

CO₂ Reforming with Ethanol for Syngas Production over SiO₂-M@CeO₂ Catalysts (M: Cu, Ni): Impact of Active Metal

Ting Li⁺,^[a] Yuhao Tian⁺,^[a] Xiaoli Yan,^[a] and Weijie Cai^{*[a]}

It is of great significance to design the high-performance catalysts with good anti-sintering and coke-resistance properties which can efficiently convert undesirable greenhouse gas CO₂ with bio-ethanol into high value-added syngas. To be addressed this issue, a series of SiO₂-M@CeO₂ (M: Cu, Ni) catalysts with typical core@shell structure were prepared via a strong electrostatic adsorption technique. Interestingly, Ni-based catalyst exhibited the higher activity towards ethanol dry reforming at the relatively low temperature. Meanwhile, SiO₂-Ni@CeO₂ catalyst presented good stability after a 50 h tests

while a serious deactivation occurred for SiO₂-Cu@CeO₂ within 20 h reaction due to heavy carbon deposition and reactor blockage. Herein, the higher catalytic performance of SiO₂-Ni@CeO₂ catalyst compared to SiO₂-Cu@CeO₂ sample was attributed to the combination effect of its mesoporous structure, higher Ni dispersion as well as stronger Ni-Ce interaction as depicted by BET, TEM, XPS, H₂-TPR and XRD findings. This work might provide meaningful information to other reforming processes involving coke formation and active metal sintering problems.

Introduction

In the past decades, global warming mainly caused by the enormous discharge of the greenhouse gas CO₂, has attracted more and more attention.^[1] To solve this problem, great efforts have been devoted to the depletion of CO₂ including the physical capture and chemical utilization to minimize its harmful impacts.^[2] Among the developed techniques for the chemical conversion of CO₂, methane dry reforming (MDR, CH₄ + CO₂ → 2CO + 2H₂) and CO₂ reforming with ethanol (EDR, C₂H₆O + CO₂ → 3CO + 3 H₂) are regarded as the promising processes.^[3] Compared to MDR, EDR is more environmentally-friendly. More importantly, CO₂ reforming with ethanol could not only consume greenhouse gas CO₂ but select the renewable bio-ethanol as reactant instead of the conventional fossil fuel methane, which could conform to the green chemistry. In addition, EDR can produce syngas, which can be used as feedstock for the important Fischer-Tropsch (FT) synthesis.^[4] Indeed, ethanol reactants derived from the biomass such as corn or agriculture residues are more available and renewable in comparison with fossil fuel methane, thereby meeting with the sustainable development. However, several bottleneck problems such as the fast catalyst deactivation due to carbon deposition and/or the serious sintering of active metal still greatly retard the wide application of EDR reaction. Therefore, the research on the efficient catalysts that can resist carbon

deposition and active metal sintering is one of the research topics of EDR reaction.

Up to date, several authors have developed many kinds of catalysts based on precious or noble metals,^[5] which have presented the promising results. However, the high costs of these materials have led researchers to investigate other alternatives based on low-cost materials. Hence, numerous articles focused on transition metals together with ceria composites have been published, in which CeO₂ plays a fundamental role in redox reactions because of its specific property to release and storage oxygen.^[6] Typically, CeO₂, as support or dopant, could enhance oxygen mobility as well as forming surface and bulk vacancies, thereby improving the catalytic performance of the composite oxides. On the other hand, SiO₂ with low price and high availability has been widely selected as support to prepare the transition metal-based catalysts like Ni and Co. However, some drawbacks of transition metal catalysts like unsatisfactory catalytic activity and stability still need to be overcome.^[7]

It is accepted that catalyst nanoparticles are unstable at high reaction/calcinations temperature, in which the serious aggregation can easily occur, thus eliminating catalytic activity/stability. Herein, encapsulating nanoparticles with a stable shell layer can not only enhance the thermo-stability of nano-materials but prevent the core species (active metal) suffer from the aggregation. In addition, the catalysts with core-shell structure might present many advantages, such as large surface area, ordered structure, controllable particle size, which guarantee their broad application prospects in the field of catalysis.^[8] Common shells include metal oxides TiO₂, Al₂O₃, CeO₂, ZrO₂ etc.^[9] Cerium oxide is one of the attractive shell candidates for redox processes such as combustion and reforming considering its high oxygen storage capacity. Cargnello et al.^[10] uniformly deposited Pd@CeO₂ core-shell nanoparticles on modified hydrophobic alumina (Pd@CeO₂/H-Al₂O₃), showing excellent thermal stability and activity to methane oxidation. CeO₂ shell pre-

