Nanoreactors



Confined Transformation of UiO-66 Nanocrystals to Yttria-Stabilized Zirconia with Hierarchical Pore Structures for Catalytic Applications

Runze Qin and Hua Chun Zeng*

Solid acids as a substitution for hazardous liquid acids (e.g., HF and H₂SO₄) can promote many important reactions in the industry, such as carbon cracking, to proceed in a more sustainable way. Starting from a zirconium-based metal-organic framework (UiO-66 nanocrystals), herein a transformative method is reported to prepare micro/mesoporous yttria-stabilized zirconia (YSZ) encapsulated inside a mesoporous silica shell. It is then further demonstrated that the resultant reactor-like catalysts can be used for a wide range of catalytic reactions. The acidity of the YSZ phase is found with rich accessible Lewis acid and Brønsted acid sites and they display superior performances for esterification (acetic acid and ethanol) and Friedel-Crafts alkylation (benzylation of toluene). After being loaded with different noble metals, furthermore, hydrogenation of CO₂ and a one-pot cascade reaction (nitrobenzene and benzaldehyde to N-benzylaniline) are used as model reactions to prove the versatility and stability of catalysts. Based on the findings of this work, it is believed that this class of reactor-like catalysts can meet future challenges in the development of new catalyst technology for greener heterogeneous catalysis.

1. Introduction

Catalytic solid acids, such as zirconium oxide, niobium oxide, and molybdenum oxide with high oxidation states for metal cations, are a class of well-established solid materials used in chemical industry which can help protonating hydrocarbon molecules to form carbocations and promote many important catalyzed reactions, such as cracking, hydrocracking, isomerization, alkylation, and aromatization through surface complexes or transition states.^[1] Compared to conventional Lewis acid (e.g., BF₃ and AlCl₃) and Brønsted acid (H₂SO₄ and HF) catalysts, which are hazardous, solid acids are more environmentally friendly in accordance with process sustainability and catalyst recyclability. Mostly being used as heterogeneous catalysts, solid acids function via their active surfaces to reactants

R. Z. Qin, Prof. H. C. Zeng Department of Chemical and Biomolecular Engineering Faculty of Engineering National University of Singapore 10 Kent Ridge Crescent, Singapore 119260, Singapore E-mail: chezhc@nus.edu.sg

D The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201903264.

DOI: 10.1002/adfm.201903264

and thus their catalytic performances are determined to a great extent by their workable surface areas. Porous solid acids with high specific surface area can provide more accessible acid sites, which will significantly enhance catalyst efficiency.^[2] Furthermore, compared with simply single pore size featured (e.g., micropore or mesopore) porous materials, hierarchical pore structures could endow them with better mass diffusion properties.^[3] Meanwhile, functionalization of solid acids with active metal components has also been found to play a crucial role in many common reactions, such as the conversion of organic intermediates to synthetic drugs;^[4] in those cases, engineering porosity for solid acid materials is also of vital importance because it endows them with a high loading capacity and uniform distribution of added components. Furthermore, topology of such supporting materials has been employed recently to

resist sintering through size confinement,^[5] which is one of the commonest impediments to nanoparticle catalysis. In this regard, ordered porous solid-acid catalysts could also play such a role to combat the sintering of their loaded metals. However, attention being devoted to this class of composite materials is found relatively lacking.

On the other hand, in searching newer acid materials, it is recognized that metal-organic frameworks (MOFs) have drawn enormous attention in the last 20 years. Because of their high specific surface area, tunable porosity, and other functionalizable physicochemical properties, MOFs have been widely used in a variety of applications including molecular adsorptiondesorption, membrane separation, gas sensing, heterogeneous catalysis, encapsulation and controlled releases.^[6] In particular, with coordinative unsaturation or open active metal sites on metal secondary building units, many MOF materials can provide abundant intrinsic acid sites.^[7] However, although design of acidity of moderate strength can be achieved for MOF materials, the ability to produce superacidity remains challenging with only few successful examples.^[8] Besides, most MOF materials cannot survive in a harsh environment such as high temperature and extreme pH values. Nevertheless, it is noted that except for their direct utilizations, MOFs are also extensively used as chemical precursors or templates to derive advanced functional materials with special structural or architectural



merits that conventional processing methods cannot provide. These resultant solid derivatives include, for instance, porous carbon materials, porous metal oxides and carbon-supported nanoscale metal particles.^[9] Through mostly thermal decomposition of MOFs or MOF nanocomposites under a reactive or inert atmosphere, specific morphology and composition can be attained owing to high carbon content and high-density metal nodes in MOFs. Prior to thermal decomposition of pristine MOFs, in many cases, post-synthesis modification or addition of other functional materials can be carried out in order to adjust properties of product.^[10] Thus it is desirable to obtain materials that maintain rich acid sites for porous solid acids similar to MOF materials and meanwhile possess high stability. In a previous literature,^[11] direct calcination of yttrium-doped UiO-66 was conducted to produce YSZ with maximum BET surface of 34.6 m² g⁻¹. However, this almost nonporous structure could make it difficult to be used as support for catalysts. To the best of our knowledge, there have been no reports yet on employing MOF as a precursor to prepare highly porous yttria-stabilized zirconia (YSZ) to work as a solid acid and as a catalyst support at the same time, although YSZ is one of the most studied materials in ceramic science and technology. In this regard, we believe that utilizing MOFs as solid precursors holds a number of advantages. First, UiO-66 used in this work is a highly porous material and thus other metal modifiers such as yttrium can be readily dispersed into the entire host structure compared with their nonporous bulk counterparts. Second, conversion of UiO-66 to its product metal oxide (ZrO_2) upon heating would generate gaseous species like CO2 and slow release of the gas product would help to create pores for resultant ZrO_2 confined with a mesoporous silica ($mSiO_2$) shell. Third, except meso- and micropores formed inside the metal oxide of ZrO₂, void spaces inside the mSiO₂ shell could be generated, which results in creating macro-porosity for the ZrO₂ phase, due to much larger volume of UiO-66 material compared to that of solid ZrO₂. Finally, ZrO₂ form within the mSiO₂ shell could be better protected in addition to targeted structural merits of the ZrO₂ phase.

The above prepared confined ZrO_2 phase should benefit numerous catalytic applications, as will be elucidated in the present work. For example, hydrogenation of CO₂ to produce C1 chemicals (such as CH₄, CO and CH₃OH) has been identified as a promising strategy to mitigate greenhouse effect and enormous work has been put on utilizing nanocatalysts to reduce CO₂ to useful products. However, activity loss caused by aggregation of active catalytic components remains a challenge for this type of catalysts and meanwhile there is still room for elevation of yield and versatility.^[12] Thus catalysts with high conversion, selectivity and meanwhile stability and versatility are highly demanded.

