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COMMUNICATION

CeO₂ nanorods anchored on mesoporous carbon as an efficient

catalyst for imine synthesis

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CeO₂ nanorods anchored on mesoporous carbon exhibit high activity and stability in aerobic oxidative coupling of alcohol and amine to imine. The abundant surface Ce3+ and the suitable interaction between CeO₂ nanorods and carbon support should be responsible for the excellent catalytic behaviors.

Ceria (CeO₂) is an interesting metal oxide that has wide applications in fields such as catalysis, electrochemistry and optics.¹⁻⁵ In heterogeneous catalysis, materials based on CeO₂ have been practically used in the production and purification of hydrogen, and the purification of exhaust gases in threeway automotive catalytic converters.⁶⁻¹⁰ CeO₂ can also be applied in catalyzing organic synthesis.¹¹⁻¹⁴ Recently, an interesting low temperature catalytic behavior of CeO₂ was reported in oxidative coupling imine synthesis.¹³ Imine is a kind of nitrogen sources containing a reactive C=N moiety, which is widely used in biological, agricultural and pharmaceutical synthetic processes.¹⁵⁻¹⁷ Aerobic oxidative coupling of alcohol and amine to imine is an environmentally friendly synthesis route, in which air is used as oxygen source and only water is produced as a by-product.¹⁸⁻²³ CeO₂ could catalyze this redox reaction even at 30 °C without using any inorganic or organic base as additives.¹³ The shortcoming is that the activity of current CeO₂ materials is relatively low and not satisfied for large-scale application.

Controlling size and morphology are regarded as efficient strategies to tune the catalytic performance of metal oxides. It usually brings some exceptional qualities, including high surface-to-bulk atomic ratio, altered surface energies, quantum confinement effects etc.²⁴⁻³⁰ These features could significantly influence the redox properties of metal oxides. Some successes have been achieved on the synthesis of CeO₂ with controllable particle size and morphology, and examples with enhancing redox catalytic activities were also reported.³¹⁻

However, the increase in surface energy with reduction in particle size and exposing special facet usually gives rise to aggregation and shape changes during a catalytic reaction,^{35, 36} which subsequently limit the recyclability of nanocrystal catalysts. Most of these nanocrystal catalysts were confined to fundamental researches. For practical application, much more efforts are still needed to develop nanocrystal catalysts with both high activity and high stability.

In this work, it was found CeO₂ nanorods anchored on mesoporous carbon (denoted as CeO₂/MC) exhibit excellent activity and stability in imine synthesis. The activity of CeO₂/MC is much higher not only than that of bulk CeO₂, but also than that of naked CeO₂ nanorod catalysts. It is interesting that the morphology of CeO₂ nanorods of CeO₂/MC could be maintained during the reaction process, and the activity of used CeO2/MC has no obvious change compared with that of fresh one, exhibiting a relatively high stability.

CeO₂/MC was prepared with a wet impregnation method followed by a fine thermal-treatment in argon condition (details see in supporting information). The loading amount of CeO₂ is 10 wt%. A kind of mesoporous carbon (MC) with pore size of 6.5 nm and surface area of 1392 $\text{m}^2{\cdot}\text{g}^{\text{-1}}$ was used as carbon support. This carbon material was prepared with a modified hard-template route, which was reported by our group previously.^{37, 38} Fig. 1 shows the SEM and TEM images of CeO₂/MC. It reveals that CeO₂ nanorods were with a diameter of 20-35 nm and a length within 200-400 nm. These CeO₂ nanorods are highly dispersed on the surface of carbon support. HRTEM image demonstrated that \mbox{CeO}_2 nanorods possess well crystallinity (Fig. 1d). From the Fourier transform (Fig. 1d inset) analysis, three kinds of lattice fringe directions attributed to (111), (002), and (220) were observed for the anchored CeO₂ nanorods. The interplanar spacing of 0.32 and

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[[]details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



Fig. 1 SEM (a, b), TEM (c) and HRTEM (d) images of CeO₂/MC catalyst.

0.28 nm was identified in the HRTEM image, which is corresponded to the lattice fringes of the (111) and (002) facets, respectively. This result is consistent with that of CeO_2 nanorods prepared by hydrothermal method,³⁹ indicating CeO_2/MC has similar exposed crystal facets with CeO_2 nanorods.

Fig. 2 shows the XRD patterns of CeO_2/MC , MC support, reference CeO_2 nanorods and bulk CeO_2 . As for CeO_2/MC , the broad peak centered at 24.5° and 44° can be assigned to the diffractions from (002) and (100) graphite planes of carbon support.⁴⁰ The small peaks at 28.5 and 47.5° could be assigned to the diffractions from (111) and (220) planes of CeO_2 .³⁶ As for reference samples of CeO_2 nanorods and bulk CeO_2 , five relatively sharp diffraction peaks at 20 value of 28.5, 33.1, 47.5, 56.3, and 59.1° can be observed, which match well with the diffractions from (111), (200), (220), (311) and (222) lattice planes of cubic phase CeO_2 (fluorite structure, JCPDS 34-0394).³² These results suggest that CeO_2 in all these samples possesses cubic structure.