[a] T. Li,⁺ Y. Tian,⁺ X. Yan, Prof. W. Cai
Faculty of Light Industry and Chemical Engineering
Dalian Polytechnic University
1 Qingqongyuan, Dalian 116034 (P. R. China)
E-mail: caiwj@dlpu.edu.cn

[⁺] The first two authors contributed equally to this work.

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vented the sintering of small Pd crystals. The reaction rate of Pd@CeO₂/HAl₂O₃ was 40 times higher than that of the catalyst synthesized by wet impregnation method. Gong's group^[11] prepared and tested Pt@CeO₂ core-shell catalyst for CO oxidation reaction. It was elucidated that the CO conversion rate was 50% when the temperature was about 180 °C. Due to the formation of core-shell structure, both the high oxygen storage capacity and increased perimeter interface between Pt and cerium oxide resulted in excellent catalytic properties. Das et al.^[8b] studied the application of core-shell structure in thermal catalysis, photocatalysis and electrocatalysis, and reported that core-shell catalyst could solve the sintering and activity loss in the process of carbon dioxide conversion.

Herein, in this paper, transition metal-based catalysts with core-shell structure (SiO₂-Cu@CeO₂ and SiO₂-Ni@CeO₂) were synthesized via a strong electrostatic adsorption technique

(SEA). The as-prepared catalysts were characterized in detail by XRD, BET, SEM, TEM, H₂-TPR, Raman, CO₂-TPD and XPS technique to establish the relationship between the physico-chemical properties and the catalytic performance. On the other hand, the influence of various transition metals on the catalytic behavior was also deeply investigated in this work.

Results and Discussion

The morphology structure of the synthesized catalyst was evaluated via TEM technique. Figure 1a and Figure 2(b,c) depict the preparation procedures and TEM images of SiO₂-Cu and SiO₂-Cu@CeO₂ samples. Meanwhile, Figure 2(f,g) shows the related information of SiO₂-Ni and SiO₂-Ni@CeO₂ samples which were prepared by the same technique. As shown in Figure 2a, SiO₂ synthesized by the Stöber method presented the nanosphere shape with a diameter of ca. 150 nm.^[12] TEM images of SiO₂-Cu sample revealed the high dispersion of copper species over SiO₂ nanospheres. However, upon the addition of CeO₂ shell, the serious aggregation occurred for SiO₂-Cu@CeO₂ catalyst. This result indicated that the weaker Cu-Ce interaction resulted in the sintering of copper species during the second calcination process. On the other hand, the fibrous lamellae over the nanospheres were clearly observed for SiO₂-Ni, probably suggesting the formation of nickel phyllosilicate.^[13] It was reported that nickel phyllosilicate species might be formed in the ammonia evaporation technique with SiO₂ nanosphere acting as a silica source.^[14] Upon the second calcination step to prepare SiO₂-Ni@CeO₂, the decomposition of the Ni-phyllosilicate layer took place, leading to the formation of Ni nanoparticles over SiO₂ nanosphere support. More importantly, the sizes of nanoparticles over silica support were much less compared to SiO₂-Cu@CeO₂ sample. This finding indicated the strong Ni-Ce interaction which might efficiently prevent the apparent aggregation. In addition, a clear shell of CeO₂ coating

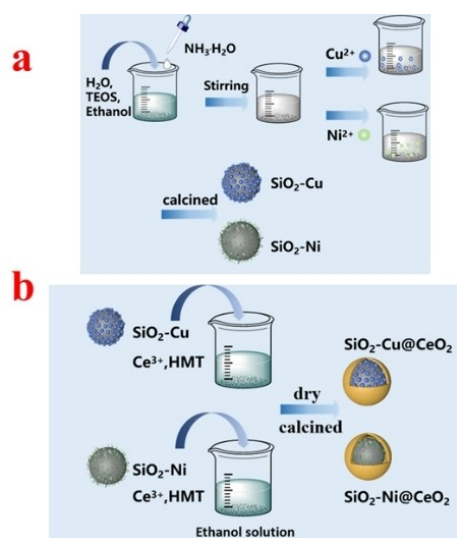


Figure 1. (a) synthesis process of SiO₂-M (M: Cu, Ni); (b) Synthesis process of SiO₂-M@CeO₂ (M: Cu, Ni).