Herein, we report a synthetic approach to obtain micro/ mesoporous YSZ encapsulated inside a mesoporous silica shell by using UiO-66 MOF as a solid precursor. In this preparation, calcination of yttrium-modified and silica-encapsulated UiO-66 in air would produce high surface-area micro/mesoporous YSZ nanostructure inside the silica shell. Compared to previous methods to fabricate porous metal oxide with soft templates (e.g., P-123, CTAB, etc.) or hard templates (e.g., SBA-15),^[2,13] this approach achieved high specific surface areas without

needing extra steps to remove the included templates. With the addition of yttrium, zirconium oxide gets stabilized and vttrium also shows positive role for catalyst activity probably through electronic structure tuning. The resultant core-shell (namely, the YSZ@mSiO₂) contains high-density accessible acid sites along the generation of porous structure, exhibiting superior performance for catalytic esterification. Furthermore, using the YSZ@ mSiO2 as a catalyst carrier, ultrasmall metal particles can be easily loaded inside the micro- and mesoporous YSZ through simple impregnation with the strong interaction between the YSZ phase and supported noble metal catalyst, which displays remarkable performances for catalytic CO₂ hydrogenation and a one-pot three-step cascade reaction of benzaldehyde and nitrobenzene, proving its ability to serve as a versatile nanoreactor for various reactions. Moreover, the micro- and mesoporous YSZ developed in this work demonstrates great chemical stability in extreme pH value environments and/or at high temperatures up to 700 °C. The loaded metal nanoparticles also exhibit excellent stability up to 500 °C without noticeable aggregation.

2. Results and Discussion

2.1. Synthesis and Morphology of M/YSZ@mSiO₂

In this work, the synthetic procedure is illustrated in Scheme 1. As can been from Figure 1a,b, uniform octahedrons of UiO-66 nanocrystals can be formed by adding acetic acid into the system to effectively reduce the nucleation rate. Varying sizes of UiO-66 nanocrystals can be controlled by adjusting the reaction time and reactant concentration, which in turn will determine the product size generated in subsequent steps (Scheme 1 and Figure S1, Supporting Information). A layer of mesoporous silica (mSiO₂) shell is then added onto the external surface of the UiO-66 nanocrystals (Figure 1c), after which yttrium is also introduced into the UiO-66@mSiO2 through impregnation, which gives rise to the Y-UiO-66@mSiO₂. This resultant precursor is then calcined at a relatively high temperature of 700 °C in order to produce thermally stable YSZ phase (in the YSZ@mSiO2; Figure 1d) to withstand any harsh reaction conditions. PXRD pattern of YSZ@mSiO2 fits well with that of the pseudo-fluorite-type tetragonal and cubic mixed structures of YSZ (Figure 1e), confirming the generation of YSZ phase inside the amorphous silica shell. Displayed in Figure 1, different batches of the synthesized samples were mixed first and then characterized in order to prove the consistency and reproducibility of our products.

We found that the appropriate calcination time, heating rate and silica shell thickness are all important process parameters in forming the YSZ@mSiO₂ core–shell structure. If calcination time is too short, the decomposition of Y-UiO-66 inside the mesoporous silica is incomplete, leaving an unevenly distributed intermediate (Figure S2, Supporting Information). Besides, when the thickness of silica shell is too thin to withstand the transformation of octahedral Y-UiO-66, the whole Y-UiO-66@mSiO₂ structure would collapse and part of YSZ would not be encapsulated (Figure S2, Supporting Information). With the Thermogravimetric analysis (TGA) technique (Figure S3,





Scheme 1. Illustration of the stepwise preparation of the $M/YSZ@mSiO_2$ nanoreactors in this work (UiO-66, starting nanocrystals; SiO₂, silica precursors; $mSiO_2$, mesoporous silica shell; Y, yttrium; M = catalytic metal nanoparticles depicted as small shining spheres).

Supporting Information), the UiO-66 phase was fully decomposed into the monoclinic zirconia readily at around 540 °C,^[14] and in particular the gradual weight loss of UiO-66@mSiO₂ in the temperature range of 200–300 °C was attributable to the decomposition of cetyltrimethylammonium chloride solution (CTAC) trapped in the mSiO₂ shell.

As shown in Figure 1d (YSZ@mSiO₂), the resultant YSZ inside the mesoporous silica shell mostly sticks to the shell and exists in a porous, incompact form, which was further proven by the N₂ adsorption/desorption isotherm and pore size distribution of this sample (Figure 2). For the YSZ@mSiO₂ coreshell, an evident hysteresis loop is observed within the range of relative pressure (P/P_0) from 0.5–0.8, proving the existence of mesopores in this sample. The specific surface area of the YSZ@mSiO₂ is 498 m² g⁻¹ with the pore volume of 0.286 mL g⁻¹ obtained at $P/P_0 = 0.980$. In the pore size distribution of this sample, typically five prominent peaks were found at 0.39, 0.68, 1.48, 2.73, and 3.43 nm, confirming a micro/mesoporous structure in the YSZ@mSiO₂. Essentially, this pore structure still remains after etching silica shell with alkali, with only a small shift to the right (i.e., only a slight pore enlargement). The disappearance of 0.39 nm pore could be attributed to the alkaline etching which eliminated contact interstitials between the YSZ and *m*SiO₂ shell. The differential pore volumes for 0.39 nm and 0.68 nm remain almost the same but the differential pore volumes for 2.73 nm and 3.43 nm were reduced by half, which implies that pore size for etched silica shell lies in this range.

To investigate the pore formation mechanism, several control experiments were also conducted. For example, the mesoporous YSZ still displayed a BET surface of 324 m² g⁻¹ after etching off the silica shell, which is among the highest specific surface areas of YSZ reported.^[15] In contrast, the specific surface area of the calcined UiO-66 sample under the same calcination condition is only 29 m²·g⁻¹. In addition to this,

transmission electron microscopy (TEM) images further disclose the same porous feature of the YSZ core phase but comparatively nonporous appearance of the ZrO₂ formed from the calcined UiO-66 sample (Figure S4, Supporting Information). Furthermore, the Y-UiO-66 sample was prepared from impregnating UiO-66 nanocrystals with the same yttrium salt solution, but the calcined Y-UiO-66 sample shows a very low BET surface area of only 34 m²·g⁻¹, excluding a major impact of yttrium in pore formation. Hence, it is deduced that the encapsulation of mesoporous silica shell on the UiO-66 is a key factor in pore formation. In the calcination process in air, the yttriumimpregnated UiO-66 would decompose into the solid YSZ and gaseous carbon dioxide, carbon monoxide and water vapor, as well as a trace amount of gaseous species from decomposition of the yttrium salt. Nevertheless, due to the confinement of mesoporous silica shell, these gaseous species cannot be released instantly, and thus this slow gas evolution process leads to formation of

