H_2O_2 through one-pot ammoximation and rearrangement.

The procedure of catalyst synthesis and possible one-pot reaction mechanism for the $Rh(OH)_3$/TS-1@KCC-1 catalyst are illustrated in Scheme 1. A typical synthesis was conducted in a microemulsion system of water–cyclohexane–*n*-pentanol (experimental details shown in ESI†), in which tetraethyl orthosilicate



Scheme 1 Preparation procedures for $Rh(OH)_3$/TS-1@KCC-1 and its application to one-pot synthesis of amides.

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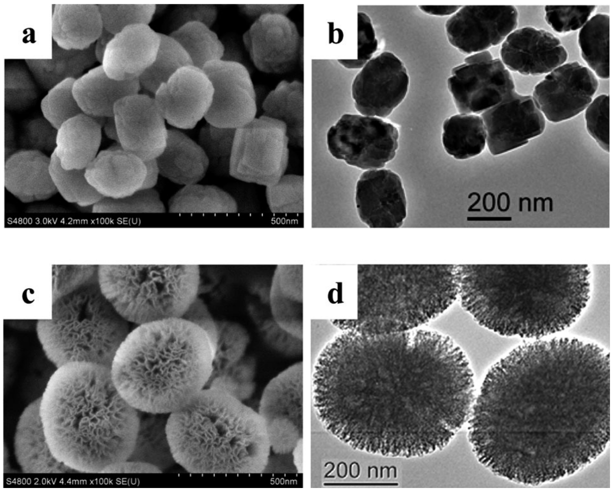


Fig. 1 SEM and TEM images of TS-1 (a and b) and TS-1@KCC-1 (c and d).

(TEOS) was assembled on the surface of TS-1 particles with the assistance of cetyltrimethyammonium bromide (CTAB) and urea. Under basic conditions, the negatively charged TS-1 nanoparticles preferred to adsorb positively charged cationic CTAB micelles. The silica precursor from TEOS hydrolysis was favourable to be assembled around the micelles catalysed by urea in the water–oil microemulsion, giving rise to the core–shell structured material TS-1@KCC-1 that possessed a fibrous mesosilica shell orientedly grown on the zeolite crystals.

Fig. 1 shows typical scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of TS-1 and TS-1@KCC-1. The core TS-1 had a particle size of 250–300 nm (Fig. 1a and b). After coating with a fibrous silica shell, the size increased to 330–380 nm (Fig. 1c and d). The flower-like fibrous silica structure of TS-1@KCC-1 was similar to the pure silica KCC-1 (ESI,† Fig. S1), synthesized according to the literature.[19] Nevertheless, in contrast to round spheres of KCC-1, TS-1@KCC-1 was of elliptical shape, resembling the morphology of the TS-1 particles. The TEM image indicated that the shell thickness of TS-1@KCC-1 synthesized was approximately 80 nm. This observation was consistent with the SEM image.

The X-ray diffraction (XRD) pattern of TS-1@KCC-1 showed a peak at 2θ of *ca.* 1° in the small angle region, which was absent for TS-1 but similar to that of KCC-1 (ESI,† Fig. S2). It should be attributed to the mesostructure of the fibrous silica assembled by the expanded CTAB micelles in the organic solvent of cyclohexane–pentanol. TS-1@KCC-1 showed the characteristic diffractions owing to the MFI topology in the wide angle region. They were reasonably weaker in intensity than TS-1, due to the decreased amount of TS-1 and the shielding effect of the fibrous silica shell.

The nitrogen adsorption–desorption isotherm of TS-1@KCC-1 was characteristic of both I and IV types (ESI,† Fig. S3). At low relative pressure (<0.2) the adsorption was attributed to micropores in the core TS-1. Thus, the fibrous silica shell and core are believed to be interconnected with each other, and the micropores were not blocked by the mesosilica shell. The specific surface area and pore volume of TS-1@KCC-1 were 268 $m^2\ g^{-1}$ and 0.354 $cm^3\ g^{-1}$, respectively, between the values of TS-1 and KCC-1 (ESI,† Table S1). The above-mentioned results verified that we have successfully coated the fibrous silica on the surface of the TS-1 zeolite.