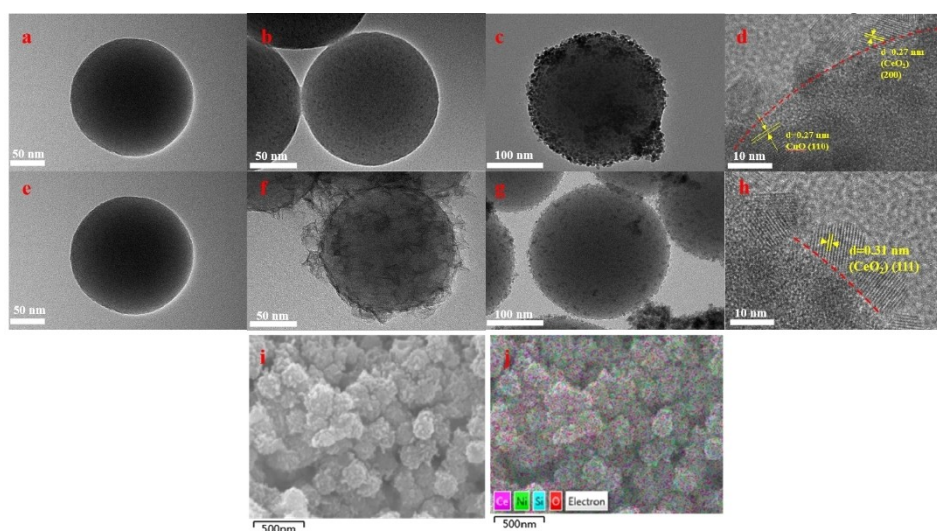


Figure 2. TEM images of the nanomaterials: (a,e) SiO₂ nano-spheres, (b) SiO₂-Cu, (c,d) SiO₂-Cu@CeO₂, (f) SiO₂-Ni and (g,h) SiO₂-Ni@CeO₂; SEM image of (i) SiO₂-Ni@CeO₂, SEM-EDX mapping of (j) SiO₂-Ni@CeO₂.

Ni nanoparticles was evidenced (Figure 2h). HRTEM image also depicted the presence of CeO_2 by its characteristic lattice fringes as presented in Figure 2h. The less crystallinity of Ni nanoparticles made it difficult to determine the lattice fringes. Meanwhile, the presence of active metal Ni was further confirmed by FESEM-EDS mappings. As presented in Figure 2j, $\text{SiO}_2\text{-Ni@CeO}_2$ sample contained elements Ni, Ce, Si and O.

H_2 -TPR measurements were conducted to depict the catalyst reducibility. It is accepted that the reduction peaks normally correspond to various metal oxide species and the same metal oxide with different particle sizes or in various chemical conditions.^[15] As presented in Figure 3a, $\text{SiO}_2\text{-Cu@CeO}_2$ sample displayed a broad peak with a wide temperature range of 150°C – 300°C , thereby suggesting the existence of CuO species with various interaction degree with other components and/or different particle sizes.^[16] Moreover, this reduction peak also might include the partial reduction of ceria. Another small shoulder at 400°C corresponded to the surface CeO_2 reduction. With respect to $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst, the first peak at 310°C was probably indexed to the reduction of NiO species with weak metal-support interaction. Indeed, another peak at 380°C was assigned to the combination reduction of NiO nanoparticles and the surface ceria which possessed stronger interaction with components in the catalyst. Obviously, the reduction peaks of $\text{SiO}_2\text{-Ni@CeO}_2$ sample shifted to the higher temperature region in comparison with $\text{SiO}_2\text{-Cu@CeO}_2$. Additionally, the peak areas of $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst were larger, implying the higher hydrogen consumption. This result suggested that the addition of CeO_2 shell resulted in a stronger

metal-support interaction (SMSI) in $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst which could enhance its sintering-resistant capacity. CeO_2 shell could create a new interfacial structure which was positive for the physicochemical features of the catalysts. As discussed in TEM analysis, the presence of smaller active metal nanoparticles in $\text{SiO}_2\text{-Ni@CeO}_2$ was helpful for the heterogeneous catalysis reactions. On the other hand, the doping of Ni^{2+} ions into ceria framework might cause the distortion of ceria lattice, thereby generating oxygen vacancies and facilitating the reduction of CeO_2 .