FUNCTIONAL

www.afm-journal.de

micro/mesoporous YSZ phase, noting that the exterior mSiO₂ shell itself is also undergone thermal decomposition of its trapped surfactant molecules (CTAC). In this process, on the other hand, the silica shell also provides a boundary support for the shrinking YSZ core generated from Y-impregnated UiO-66, which results in a loosely packed particles of porous YSZ (Figure S4a, Supporting Information), instead of contracting inward into a compact form. The YSZ formed from this process is very stable up to 700 °C and in the pH range of 0-13 (i.e., the silica shell would be etched in alkaline environment but the porous YSZ core remains). It is worth noting that with the uniform morphologies for the solid precursors (UiO-66@mSiO₂ and thus Y-UiO-66@mSiO₂), consistent pore size distribution for the final YSZ phase can be easily obtained among samples from different batches of synthesis. Another noteworthy feature about porous YSZ inside mSiO2 shell is that because YSZ, which has a much higher density than the UiO-66 phase, can only occupy a small volume of the space left by the decomposition of a UiO-66 crystal core; therefore a large part of the interior space, especially the space in the central location, is still empty (Figure S4a, Supporting Information). Besides obvious micro- and mesopore observed in BET pore size distribution, formation of these empty cavities creates some macropores inside porous YSZ, thus producing unique macro-meso-micro hierarchical pore structure (see Scheme 2). The improved mass diffusion properties of such hierarchical frameworks could endow them with superior catalytic activity,^[3] which could further be confirmed by their versatility for a range of catalytic reactions. It is proposed that this structural feature will create localized concentration gradients if the YSZ@mSiO₂ core-shell structure is used as a catalyst carrier for constructing nanoscale reactors with other catalytically active metals in consecutive cascade reactions, noting that the tiered porosities in the YSZ core will ease required mass transport processes for





www.afm-journal.de



Figure 1. a) FESEM image of the UiO-66 nanocrystals, TEM images of b) the UiO-66 nanocrystals, c) the UiO-66@mSiO₂ sample, d) the YSZ@mSiO₂ sample, and e) XRD pattern of the YSZ@mSiO₂ sample (black curve), compared with the XRD patterns of tetragonal YSZ (red vertical lines) and cubic YSZ (light blue lines) from XRD database.

reactions too. Indeed, apart from the catalytic activity of YSZ itself, multiple active metal components can also be loaded into the YSZ@mSiO₂ through simple metal impregnation. As shown in **Figure 3**a, metal NPs are homogenously distributed throughout the interior YSZ phase. In principle, both the porous silica shell and the YSZ can support these metal NPs. However, much fewer nanoparticles were found in mesoporous silica shell based on our investigations of TEM and energy-dispersive X-ray spectroscopy (EDX) elemental mapping, which could possibly result from contraction of metal solution from outside to inside in drying process after impregnation. Furthermore, surface hydrophilicity and chelating ability to metal precursors (which were dissolved in an aqueous solution) can also be attributed to the observed difference between the mSiO₂



Figure 2. a) N₂ adsorption–desorption isotherms and b) differential volumetric pore size distribution (using BJH method based on the desorption data) of the YSZ@mSiO₂ sample, the etched YSZ@mSiO₂ sample, the calcined Y-UiO-66 sample, and the calcined UiO-66 sample.

and YSZ. In our X-ray diffraction (XRD) investigation for the $M/YSZ@mSiO_2$ samples, we found that XRD peaks for the corresponding metals (M) can totally disappear by adjusting reducing temperature, indicating ultrasmall size of metal NPs formed in the micro/mesoporous YSZ phase (Figure S5, Supporting Information). Furthermore, mixed domains of YSZ can





Scheme 2. Schematic illustration of hierarchical pore structures in metal loaded YSZ for catalytic applications.

be observed under high-resolution TEM (HRTEM) (e.g., Pd/ YSZ@mSiO₂; Figure 3b) after etching away the mesoporous silica shell and the lattice fringe with an interplanar distance of 0.30 nm corresponds to the plane distance of *t*-YSZ {011} and/ or *c*-YSZ {111}, which indicates a possible structural mixture of tetragonal phase and cubic phase.^[16] However, the loaded noble metal nanoparticles cannot be located unambiguously in the same image, thus indicating that the loaded Pd is indeed extremely small, probably in sub-nanoscale (Figure 3b). Similarly, other metal loadings (such as Pt and Ru) are also difficult to observe with the HRTEM technique, indicating their sizes are indeed ultrafine. Accommodation and homogenous distribution of more than one kind of metal in the host system of YSZ@mSiO₂ can also be realized simultaneously (see Figure S6, Supporting Information).

2.2. Acidity of YSZ@mSiO₂

YSZ is a very common support for catalysts nowadays with strong acidity as solid superacid.^[17] To investigate the acidity and accessibility of acid sites for the YSZ inside the mesoporous silica shell, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) IR was used to characterize the acid sites distributed in the YSZ@mSiO₂ sample by using pyridine as a probing molecule. With this in situ technique, the IR peaks for pyridine would shift according to whether it is adsorbed on a Lewis acid site or protonated by a Brønsted acid site.^[18] After the adsorption of pyridine, first, peaks for pyridine adsorbed on Lewis acid sites can be found on IR spectrum (Figure 4). According to an early paper in literature,^[19] these peaks correspond to the normal modes v_{8a} and v_{19a} of ring-breathing (vCCN) vibrations of pyridine with A1 symmetry (1598 and 1490 cm⁻¹, respectively) and the v_{19b} modes with B₂ symmetry (1446 cm⁻¹),^[19] which coincide with those found for Lewis-site coordinated pyridine on ZrO2.^[20] Indicated by vibrational band





Figure 3. a) HRTEM-EDX elemental mapping study of the Pd/ YSZ@mSiO₂ sample, and b) HRTEM image of the Pd/YSZ sample at high magnification. Parts of lattice fringes are circled in yellow.

at 1545 cm⁻¹ typical for pyridinium ions bonded to Brønsted sites,^[20] furthermore, Brønsted acid sites also exist in the same YSZ@*m*SiO₂. All the above data confirm that both Lewis and Brønsted acid sites of the YSZ inside the silica shell remain accessible by pyridine molecules. When temperature is raised from room temperature to 300 °C, it is observed that two peaks (1446 and 1490 cm⁻¹) assigned to the adsorption on Lewis acid sites decrease significantly, but other two peaks (1545 and 1598 cm⁻¹) basically remain their original intensity. All these peak changes, including a blue shift observed for the original







Figure 4. DIRFTS-IR pyridine adsorption data for the YSZ@*m*SiO₂ sample of varying temperatures. L denotes Lewis acid sites and B denotes Brønsted acid sites. Pyridine IR data are from NIST Chemistry WebBook (https://webbook.nist.gov/cgi/cbook.cgi?ID=C110861&Type=IR-SPEC&Index=2).

1598 cm⁻¹ peak, suggest some desorption of pyridinium ions and/or alternation of their adsorption configuration upon heating. Nevertheless, the DRIFTS study confirms the strength of acid sites in our samples.