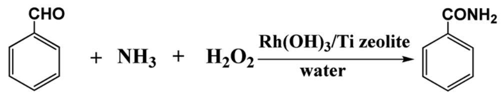
The fibrous core–shell material was used to support the $Rh(OH)_3$ species, leading to a bifunctional catalyst $Rh(OH)_3$/TS-1@KCC-1 (for detailed preparation procedure, see ESI†). The amount of Rh loaded was 1.6 wt% as determined by ICP analysis. The $Rh(OH)_3$ species were highly dispersed probably inside the mesopores of TS-1@KCC-1, but not as oxide particles as they were not detected either by XRD or by TEM measurements (ESI,† Fig. S4 and S5). $Rh(OH)_3$/TS-1@KCC-1 showed in the XPS spectrum the Rh $3d_{5/2}$ and Rh $3d_{3/2}$ peaks at electron binding energies of 309.0 and 313.7 eV, respectively (ESI,† Fig. S6), indicating that the Rh species existed in the oxidation state of +3.[23]

The $Rh(OH)_3$/TS-1@KCC-1 catalyst was employed for one-pot synthesis of benzamide through tandem reactions, that is, direct ammoximation of benzaldehde with ammonia and hydrogen peroxide and subsequent rearrangement of the corresponding oxime formed. Titanosilicates are capable of catalysing the oxidation of NH_3 with H_2O_2 to yield the hydroxylamine intermediate, which then reacts with aldehydes or ketones *via* non-catalytic oximation to produce oximes.[12] On the other hand, the $Rh(OH)_3$ species are considered to be the catalytic sites for the rearrangement of aldehyde oximes to amides.[7] These tandem reaction steps are expected to take place on the bifunctional $Rh(OH)_3$/TS-1@KCC-1 catalyst as illustrated in Scheme 1.

$Rh(OH)_3$/TS-1@KCC-1 and related materials were first checked for their catalytic activity in the rearrangement of benzaldehyde oxime to benzamide. In the case of TS-1 and TS-1@KCC-1, the oxime conversion and benzamide selectivity were both very low, nearly close to the results without catalyst (ESI,† Table S2, no. 1–3). Instead of amide, benzaldehyde as a result of oxime hydrolyzation and other products were produced as the main products. The $Rh(OH)_3$ species supported on TS-1 and TS-1@KCC-1, however, gave an oxime conversion of *ca.* 99% and a benzamide selectivity of 82–84% (no. 4 and 5). When $Rh(OH)_3$/TS-1@KCC-1 was converted to Rh_2O_3/TS-1@KCC-1 by calcination at 573 K for 5 h in air, the rearrangement of oxime was retarded obviously, giving only 33.8% oxime conversion (no. 6). Thus, the $Rh(OH)_3$ species are essential to the oxime rearrangement, which was in agreement with the mechanism proposed previously.[23]

Table 1 shows the results of one-pot synthesis of benzamide from benzaldehyde, ammonia and hydrogen peroxide in water solvent. TS-1 and TS-1@KCC-1 catalysed efficiently the ammoximation of benzaldehyde to benzaldoxime, but gave an extremely low amide selectivity (1.2%) (Table 1, no. 1 and 2). Obviously, the tandem reactions terminated at the ammoximation step in the absence of $Rh(OH)_3$ species. $Rh(OH)_3$/KCC-1 free of Ti active sites, on the other hand, converted benzaldehyde mainly into benzoic acid as a result of oxidation by H_2O_2 on the Rh species, but showed a low selectivity to oxime and amide (no. 3). Only when the $Rh(OH)_3$ species were supported on TS-1 or TS-1@KCC-1, the amide selectivity reached *ca.* 95%, while the oxime selectivity decreased to low levels (no. 4 and 5). The benzaldehyde conversion of $Rh(OH)_3$/TS-1 was higher than that of $Rh(OH)_3$/TS-1@KCC-1, simply because the latter contained a less active TS-1 component available for the ammoximation.