Crystalline structure of the catalysts were probed by XRD patterns. As presented in Figure 3b, the bands located at $2\theta = 28.64, 33.24, 47.92, 56.42^\circ$ were observed, which corresponded to typical lattice planes of cubic CeO_2 (JCPDS card no. 34–0394).^[17] Interestingly, the peaks for NiO phase were broad and almost invisible in $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst. On the contrary, two peaks at 35.42° and 38.71° were clearly noted in $\text{SiO}_2\text{-Cu@CeO}_2$ catalyst which were related to CuO species. This result revealed that NiO nanoparticles exhibited lower crystallite size than that of CuO nanoparticles. This was in accordance with the findings of TEM images in which the relatively serious aggregation occurred for $\text{SiO}_2\text{-Cu@CeO}_2$ catalyst. The mean particle size of CuO phase calculated from the Scherrer equation was 3.5 nm. It should be noted that the average crystal size of CeO_2 in $\text{SiO}_2\text{-Cu@CeO}_2$ was 5.26 nm which was larger than the value of $\text{SiO}_2\text{-Ni@CeO}_2$ (2.82 nm). As demonstrated in experimental section, $\text{SiO}_2\text{-Cu}$ and $\text{SiO}_2\text{-Ni}$ samples were synthesized by the same method. However, the addition of CeO_2 led to the above difference. This might be explained by the fact that Ni sites

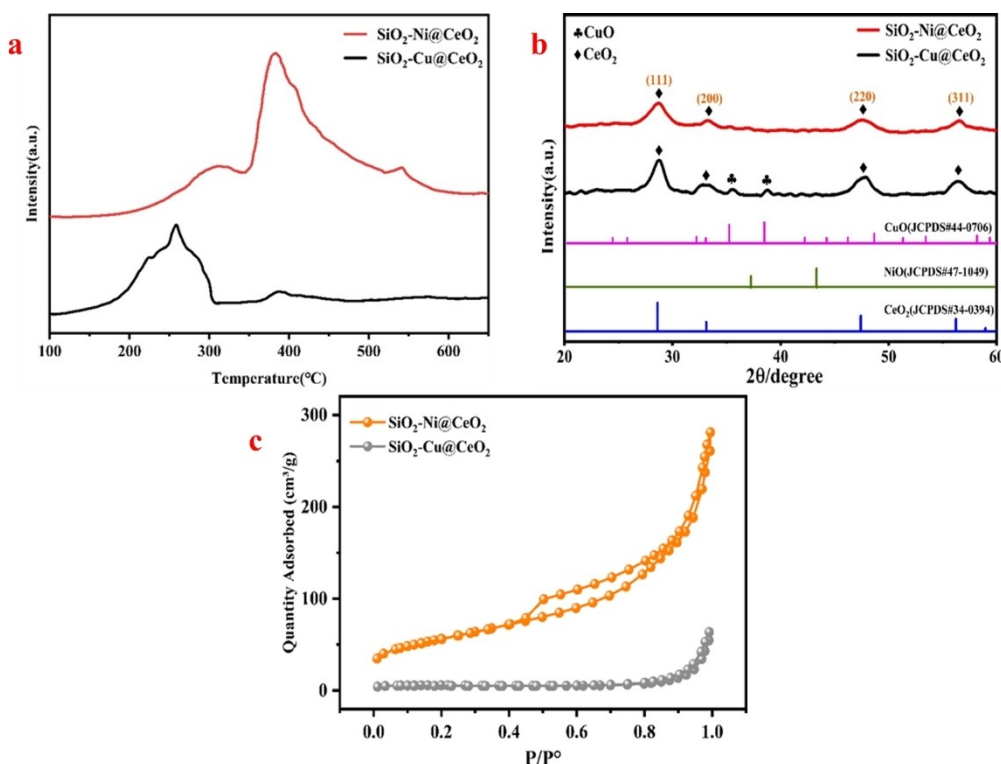


Figure 3. (a) H_2 -TPR profiles of $\text{SiO}_2\text{-Cu@CeO}_2$ and $\text{SiO}_2\text{-Ni@CeO}_2$ catalysts; (b) XRD profiles of the as-prepared catalysts; (c) N_2 adsorption-desorption isotherms of the catalysts.