Apart from the acidity probing, esterification of acetic acid and ethanol, which is a very common reaction catalyzed by acid catalysts, was employed as a model reaction to demonstrate the activity for the YSZ@mSiO2 as a solid superacid. Our YSZ@mSiO₂ exhibits much higher rate of the esterification of acetic acid than bulk nonporous YSZ. Since catalytic activity of the $mSiO_2$ shell can be neglected compared to the YSZ phase (Figure S7, Supporting Information), performance of the YSZ@mSiO₂ was calculated based on the mass of YSZ instead of YSZ@mSiO2 in which the YSZ component accounts for 40.4 wt% (see the Experimental Section in the Supporting Information). It is revealed that the catalytic performance of our YSZ achieves a reaction rate of 1.80 mmol g⁻¹ min⁻¹, surpassing the best conventional solid acid catalysts and other catalysts reported in literature.^[2,21] As shown in Figure S7 (Supporting Information), the reaction rate was higher than that of sulfated mesoporous niobium oxide,^[2] 2 times that of Amberlyst-15, and 6 times that of bulk nonporous YSZ with the same yttrium oxide weight percentage. Besides, the content of yttrium and thus its weight percentage could be adjusted in our YSZ samples. Esterification reaction and related XRD characterization were conducted using these samples (Figures S8 and S9, Supporting Information). In addition to this, our YSZ@mSiO₂ also shows high activity for Friedel-Crafts alkylation, more specifically benzylation of toluene, which is another common reaction catalyzed by acid catalysts.^[22] The observed high activity of our YSZ is again attributed to the presence of much higher acid site density in its micro/mesoporous texture. On the contrary, the relatively low reaction rate of UiO-66 is probably the result of both low oxozirconium clusters density compared with the YSZ and higher diffusing barrier for mass transfer due to lacking mesoporosity.

2.3. CO₂ Hydrogenation

The global warming has been a big challenge raising concern widely and CO₂, one of main green gases causing issue above, can be reduced to produce CO as a fuel or a synthetic feedstock by using many catalysts.^[12a] In this regard, supported Pt catalysts have been widely investigated to realize CO₂ reforming to syngas. It has been well known that the catalytic activity is largely determined by the accessibility of Pt catalysts on the support interface. In particular, the importance of support has been be elucidated by the low activity of Pt black and Pt/SiO₂ catalyst, because of lacking the ability to form carbonates on the support.^[23] In this part of study, we will use the above prepared YSZ@mSiO₂, in combination with Pt NPs, to demonstrate realizations of high conversion of CO₂ and high selectivity over CO.

As can be seen from Figure 5a, the main product for CO_2 hydrogenation is CO with a small amount of CH_4 using Pt as an active catalytic component. The selectivity of CO for the Pt/ YSZ@*m*SiO₂ dropped slightly from 100% to 96.2% when temperature was increased from 200 to 400 °C. Meanwhile, the conversion of CO₂ increased significantly and finally reached 26.5%, which gave a yield of 25.5% for the desired product CO. Therefore, the catalyst activity for CO₂ hydrogenation to CO increases with temperature, which is also supported by the increasingly high intensity for some intermediates formed in the CO₂ hydrogenation process (Figure S10, Supporting Information).

The reaction mechanism for CO_2 hydrogenation was further explored using the same in situ DRIFTS-IR technique (**Figure 6**). In this measurement, H₂, CO₂, and N₂ were used, either respectively or in combination, as purging (as well as adsorbing) gases for the catalyst in a deliberated sequence. For example, on the basis of IR peak changes (i.e., appearance, disappearance, and/or persistence) of certain reaction species, the hydrogenation mechanism of CO₂ can be investigated and deduced.

First, the catalyst was reduced with H₂ in the cell at 200 °C for 3 h, after which the catalyst was purged with N₂ for 10 min. In stage 1 of reaction, the temperature was raised to 400 °C and the catalyst was purged with CO₂. After this CO₂ purging, IR peaks of gases CO₂ (2350 cm⁻¹), O-C-O stretching of carboxylates (1281 cm⁻¹) and bicarbonates (1224 cm⁻¹) were observed.^[24] In particular, two peaks indicating the presence of adsorbed CO appear at 2175 and 2118 cm⁻¹, respectively,^[25] which was probably produced from the reaction between adsorbed hydrogen and carbonate and bicarbonate species. It was further confirmed that no such CO peaks appeared when catalysts were placed in air for a few days to remove the hydrogen adsorbed. In stage 2, the input of CO₂ flow was ceased and instead purging gas N₂ was then introduced. It can be found that IR peaks for gases CO₂, carbonates and bicarbonates are weakened significantly, revealing that most reaction intermediates were purged away; the CO peaks totally disappeared also in this stage. In stage 3, the N₂ stream was shut down and a mixture of H₂ and CO₂ was sent to the cell at a molar ratio of 3:1. Interestingly, IR peaks of formate species appear at 1395 and 1374 cm⁻¹ at this stage though with a very weak intensity.^[26] Nevertheless, this observation is consistent with our result that CH4 accounted for less than 8% of final product (Figure 5). Two CO peaks at 2175 and

www.advancedsciencenews.com

DVANCED



Figure 5. a) The conversion of CO_2 and the selectivity of CO for the Pt/YSZ@*m*SiO₂ catalyst (red lines) and the Pt/ZrO₂@*m*SiO₂ catalyst (blue line), and b) working stability tests of the Pt/YSZ@*m*SiO₂ catalyst: conversion of CO₂ (blue line) and selectivity of CO (red line).

2118 cm⁻¹ were again observed with stronger intensity than those of stage 1, confirming CO as a main product from CO₂ hydrogenation. It should be mentioned that when both CO₂ and H₂ were introduced (stage 3), IR peak of CH₄ at 3016 cm⁻¹ (Figure 6a) became observable. The phenomenon observed on DRIFTS is also consistent with our previous study that the formate is an intermediate in the reaction path for CH₄ formation and carbonate and bicarbonate species are responsible for the production of CO.^[12a]

The presence of Pt metal as well as its chemical states in the above catalyst (Pt/YSZ@mSiO₂) was also investigated



with X-ray photoelectron spectroscopy (XPS) after etching of mesoporous silica shell (Figure S11, Supporting Information). Our XPS spectra indicate that there existed mixed valent states of Pt metal. The peak deconvolution was conducted based on reported binding energies of $4f_{7/2}$ electron for Pt⁰, Pt²⁺, and Pt⁴⁺ as 71.6, 72.7, and 74.2 eV, respectively.^[27] The surface species of Pt in the Pt/YSZ were made up from Pt⁰ (68.6%), Pt²⁺ (19.5%), and Pt⁴⁺ (11.9%). However, one should note that the highly oxidized Pt species were resulted from ambient oxidation of laboratory air when handling the sample. Under our actual reaction conditions (i.e., CO₂ with H₂), such high oxidation state Pt species are unlikely present.