Raman spectra showed that all these CeO₂ samples had a strong band at ~455 cm⁻¹ and a weak band at ~600 cm⁻¹. The band at ~455 cm⁻¹ is ascribed to the Raman-active vibrational mode $(F_{2\alpha})$ of the fluorite-type structure, while the band at ~600 cm⁻¹ demonstrates the intrinsic oxygen vacancies due to the existence of Ce^{3+} in CeO_2 .⁴¹ As for CeO_2/MC , the red shift of the later band to 645 cm⁻¹ should be due to the presence of interaction between CeO₂ nanorod and MC support. According to the literature, the ratio of the integral area of the two peaks, i.e. A_{600}/A_{455} , can be used to evaluate the difference of oxygen vacancies. $^{42,\,43}$ The value of A_{600}/A_{455} is 0.12, 0.05, and 0.03 for CeO₂/MC, CeO₂ nanorods and bulk CeO₂. This result suggests that CeO_2/MC possesses much more oxygen vacancies than other two samples. XPS measurement was also carried out to detect the chemical state of Ce on the surface CeO₂/MC, CeO₂ nanorods and bulk CeO₂. According to the literature,^{44, 45} eight peaks associated with the 3d electrons of Ce can be fitted, which corresponded to four pairs of spin-orbit doublets. Peaks marked as u/v, u''/v'' and u'''/v''' are assigned to the Ce⁴⁺ species, while peaks denoted as u'/v' are attributed to the Ce³⁺ species. Calculated from the integrated areas of the



Fig. 2 (A) XRD patterns and (B) Raman spectra of MC support, CeO_2/MC , CeO_2 nanorod and bulk CeO_2 catalysts. (C, D) Ce 3d and O 1s XPS spectra of CeO_2/MC , CeO_2 nanorod and bulk CeO_2 catalysts.

respective peaks, the fractions of the surface Ce^{3+} followed the trend of CeO_2/MC (0.48) > CeO_2 nanorods (0.13) > bulk CeO_2 (0.06). As for the O 1s spectra, the two peaks centered at 530.1 eV (peak I) and 531.9 eV (peak II) could be ascribed to "O²⁻" ions in lattices and surface -OH or oxygen vacancies. The new peak (peak III) at 533.5 eV for CeO_2/MC can be attributed to the oxygen groups remained on MC support. The area ratio of peak II/ peak I is 7.17 for CeO_2/MC , which is much higher than that of CeO_2 nanorods (0.76) and bulk CeO_2 (0.25).

Oxidative coupling of benzyl alcohol and aniline to imine was carried out to detect the catalytic performance of CeO_2/MC , naked CeO_2 nanorods and bulk CeO_2 . Fig. 3 shows that all these samples are active in the title reaction. The samples with nanorod morphology exhibit much higher activities than bulk one. The reactivity trend in this system follows $CeO_2/MC > CeO_2$ nanorods > bulk $CeO_2 > MC$. As for CeO_2/MC , a 99.2 % yield of imine was obtained after 2 h reaction at 80 °C. In addition, the catalytic performance of



Fig. 3 Time dependence of imine formation from oxidative coupling of benzyl alcohol and aniline over CeO₂/MC, CeO₂ nanorod, bulk CeO₂ and MC catalysts. Reaction conditions: benzyl alcohol (1 mmol), aniline (2 mmol), catalyst (0.3 g), solvent (toluene 10 mL), 80 °C, air (1 bar).

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CeO₂/MC at different temperature was also detected (Fig. S3). The yield of imine was 77.6% at 60 °C and 46.5% at 40 °C, respectively. This result is much higher than other non-noble metal catalysts and CeO₂ with other morphologies in the imine synthesis (Table S1 and Fig. S4). Based on the initial reaction rate, the apparent activation energy (*Ea*) of reaction over CeO₂/MC, CeO₂ nanorods and bulk CeO₂ was also calculated (Fig. S5). The *Ea* of CeO₂/MC is about 26.04 kJ·mol⁻¹, which is much lower than that of naked CeO₂ nanorods (57.89 kJ·mol⁻¹) and bulk CeO₂ (64.86 kJ·mol⁻¹).