could strongly interact with ceria, thereby preventing the aggregation and maintaining the high dispersion during the calcination process. H_2 -TPR profiles also exhibited the stronger interaction between Ni species with components in SiO_2 -Ni@ CeO_2 catalyst, supporting the XRD findings. Wang et al.^[18] also depicted that the ceria dopant could greatly reduce the Ni particle size in Ni/ Al_2O_3 catalyst which was below XRD detection limit. This might be due to the redox properties of CeO_2 , in which Ce^{4+}/Ce^{3+} couple species could form surface and bulk oxygen defects, leading to the generation of metal-oxygen complexes. It is accepted that the adequate O vacancies is favorable for dry reforming process. Indeed, carbonaceous deposits in heterogeneous catalysis reactions are indexed with the particle size/dispersion of active metal. Normally, small metal particles might prevent the metal aggregation and carbon deposition. Some literatures have focused on the design of efficient reforming catalysts with good coke-resistance via precisely controlling the particle size of active metal.^[19]

It is widely known that high surface area which might provide adequate active sites could enhance the catalytic performance.^[20] Figure 3c depicts the N_2 adsorption-desorption profiles to measure the specific surface areas. Based on the IUPAC classification, the isotherm curve of SiO_2 -Ni@ CeO_2 catalyst might be attributed to typical type IV isotherm, corresponding to mesoporous material. Indeed, the obvious capillary condensation phenomenon at low P/P_0 value was related to the uniform mesopores and another hysteresis loop at $P/P_0=0.8-0.9$ was assigned to N_2 condensation within void space and/or structural defects. In contrast, SiO_2 -Cu@ CeO_2 sample presented type II isotherms which was typical of non-porous or microporous materials. Additionally, the variations of the porous structure between SiO_2 -Ni@ CeO_2 and SiO_2 -Cu@ CeO_2 were obvious as shown in Table 1. Clearly, the less surface area as well as the larger pore size for SiO_2 -Cu@ CeO_2 catalyst was caused due to the filling of the pores by copper nanoparticles, thereby leading to the pores inaccessible for N_2 adsorption. Because the smaller pores were firstly plugged, it explained the increase of pore size as previously illustrated by the previous literature. More importantly, the discussion of TEM images and H_2 -TPR profiles depicted the obvious aggregation and less synergistic interaction between Cu species and CeO_2 in SiO_2 -Cu@ CeO_2 catalyst which could result in the blocking of pores by copper species. Indeed, the higher surface area was attributed to the smaller particle size and the broader band. More importantly, the mesoporous CeO_2 shell could maintain SiO_2 -

Ni@ CeO_2 nanoparticles with well permeability for reactant gas, thereby enhancing the catalytic activity in dry reforming process.^[21]

Both the surface chemical states and chemical interaction of the investigated catalysts were determined by XPS technique. The full survey scan spectra (Figure 4a) revealed the presence of Cu, Ce, O elements in SiO_2 -Cu@ CeO_2 and Ni, Ce, O elements in SiO_2 -Ni@ CeO_2 catalyst. As presented in Figure 4b, Ce 3d XPS spectra for all samples could be fitted with eight peaks corresponding to Ce 3d_{5/2} and Ce 3d_{3/2}, respectively. Herein, the peaks at (901.9 eV) and (883.9 eV) were indexed with Ce^{3+} species while the peaks at (916.1 eV), (897.6 eV), (900.3 eV), (881.9 eV), (906.9 eV) and (888.5 eV) were attributed to Ce^{4+} sites, thereby suggesting the co-existence of Ce^{3+} and Ce^{4+} ions in the catalysts. The presence of Ce^{3+} species was closely connected with the generation of O defects that could positively facilitate the coke gasification during reforming reaction to inhibit coke accumulation. Moreover, It was reported that CO_2 gas preferentially adsorbed onto the Ce^{3+} species rather than the oxidized Ce^{4+} sites.^[22] The relative content of Ce^{3+} species was calculated by integrated areas of XPS bands. The results declined as following: SiO_2 -Ni@ CeO_2 (30.2%) > SiO_2 -Cu@ CeO_2 (18.3%). Typically, the value in SiO_2 -Ni@ CeO_2 catalyst was larger compared to the previous reports like CeO_2 @ Co_3O_4 (27%) and Ni/ CeO_2 (16%).^[23] This might be due to the SMSI as elucidated in XRD and H_2 -TPR results. The concentration of Ce^{3+} species was positively in associated with the catalytic performance of dry reforming reaction considering that Ce^{3+} sites accompanying with O defects played an important role in coke elimination.