Existence of yttrium in ZrO₂ phase was also proven to be essential to improve the selectivity and conversion of CO2 hydrogenation. Contrast experiments were thus conducted to compare the conversion and selectivity of the Pt/YSZ@ mSiO2 and Pt/ $ZrO_2@mSiO_2$. As can be seen in Figure 5a, at lower temperatures, the difference between these two catalysts is not pronounced due to their low activity. However, at higher temperatures, the Pt/YSZ@mSiO₂ demonstrates both better conversion of CO₂ and selectivity of CO over CH4 with the addition of yttrium. With the addition of yttria, zirconia could be stabilized into the tetragonal phase which usually only exists above 1173 °C by incorporating an trivalent vttrium into the structure; and this tetragonal (and/or cubic, Figure 1e) polymorph has an enhanced ionic conductivity than the ambient temperature monoclinic form.^[28] It is postulated that addition of yttrium enhanced electronic interactions in catalyst and thus improved the catalyst activity. Furthermore, the slightly increased specific surface area due to lattice incorporation of yttrium may be counted as another factor responsible for its better performance.

The Pt/YSZ@mSiO₂ has been demonstrated to be very stable by extending reaction time at 400 °C for 30 h (Figure 5b). As

is shown in Figure 5b, the selectivity of CO was measured as 93.5% on average with a small variation below 0.2%. The conversion rate of CO₂ basically remains the same over the reaction period of 30 h with an average conversion of 30.8 with a variation below 0.5%. It shows that the Pt/YSZ@*m*SiO₂ performance toward CO₂ hydrogenation remain stable at a temperature as high as 400 °C. Furthermore, the morphology and crystallographic phase remain unchanged after the reaction, which is confirmed by both TEM and XRD characterizations (Figure S12, Supporting Information), demonstrating the effective protection provided by this reactor configuration





Figure 6. a) DRIFT-IR spectra collected at 400 °C as a function of process time: red/orange lines, yellow/green lines, and light-blue/blue lines show the spectral results when CO₂ (stage 1, 30 mL min⁻¹), N₂ (stage 2, 30 mL min⁻¹), and CO₂/H₂ (stage 3, CO₂ at 20 mL min⁻¹ and H₂ at 60 mL min⁻¹) were passing through the cell, respectively, and b) three representative DRIFT-IR spectra selected from each purging stage. Peak values in wavenumber indicated in (b) were highly repeatable in eight consecutive runs, including those with a very small peak intensity.

to stabilize catalytic Pt. CO_2 hydrogenation for Pt loaded commercial YSZ with same Pt content was also conducted as reference of which performance is similar to our catalyst (see Figure S13, Supporting Information). Similarly, nanoscale Ru was loaded to the YSZ@*m*SiO₂ using the same synthetic method as that used in the Pt/YSZ@*m*SiO₂ and the resultant Ru/YSZ@*m*SiO₂ also performed well in CO₂ hydrogenation but with a high selectivity for CH₄ (Figure S14, Supporting Information) instead of CO.



2.4. Cascade Reaction

The acidity from the YSZ phase and catalytic activity toward different reactions from a variety of loaded active metals enable our reactor-like M/YSZ@ mSiO2 to serve as a multifunctional catalyst for a plenty of reactions. To demonstrate its capacity as a general platform for catalysis, a one-pot multistep conversion of nitroarene to valueadded secondary arylamine, which is widely used for fungicides, drugs and pesticides,^[29] has also been explored over our Pd/ YSZ@mSiO2 catalyst. As can be seen from Table 1, the entire tandem reaction can be divided into 3 steps. The first step (formation of D) and third step (formation of F) are hydrogenations catalyzed by palladium and the second step is dehydration reaction to form Schiff base (E) catalyzed by acid catalysts. In this work, Pd was also loaded into the YSZ@mSiO2 nanoreactor to carry out this one-pot cascade transformation of benzaldehyde (A) and nitrobenzene (B) to their final products (C, E, and F; Table 1). Indeed, the Pd/YSZ@mSiO2 catalyst shows superior performance for this reaction. Under merely ordinary pressure, the 200 °C reduced catalyst showed a high conversion of reactant A (87%) and meanwhile realized a very high selectivity of 80% toward the desired final product F, achieving a higher yield than an industrial catalyst and a bifunctional catalyst at 2 atm reported in literature.^[29] Apart from the easiness of mass transport in the micro/ mesoporous Pt/YSZ, the presence of central cavity of the Pd/YSZ@mSiO2 nanoreactor may be able to create a centration gradient between the liquid phase within the reactor and the liquid phase outside the reactor. Due to the holding capacity of the central space,^[30] for example, it is expected the concentration of intermediate product E inside the reactor must be higher than that outside the reactor, thus expediting the conversion of E to F. The 300 °C reduced Pd/YSZ@mSiO2 also demonstrated a slightly worse but still better yield than aforementioned contrasts (entries 1 and 2), which is probably due to resulted larger nanoparticles formed in the reducing

process. In a catalyst stability test, the Pd/YSZ@*m*SiO₂ was recycled for 3 times and no obvious activity deterioration was observed (Figure S15, Supporting Information). Also, no morphological degradation of the spent catalyst was found with our TEM examination (Figure S16, Supporting Information).

In comparison, as reported in **Figure 7**, a similar catalytic nanostructure, YSZ@Pd@*m*SiO₂, was synthesized using NH₂-functionalized UiO-66 as a core precursor. First, NH₂-UiO-66 nanocrystals were synthesized based on a previously reported



www.advancedsciencenews.com

DVANCED

 Table 1. Cascade reaction of nitrobenzene and benzaldehyde to N-benzylaniline.



Entry	Catalyst	Pressure	Conversion of A [%]	Selectivity [%]		
			-	F	E	С
1	Pd@MIL-101 ^[29]	2 bar	100	56	1	43
2	Pd@Al ₂ O ₃ ^[29]	2 bar	67	53	20	27
3	Pd/YSZ@ <i>m</i> SiO ₂ (200 °C)	1 atm	87	80	7	13
4	Pd/YSZ@ <i>m</i> SiO ₂ (300 °C)	1 atm	98	64	3	33
5	YSZ@Pd@ <i>m</i> SiO ₂	1 atm	66	80	7	13
6	Pd/bulk YSZ	1 atm	<1	0	<1	0

Notes: For entries 1 and 2,^[29] the catalytic reaction was performed in a 10 mL Teflon-lined stainless-steel autoclave equipped with pressure gauge and a magnetic stirrer. A 20 mg portion of dried catalyst was dispersed in 4 mL of ethanol containing 1 mmol of nitrobenzene and 1 mmol benzaldehyde. The vessel was purged with H₂ 10 times and pressurized to 2 bar for the reaction under room temperature. For entries 3–5, same amount of reactants and catalyst were used and the reaction was conducted in round bottle flask with stirrer which is purged with H₂ and connected to a balloon full of H₂. The catalyst Pd/YSZ@*m*SiO₂ (200 °C) and Pd/YSZ@*m*SiO₂ (300 °C) were reduced in H₂ at 200 and 300 °C respectively. The Pd content for all the entries were =1 wt%. Conversion of A was analyzed by GC.