In order to confirm the heterogeneous nature of the CeO2/MC catalyst, a hot filtration test was carried out. The result showed that no subsequent conversion of benzyl alcohol was detected in the filtrate, proving that CeO₂/MC is a really heterogeneous catalyst (Fig. S6). In addition, multiple aerobic oxidation cycles were also carried out to examine the recoverability of CeO_2/MC (Fig. 4A). After four cycles test, the catalyst still maintains a relatively high activity and no obvious changes can be observed. SEM measurement shows that CeO₂ still maintains the morphology of nanorod and highly dispersed on the surface of carbon support. No aggregation of CeO_2 species could be observed in the CeO_2/MC (Fig. 4B). All these results suggest that CeO_2 nanorod in the CeO_2/MC be stable during the reaction. This should be an impressive advantage of CeO₂/MC, since the aggregation of nanorod during a catalytic reaction even the preparation process is a major drawback limiting their application.

The general application of CeO₂/MC catalyst was also investigated. At least twelve kinds of imines could be obtained by oxidative coupling of different alcohols with amines. Table 1 shows that CeO₂/MC catalyst is active in the reactions using benzyl alcohol derivatives with either electron-rich- or electron-poor- substituent groups, and excellent imine yields were obtained especially for 4-chlorobenzyl alcohol (98 % imine yield after 2 h reaction) and p-methyl benzyl alcohol (96 % imine yield after 8 h reaction). Notably, CeO₂/MC catalyst also worked well in catalysing oxidative coupling of benzyl alcohol with substituted anilines, and obtained a high imine yields. In addition, aliphatic amines such as cyclohexane and nbutylamine can also reacted efficiently with benzyl alcohol to afford the desired imines in good yields. The above catalytic tests clearly show that CeO_2/MC is a robust catalyst in imine synthesis with oxidative coupling route.

Our previous work has shown that large amount of oxygencontaining functional groups (detected by Boehm titration) present on the surface of MC support, including carboxylic Table. 1 Oxidative coupling of alcohols and amines to imines over \mbox{CeO}_2/\mbox{MC} catalyst a



 $^{\rm a}$ Reaction conditions: alcohol (1 mmol), amine (2 mmol), catalyst (0.3 g), solvent (toluene 10 mL), 80 °C, air (1 atm). Numbers in parentheses are imine yield. $^{\rm b}$ Reaction time: 6 h.

 $(0.92 \text{ mmol}\cdot\text{g}^{-1})$, lactonic $(0.91 \text{ mmol}\cdot\text{g}^{-1})$, phenolic groups (1.40 mm)mmol·g⁻¹). These functional groups may serve as anchor sites for CeO₂ nanorod. In this work, ¹³C cross polarization (CP) magic angle spinning (MAS) NMR and ¹H MAS NMR experiments were used to confirm the fact that a variety of oxygen-containing functional groups are present on the surface of MC (Fig. S7). The ¹³C NMR spectrum of MC shows a major peak at 127 ppm with a shoulder at approx. 170 ppm, corresponding to sp^2 carbon in the bulk part of MC and -COOH/-COOR environments of MC, respectively. In addition, relatively weak signals at lower frequencies, i.e., 10~70 ppm can be observed. These peaks can be ascribed to the alkyl groups in the surface -COOR sites. The absence of the alkyl groups in the ¹³C NMR spectrum of CeO₂/MC (10-70 ppm) may indicate the reaction between carboxylic and ester sites of MC and rich hydroxyl groups of CeO2.46 Large amount of Ce3+ should form in this process due to the reduction behaviour of carbon support in the inert atmosphere. And this interaction between CeO₂ and MC is very important for the improvement of catalytic performance.

The Ce³⁺ species are tightly correlated with redox properties and then the catalytic performance of Ce-based catalysts. In our case, O₂-TPD showed an improvement of oxygen adsorption capacity over CeO₂/MC (Fig. S8). H₂-TPR reflects that CeO₂/MC possess a relatively high reduction temperature compared with that of CeO₂ nanorods and bulk

CeO₂ (Fig. S9). These results are all correlated well with the amount of Ce^{3+} over CeO_2/MC . It results in a high concentration of oxygen vacancies, which could significantly improve the catalytic performance for molecular O₂ activation and subsequent oxidation of benzyl alcohol, especially under the relatively low reaction temperature. The oxidation of benzyl alcohol to benzaldehyde is the rate-determining step for imine synthesis over metal oxides catalysts.¹³ The weak acid-base properties were also detected (Fig. S10 NH₃-TPD and CO2-TPD). The relatively large amount of surface weak acid sites on CeO₂/MC could facilitate the coupling of benzaldehyde and aniline.⁴⁷ Additionally, it can be imaged that the isolated state of CeO₂ nanorods on the surface of carbon support could make the facet of CeO₂ have more opportunity to contact with reagents. At the same time, the anchored CeO₂ nanorods have little opportunity to contact with each other, limiting the aggregation of these CeO₂ nanorods.

In summary, CeO_2 nanorods highly dispersed on the surface of mesoporous carbon have been obtained, and were highly efficient in aerobic oxidative coupling of alcohol and amine to imine. The presence of large amount of surface Ce^{3+} and the suitable interaction between CeO_2 nanorods and carbon support should be responsible for the high activity and stability in the reaction.

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