O 1s profiles are presented in Figure 4c. Obviously, O 1s spectra were broad and complex in all cases which could be fitted with two peaks. This indicated the existence of various oxygen species. Indeed, the peak at ca.530 eV was related to lattice O sites (O_a) while another peak at ca. 532 eV corresponded to the surface O sites (O_b). Particularly, surface O species like adsorptive or defective O species was favorable to enhance the catalytic behavior. The ratio of O_b/O_a in SiO_2 -Ni@ CeO_2 (9.76) was higher than that of SiO_2 -Cu@ CeO_2 (4.02) which was in accordance with the concentration of Ce^{3+} species.^[24]

Ni 2p XPS spectrum in Figure 4d shows two main peaks and two shake-up satellites. The peak located at 856.4 eV corresponded to the binding energies of Ni 2p_{3/2} while another peak at 874.3 eV was attributed to Ni 2p_{1/2}. This result implied the existence of NiO species as reported in the previous literature. This was caused by the non in-situ reduction treatment in which metallic Ni species were re-oxidized. The peak ascribed to Ni 2p_{3/2} in pure NiO was 854 eV as reported in the previous literature. Interestingly, the shift to higher binding energy of Ni 2p_{3/2} depicted a strong interaction between Ni and the components in catalyst. The observed blue shift of O1s in SiO_2 -Ni@ CeO_2 further provided the evidence. Cu 2p spectra presented two main peaks, one at 932 eV (Cu 2p_{3/2}) and the other at 952 eV (Cu 2p_{1/2}) which suggested the presence of Cu⁰ and/or Cu⁺ species. Another two prominent satellite peaks at 942 eV and 962 eV implied the existence of Cu²⁺ species.^[25]

Table 1. Physicochemical properties of the catalysts.

Catalysts	BET ^[a] [m ² /g]	Ni si- ze ^[b] [nm]	Cu size ^[b] [nm]	CeO ₂ size ^[b] [nm]	Pore size ^[a] [nm]	Pore vol- ume ^[a] [cm ³ /g]
SiO_2 - Cu@ CeO_2	18.9	–	3.51	5.26	30.9	0.098
SiO_2 -Ni@- CeO_2	201.4	–	–	2.82	7.9	0.434

[a] obtained from N_2 adsorption-desorption; b: calculated from XRD patterns.