method with minor modification (see the Experimental Section in the Supporting Information).^[31] Then Pd NPs were anchored on the surface of NH₂-UiO-66 nanocrystals utilizing affinity of $-NH_2$ groups (from the organic linker) to Pd (Figure 7a). After the encapsulation of mesoporous silica shell (Figure 7b), calcination was conducted, followed by the impregnation of yttrium (see the Experimental Section in the Supporting Information). In the YSZ@Pd@mSiO₂ produced from this process (Figure 7c), however, the Pd NPs were not distributed inside the micro/ mesopores of YSZ and thus there is no size confinement for Pd NPs, which leads to metal sintering after calcination and further metal agglomeration after the cascade reaction (Figure 7d). Because of the process and structural disadvantages in this catalyst, both stability and activity of the YSZ@Pd@*m*SiO₂ are low, as indicated by the TEM study of Figure 7d and its low conversion rate (66% conversion of A) in entry 5 of Table 1.

3. Conclusion

In summary, using shape-controlled UiO-66 as a solid precursor, we have synthesized a highly porous YSZ phase encapsulated inside a mesoporous silica shell, obtaining a reactor-like

configuration. This synthetic strategy endows the resultant solid superacid catalyst with high specific surface area and hierarchical porosity, which provides rich accessible Lewis acid and Brønsted acid sites and easy mass transports for many chemical reactions. For example, our YSZ@mSiO₂ can actively catalyze the esterification of acetic acid and ethanol and Friedel-Crafts alkylation reactions. Furthermore, ultrafine metal NPs can be homogenously distributed in the YSZ phase and the synergistic effect can be built between the catalytic metals and YSZ support. By loading various metals, furthermore, a great number of reactions can be conducted in our M/YSZ@mSiO2. With the loading of Pt, for instance, hydrogenation of CO₂ can be realized with high conversion and high selectivity of CO. On the other hand, replacing Pt with Ru for the same CO₂ hydrogenation leads to the high selectivity of CH4. After loaded with Pd, a one-pot three-step tandem reaction for direct conversion of nitrobenzene and benzaldehyde to N-benzalaniline exhibits remarkable catalyst activity and selectivity to the targeted product; this process can be viewed as a greener approach, as it significantly simplifies operational requirements. Our M/YSZ@mSiO2 have also demonstrated high working stability because of formation of stable YSZ and space confinement of mSiO₂ shell which prevents metal catalysts from sintering. Their workability in harsh reaction environments such as at temperatures up to 700 °C and extreme pH values of 0-13 will allow this class of reactor-

like catalysts to meet future challenges in development of new catalyst technology in the field of sustainable heterogeneous catalysis.

4. Experimental Section

Materials: Zirconium chloride (Merck, 98%), terephthalic acid (H₂BDC, Aldrich), acetic acid (Merck, 99.8%), sodium hydroxide (Merck, 99%), dimethylformamide (DMF, VWR Chemicals, 99.90%), 2-methylimidazole (2-MeIM, Aldrich, 99%), CTAC (Sigma, 25 wt%), tetraethyl orthosilicate (TEOS, Aldrich, \geq 99.0%), yttrium (III) nitrate hydrate (STREM Chemicals, 99.9%), ethylenediamine (EDA, Alfa Aesar, 99%), palladium chloride (PdCl₂, Aldrich, 99.9%), ruthenium chloride (Aldrich, 99.98%), zirconium oxide (Dupont), ammonia solution (Merck, 25%), nitrobenzene (TCI, 99.5%), benzaldehyde (Sigma-Aldrich, 99.5%), hexadecane (Sigma-Aldrich, 99%), pyridine (Sigma, 99.8%), methanol (VWR Chemicals, analytical reagent grade). Deionized water was used for all experiments.

Synthesis of SiO₂ Spheres: The SiO₂ spheres were synthesized by a reported method with modification.^[28] Briefly, 3 mL of tetraethyl orthosilicate was dissolved in a mixture of 6 mL of water and 40 mL of ethanol, followed by the addition of 1 mL of 32 wt% ammonia solution and 6 h of stirring at ambient temperature. The SiO₂ spheres were





Figure 7. TEM images of a) the NH_2 -UiO-66@Pd, b) the NH_2 -UiO-66@Pd@mSiO₂, c) the YSZ@Pd@mSiO₂, and d) the YSZ@Pd@mSiO₂ after the cascade reaction.

separated by centrifugation and washed with 1:1 ethanol/ water solution. The product was then dispersed in deionized water at a concentration of 1 mol L^{-1} .

Synthesis of UiO-66: The UiO-66 nanocrystals were synthesized by a reported method with some minor modification.^[32] Briefly, 133.7 mg of zirconium chloride and 100 mg of terephthalic acid were dissolved in 40 mL of DMF in a 100 mL glass flask and then 3 mL of acetic acid was added. The mixture was sonicated for 5 min and then heated in oil bath at 130 °C for 24 h. The nanocrystal product was separated by centrifugation and washed with methanol for three times.

Synthesis of UiO-66@mSiO₂: 100 mg of the above prepared UiO-66 nanocrystals was dispersed in 60 mL of deionized water with 5 min sonication. Then 50 mL of 10 g L⁻¹ 2-MeIM methanolic solution was mixed with the turbid UiO-66 nanocrystal suspension and stirred for 5 min, after which, 1.1 mL of CTAC solution (25 wt%) was added and stirred for another 5 min. Finally, 0.6 mL of TEOS (99%) was added dropwise in 5 min and the mixture was further stirred for 3 h.

Introduction of yttrium to UiO-66@mSiO₂: 580 mg of yttrium (III) nitrate hydrate and 182.1 mg of EDA were dissolved in 100 mL of ethanol to produce an yttrium nitrate suspension. In this impregnation process, 25 mg of UiO-66@mSiO₂ was placed in an alumina crucible and then 150 μ L of the above yttrium-nitrate-EDA-ethanol suspension was added slowly to submerge all the powder. Then the crucible was dried in an electrical oven at 60 °C for 3 h.

Synthesis of $YSZ@mSiO_2$: The above UiO-66@mSiO₂ core-shell precursor after the yttrium impregnation was heated inside an electric furnace with a ramping rate of 10 °C min⁻¹, calcined at 700 °C for 2 h, and then cooled down to room temperature naturally.

Synthesis of $ZrO_2@mSiO_2$: Similar core-shell structure of pure porous ZrO_2 encapsulated inside the $mSiO_2$ shell (namely, the $ZrO_2@mSiO_2$) was produced through direct calcination of the UiO-66@mSiO₂ sample



www.afm-journal.de

without adding yttrium. The calcination procedure was the same as that in the synthesis of the YSZ@ $mSiO_2$ catalyst system.