Table 1 One-pot synthesis of benzamide from benzaldehyde, ammonia and hydrogen peroxide catalyzed by supported $Rh(OH)_3$ and related catalysts[a]



No.	Catalysts	Ti content (%)	Aldehyde conv. (%)	Selectivity (%)	
				Amide	Oxime
1	TS-1[b]	2.0	93.5	1.2	95.1
2	TS-1@KCC-1[b]	0.9	68.4	1.2	94.8
3	$Rh(OH)_3$/KCC-1[c]	0	56.1	0.8	1.8
4	$Rh(OH)_3$/TS-1[c]	1.96	94.9 (79.5)	94.7 (76.4)	3.4 (17.2)
5	$Rh(OH)_3$/TS-1 @KCC-1[c]	0.88	72.1 (71.2)	94.9 (94.9)	1.4 (1.9)
6	$Rh(OH)_3$/TS-1 @MS-P123[c]	1.25	85.2 (77.9)	91.2 (64.8)	8.4 (25.4)
7	$Rh(OH)_3$/TS-1 @MS-CTAB[c]	1.25	90.9 (76.3)	94.5 (45.4)	0.3 (45.4)

[a] Conditions: cat, 0.2 g; H_2O, 1.5 mL; benzaldehyde, 2 mmol; $NH_3 \cdot H_2O$, 2.5 mmol; H_2O_2, 2.5 mmol. [b] Reaction temp., 343 K; time, 1 h. [c] Reaction temp., 343 K for 1 h and then 433 K for 7 h. The values in parentheses show the results after reuse.

The reusability of $Rh(OH)_3$/TS-1@KCC-1 was compared with $Rh(OH)_3$/TS-1 in the one-pot synthesis of amide (ESI,† Fig. S7 and S8). $Rh(OH)_3$/TS-1@KCC-1 could be reused four times without obvious decrease in aldehyde conversion and amide selectivity, while it suffered a slight decrease in amide selectivity after fifth reuse. This might be attributed to a partial leaching of $Rh(OH)_3$ species as the Rh content decreased from 1.6 wt% to 1.0 wt%. In contrast, the oxime selectivity of $Rh(OH)_3$/TS-1 decreased sharply during reuse although the aldehyde conversion was maintained over 80%, indicating that it possessed a stable ammoximation ability but lost easily the activity of oxime rearrangement. ICP analysis indicated that its Rh content decreased from 1.55 wt% to 0.2 wt%. Thus, considering the advantages of confining and stabilizing effect of mesopores, $Rh(OH)_3$/TS-1@KCC-1 was found to be superior to $Rh(OH)_3$/TS-1 in terms of suppressing Rh leaching.

The advantage of using a fibrous silica shell for supporting the $Rh(OH)_3$ species was further verified by comparing the hydrothermal stability of $Rh(OH)_3$/TS-1@KCC-1 with $Rh(OH)_3$/TS-1@MS-P123 and $Rh(OH)_3$/TS-1@MS-CTAB, the mesosilica shells of the latter two catalysts were assembled by using triblock copolymer P123 and CTAB as the template, respectively. At a similar Rh loading (1.5–1.6 wt%), $Rh(OH)_3$/TS-1@MS-P123 and $Rh(OH)_3$/TS-1@MS-CTAB were both highly efficient for the amide formation in the first run, but they decreased greatly the amide selectivity in reuse (Table 1, no. 6 and 7). The SEM images indicated that the morphology of $Rh(OH)_3$/TS-1@KCC-1 was almost intact, while the mesosilica shells were totally degraded for the other two materials after catalytic reaction (ESI,† Fig. S9). TEM investigation also confirmed that the structure was well-preserved in the used $Rh(OH)_3$/TS-1@KCC-1 catalyst (Fig. S10, ESI†). The Rh species were almost undetectable for the used $Rh(OH)_3$/TS-1@MS-P123 and $Rh(OH)_3$/TS-1@MS-CTAB catalysts. The presence of water, from either added solvent or aqueous hydrogen peroxide, meant the catalyst particles were exposed to a severe hydrothermal environment. In order to prepare hydrothermally stable and reusable catalysts for one-pot production of amides, more robust and stable mesosilica shells are thus required to serve as the scaffold for supporting and immobilizing the $Rh(OH)_3$ species.

In summary, we successfully synthesized a new core–shell material consisting of center radially fibrous silica and encapsulated TS-1 in a microemulsion system. With superior hydrothermal and mechanical stability, TS-1@KCC-1 is a good support for dispersing and stabilizing the $Rh(OH)_3$ species, leading to be a reusable catalyst that combines together the catalytic properties of ammoximation and oxime rearrangement. This bifunctional catalyst makes one-pot synthesis of benzamide possible.

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