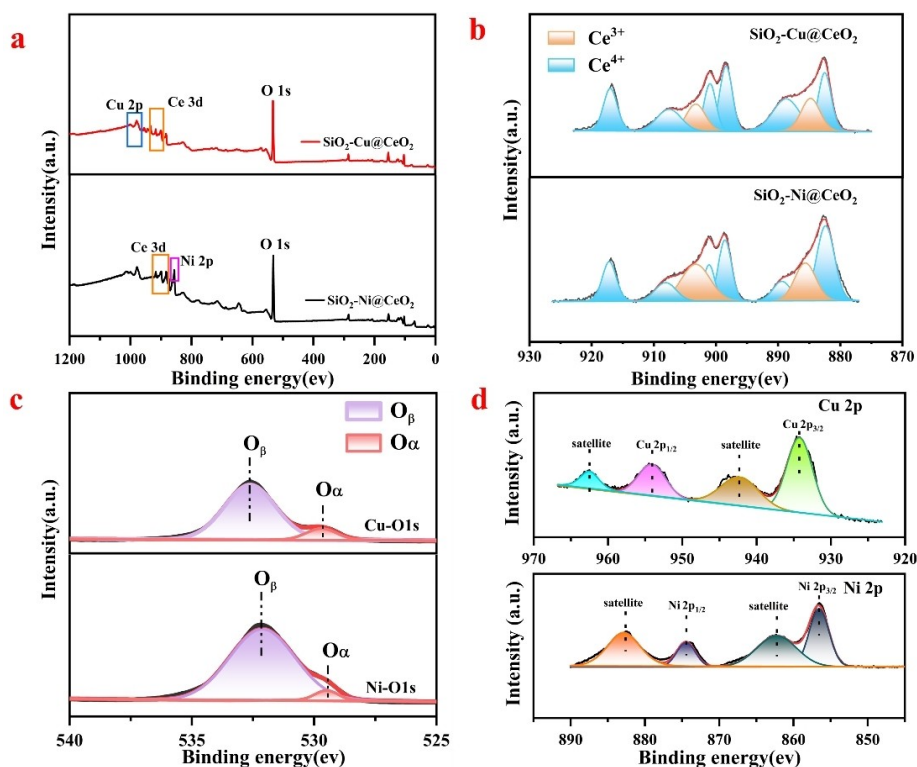


Figure 4. (a) XPS full survey spectra, (b) Ce 3d, (c) O 1s, (d) Cu 2p and Ni 2p spectra of the catalysts.

CO₂-TPD profiles were recorded to explore the basicity difference of the investigated catalysts, which was critical for the catalytic performance of the EDR reaction, especially in the adsorption/conversion of CO₂.^[26a] As presented in Figure S2, three kinds of desorption peaks were observed for SiO₂-Ni@CeO₂ catalyst. Typically, the peak at ca. 127 °C corresponded to the desorption of CO₂ bounded with the weak basic sites. The desorption bands at ca. 373 °C and 496 °C were attributed to moderate and strong basic sites, respectively.^[26b] What's more, SiO₂-Cu@CeO₂ sample exhibited three desorption peaks at lower temperature in comparison with SiO₂-Ni@CeO₂. This indicated the stronger binding affinity to CO₂ for SiO₂-Ni@CeO₂ catalyst. Indeed, increasing catalyst basicity could significantly prevent the coke accumulation through accelerating the oxidation of coke.^[26c]

The catalytic activity of ethanol dry reforming reaction was evaluated under the conditions of stoichiometric feedstocks. The experimental results are shown in Figure 5a where the activity of catalysts with different active metal has an obvious distinction. SiO₂-Ni@CeO₂ catalyst exhibited an obvious higher activity than that of SiO₂-Cu@CeO₂ sample. In detail, almost complete ethanol conversion (99.3%) could be achieved over SiO₂-Ni@CeO₂ at 500 °C while the value for SiO₂-Cu@CeO₂ was only 83%. It was conspicuous that less by-product acetone (1.01%) was formed in Ni-based catalyst in comparison with Cu-based catalyst (2.7%), implying the unfavorable occurrence of aldol condensation reaction over SiO₂-Ni@CeO₂ catalyst. Moreover, H₂/CO ratio in SiO₂-Ni@CeO₂ was 1.1, which was closer to the theoretical value and the targeted number for Fischer-

Tropsch process. As presented in H₂-TPR and XPS, the existence of the stronger synergistic interaction between active metal and other components in SiO₂-Ni@CeO₂ catalyst was noted which might enhance its C–C dissociation capacity. In addition, both larger specific surface area and higher dispersion of active metal in SiO₂-Ni@CeO₂ as depicted in BET and TEM findings could provide more active sites thereby enhancing its catalytic activity. More importantly, the sequence of activity was consistent with the characterization results.

The catalytic behavior over SiO₂-Ni@CeO₂ catalyst was studied at 500–750 °C to determine the temperature effect. Figure 5b presents the change of reactant conversion and product distributions in the outlet dry gas. Typically, ethanol was almost completely converted in the whole testing temperature region. In addition, CO concentration steadily increased while H₂ formation followed the reverse trend with increasing reaction temperature which was probably because of the favorable occurrence of reverse water gas shift reaction (H₂ + CO₂ → CO + H₂O). As for the methane concentration in the outlet gas, it steadily decreased due to methane dry reforming which was spontaneous at high temperatures.^[27] The molar concentration of another byproduct acetone gradually declined from 2.9 mol % to 0.4 mol %.