Synthesis of Micro/Mesoporous YSZ: Single-phase micro/mesoporous YSZ powder was produced by removing the $mSiO_2$ shell from the YSZ@ $mSiO_2$ with NaOH that served as an etchant. Typically, 50 mg of YSZ@ $mSiO_2$ was added to 10 mL of 1.0 M NaOH aqueous solution. The mixture was stirred under room temperature for 24 h to ensure full etching of mesoporous silica shell.

Synthesis of *M*/YSZ@mSiO₂: 200 µL of 20×10^{-3} m metal precursor (e.g., PdCl₂, RuCl₂, and K₂PtCl₄) aqueous solution was added to 100 mg of YSZ@mSiO₂ in an alumina crucible. Then the crucible was placed in 60 °C oven for 1 h for drying and then calcined in air at 350 °C for 2 h with a ramping rate of 2 °C min⁻¹. Note that the catalytic NPs of metals in the nanoreactors could be reduced to their metallic state in H₂ at 200–300 °C for 2 h with a ramping rate of 2 °C min⁻¹.

Synthesis of $Pt/ZrO_2@mSiO_2$: Preparation procedure of the $Pt/ZrO_2@mSiO_2$ catalyst was the same as the above, except for using the $ZrO_2@mSiO_2$ as a catalyst carrier.

Pyridine Adsorption: The Lewis and Brønsted acid sites were investigated using pyridine as a probe molecule. The YSZ@mSiO₂ was first placed under dynamic vacuum (=8 Torr) at 200 °C for 3 h to remove adsorbed molecules on surface. After cooling down to room temperature, excessive pyridine was evaporated to process the sample and the sample was placed back to static vacuum at room temperature for 1 h. Pyridine adsorption was analyzed by in situ DRIFT-IR spectroscopy. The cell containing sample was purged with nitrogen before measurement and heated to 200 °C to ensure no secondary contamination.

Esterification: Typically, 0.05 mole of acetic acid, 0.5 mole of ethanol, and 0.005 mole of hexadecane (an internal standard) were mixed and 50 mg of catalysts were added to the mixture solution, respectively. Esterification reaction was held in a glass flask inside an oil bath heated at 70 °C for 2 h. Samples of the reaction mixture were periodically withdrawn from the flask and analyzed using gas chromatography (GC; Agilent-7890A, coupled with a flame ion detector (FID) and an HP-5 column; the temperature was programmed from 70 to 280 °C).

Friedel-Crafts Alkylation: Benzylation of toluene using the YSZ@*m*SiO₂ catalyst was conducted with a 100 mL three-neck round-bottom glass flask which was mounted with a reflux condenser. Benzyl alcohol (5.0 mL), toluene (50.0 mL), and hexadecane (0.5 mL, as an internal standard) were added to the flask reactor with the YSZ@*m*SiO₂ catalyst (0.50 g) in each test run. Nitrogen was introduced to the reactor through one of the glass necks. The second glass neck was equipped with a septum for sample removal. The reaction mixture was heated to 130 °C in an oil bath for a desired period of time. Samples of the reaction mixture were periodically withdrawn from the flask and analyzed using the same GC system as above.

 CO_2 Hydrogenation: To start with, the Pt/YSZ@mSiO₂ catalyst was reduced at 200 °C in a tube-furnace for 3 h with a ramping rate of 3 °C min⁻¹ under a constant flow of H₂ gas at 50 mL min⁻¹ and 1 atm. After cooling down to room temperature, 170 mg of the reduced catalyst was loaded immediately into a fixed bed reactor (3/8 stainless steel tube). Hydrogenation of CO_2 was then carried out in continuous mode with a mixed gas stream ($CO_2/H_2/N_2 = 24\%/72\%/4\%$; N₂ was used as an internal standard). The gas feed was monitored by a Brooks mass-flow controller, and reaction temperature was gauged with a thermocouple pointed at the center of the catalyst bed. The pressure was controlled by a backpressure regulator. Concentrations of reactants and products were measured online by a GC system (Agilent-7890A,



equipped with both FID and thermal conductivity detector (TCD)). Unless otherwise specified, all reaction data were measured at steady state, e.g., after 30 min to 60 min on stream.

Cascade Reaction: The catalytic reaction was performed in a 50 mL glass flask. Briefly, a 20 mg portion of dried Pd/YSZ@*m*SiO₂ was dispersed in 10 mL of ethanol containing 1.0 mmol of nitrobenzene and 1.0 mmol of benzaldehyde, and the solution was sonicated in order to achieve homogenous mixing. The glass vessel was purged first with a flowing H₂ for 3 min, and then connected to a hydrogen balloon under normal atmospheric pressure. The reaction was conducted at room temperature (25 °C) with nitrobenzene and benzaldehyde as substrates. After the reaction, the catalyst was separated by centrifugation, thoroughly washed with ethanol, and then reutilized as catalyst in subsequent runs under identical reaction conditions. The yield of the product was analyzed by the same GC system (Agilent-7890A) with dodecane as an internal standard for analytical calibration.

Materials Characterization: Morphologies of sample were characterized by TEM (JEM-2010), field emission scanning electron microscopy (FESEM, JSM-6700F), and HRTEM (JEM-2100F). Crystallographic information was analyzed by XRD (Bruker D8 Advance) equipped with a Cu K_{α} radiation source. Elemental mapping examination was done by EDX (Oxford Instruments, model-7426). Specific surface area, differential pore volume and pore size distribution of samples were determined using N₂ physisorption isotherms at 77 K. Metal loading in the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 7300DV, Perkin Elmer). Surface compositions of samples were analyzed by XPS (AXIS-HSi, Kratos Analytical). In situ IR spectra were collected on a Bruker TENSOR II spectrometer equipped with a DRIFT accessory and a cell (Harrick). Each spectrum was recorded at 4 cm⁻¹ resolution and related spectral data were based on the average of 64 scans. For consecutive runs, each set of data was collected every min automatically. TGA was conducted with a scanning rate of 6 °C min⁻¹ in air (TGA-2050, TA Instruments).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

R.Q. would like to thank the National University of Singapore for providing his postgraduate scholarship. The authors gratefully acknowledge the financial support provided by the Ministry of Education, Singapore, and National University of Singapore. This project was also partially funded by the National Research Foundation (NRF), Prime Minister's Office, Singapore, under its Campus for Research Excellence and Technological Enterprise (CREATE) program.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

cascade reaction, CO_2 hydrogenation, metal-organic frameworks, micro/ mesoporous metal oxide, nanoreactor, yttria-stabilized zirconia

Received: April 24, 2019 Revised: June 11, 2019 Published online:



www.afm-journal.de

- a) G. A. Olah, Angew. Chem., Int. Ed. Engl. 1995, 34, 1393;
 b) Z. Wang, Y. Jiang, O. Lafon, J. Trébosc, K. Duk Kim, C. Stampfl, A. Baiker, J.-P. Amoureux, J. Huang, Nat. Chem. 2016, 7, 13820;
 c) J. Engelhardt, W. K. Hall, J. Catal. 1995, 151, 1; d) W. Hua, A. Sassi, A. Goeppert, F. Taulelle, C. Lorentz, J. Sommer, J. Catal. 2001, 204, 460.
- [2] C. C. Li, J. Dou, L. Chen, J. Lin, H. C. Zeng, ChemCatChem 2012, 4, 1675.
- [3] K. Shen, L. Zhang, X. Chen, L. Liu, D. Zhang, Y. Han, J. Chen, J. Long, R. Luque, Y. Li, B. Chen, *Science* **2018**, *359*, 206.
- [4] L.-Q. Lu, J.-R. Chen, W.-J. Xiao, Acc. Chem. Res. 2012, 45, 1278.
- [5] J. Liu, Q. Ji, T. Imai, K. Ariga, H. Abe, Sci. Rep. 2017, 7, 41773.
- [6] a) J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* 2009, *38*, 1477;
 b) G. Lu, J. T. Hupp, *J. Am. Chem. Soc.* 2010, *132*, 7832; c) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* 2009, *38*, 1450; d) P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.-S. Chang, Y. K. Hwang, V. Marsaud, P.-N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur, R. Gref, *Nat. Mater.* 2010, *9*, 172.
- [7] a) J. Jiang, O. M. Yaghi, *Chem. Rev.* 2015, *115*, 6966; b) B. Chen,
 M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O'Keeffe, O. M. Yaghi,
 J. Am. Chem. Soc. 2000, *122*, 11559.
- [8] J. Jiang, F. Gándara, Y.-B. Zhang, K. Na, O. M. Yaghi, W. G. Klemperer, J. Am. Chem. Soc. 2014, 136, 12844.
- [9] a) B. Liu, H. Shioyama, T. Akita, Q. Xu, J. Am. Chem. Soc. 2008, 130, 5390; b) X. Xu, R. Cao, S. Jeong, J. Cho, Nano Lett. 2012, 12, 4988; c) Z. Li, Y. Fang, J. Zhang, X. W. Lou, Adv. Mater. 2018, 30, 1800525.
- [10] a) Z. Wang, S. M. Cohen, Chem. Soc. Rev. 2009, 38, 1315;
 b) Y. Meng, G.-H. Wang, S. Bernt, N. Stock, A.-H. Lu, Chem. Commun. 2011, 47, 10479.
- [11] Z. Yue, S. Liu, Y. Liu, RSC Adv. 2015, 5, 10619.
- [12] a) J. Dou, Y. Sheng, C. Choong, L. Chen, H. C. Zeng, *Appl. Catal.*, B **2017**, 219, 580; b) G. Zhan, H. C. Zeng, ACS Catal. **2017**, 7, 7509.
- [13] a) B. Liu, R. T. Baker, J. Mater. Chem. 2008, 18, 5200; b) P. Yang,
 D. Zhao, D. I. Margolese, B. F. Chmelka, G. D. Stucky, Nature 1998, 396, 152.
- [14] W. Green ChemistryCao, W. Luo, H. Ge, Y. Su, A. Wang, T. Zhang, Green Chem. 2017, 19, 2201.
- [15] a) I. M. Hung, D.-T. Hung, K.-Z. Fung, M.-H. Hon, J. Eur. Ceram. Soc. 2006, 26, 2627; b) G. A. Ozin, M. Mamak, N. A. Coombs, Google Patents, US, 2002; c) D.-K. Seo, D. Ladd, A. Volosin, Google Patents, US, 2013.
- [16] a) T. Götsch, W. Wallisch, M. Stöger-Pollach, B. Klötzer, S. Penner, *AIP Adv.* **2016**, *6*, 025119; b) X. Yan, N. Lu, B. Fan, J. Bao, D. Pan, M. Wang, R. Li, *CrystEngComm* **2015**, *17*, 6426.
- [17] a) H. Kan, H. Lee, *Appl. Catal., B* 2010, *97*, 108; b) X. Huang,
 R. Reimert, *Fuel* 2013, *106*, 380; c) A. Toghan, L. M. Rösken,
 R. Imbihl, *ChemPhysChem* 2010, *11*, 1452.
- [18] a) M. I. Zaki, M. A. Hasan, F. A. Al-Sagheer, L. Pasupulety, *Colloids Surf., A* **2001**, *190*, 261; b) C. D. Malonzo, S. M. Shaker, L. Ren, S. D. Prinslow, A. E. Platero-Prats, L. C. Gallington, J. Borycz, A. B. Thompson, T. C. Wang, O. K. Farha, J. T. Hupp, C. C. Lu, K. W. Chapman, J. C. Myers, R. L. Penn, L. Gagliardi, M. Tsapatsis, A. Stein, J. Am. Chem. Soc. **2016**, *138*, 2739.
- [19] C. H. Kline, J. Turkevich, J. Chem. Phys. 1944, 12, 300.
- [20] S. A. Bagshaw, R. P. Cooney, Chem. Mater. 1993, 5, 1101.
- [21] C. Tagusagawa, A. Takagaki, A. Iguchi, K. Takanabe, J. N. Kondo, K. Ebitani, S. Hayashi, T. Tatsumi, K. Domen, *Angew. Chem., Int. Ed.* 2010, 49, 1128.
- [22] a) J. Dou, H. C. Zeng, J. Am. Chem. Soc. 2012, 134, 16235; b) J. Dou,
 H. C. Zeng, J. Phys. Chem. C 2012, 116, 7767.
- [23] J. H. Bitter, K. Seshan, J. A. Lercher, J. Catal. 1997, 171, 279.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com



- [24] A. Vimont, J. C. Lavalley, A. Sahibed-Dine, C. Otero Areán, M. Rodríguez Delgado, M. Daturi, J. Phys. Chem. B 2005, 109, 9656.
- [25] P. Panagiotopoulou, D. I. Kondarides, X. E. Verykios, J. Phys. Chem. C 2011, 115, 1220.
- [26] A. Erdöhelyi, M. Pásztor, F. Solymosi, J. Catal. 1986, 98, 166.
- [27] K.-P. Yu, W.-Y. Yu, M.-C. Kuo, Y.-C. Liou, S.-H. Chien, Appl. Catal., B 2008, 84, 112.
- [28] G. J. Callon, D. M. Goldie, M. F. Dibb, J. A. Cairns, J. Paton, J. Mater. Sci. Lett. 2000, 19, 1689.
- [29] Y.-Z. Chen, Y.-X. Zhou, H. Wang, J. Lu, T. Uchida, Q. Xu, S.-H. Yu, H.-L. Jiang, ACS Catal. 2015, 5, 2062.
- [30] G. Zhan, H. C. Zeng, Chem. Mater. 2015, 27, 726.
- [31] L. Shen, W. Wu, R. Liang, R. Lin, L. Wu, Nanoscale 2013, 5, 9374.
- [32] M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp, O. K. Farha, *Chem. Commun.* **2013**, *49*, 9449.