Figure 5(c, d) shows the stability tests over SiO₂-Ni@CeO₂ and SiO₂-Cu@CeO₂ catalysts, respectively. It should be noted that the reactor tube was blocked by the carbonaceous deposits for SiO₂-Cu@CeO₂ sample within 20 h reaction that inhibited the reactant gas from entering the reactor because of the increasing reaction pressure. This result suggested a rapid

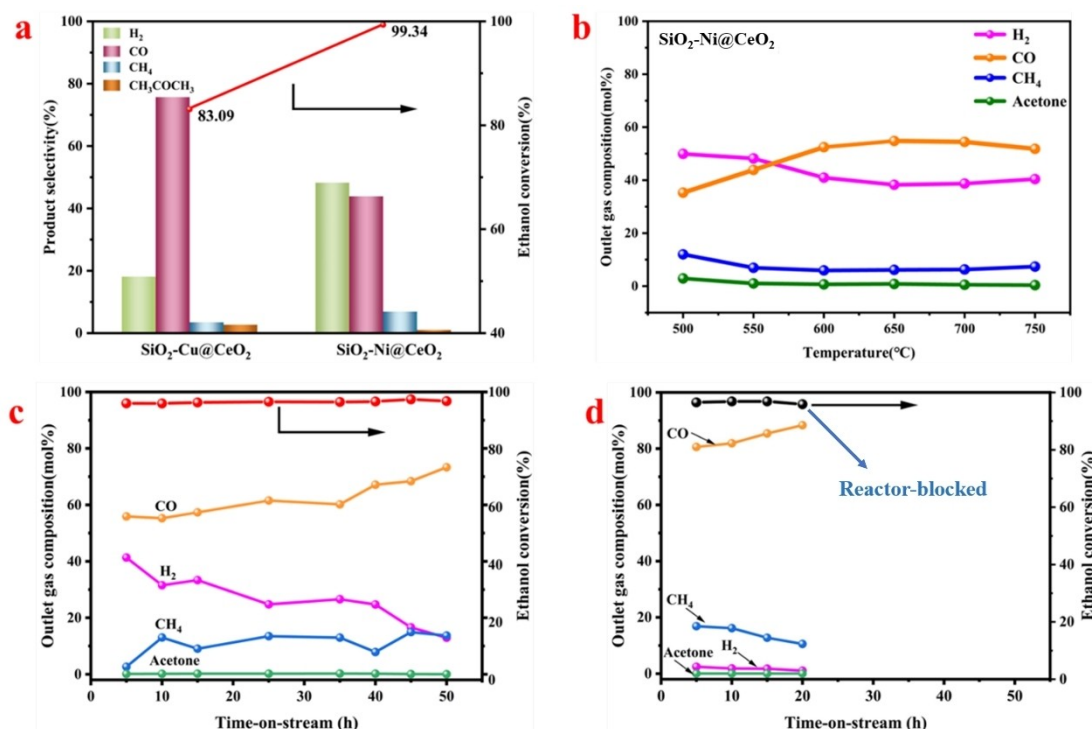


Figure 5. (a) Comparison of the catalytic activity for the investigated catalysts ($\text{CH}_3\text{CH}_2\text{OH}/\text{CO}_2/\text{N}_2 = 1/1/1.5$, molar ratio; 500 °C, GHSV = 27700 mL/g_{cat}h); (b) Influence of reaction temperature on the catalytic activity over $\text{SiO}_2\text{-Ni@CeO}_2$ catalysts. ($\text{CH}_3\text{CH}_2\text{OH}/\text{CO}_2/\text{N}_2 = 1/1/1.5$, molar ratio; GHSV = 27700 mL/g_{cat}h); (c, d) Stability tests of $\text{SiO}_2\text{-Ni@CeO}_2$ and $\text{SiO}_2\text{-Cu@CeO}_2$ catalysts (Reaction conditions: 500 °C, $\text{CH}_3\text{CH}_2\text{OH}/\text{CO}_2/\text{N}_2 = 1/1/1.5$ molar ratio, 550 °C GHSV = 27700 mL/g_{cat}h).

carbon accumulation rate in Cu-based catalyst. It was accepted that active metal nanoparticles with large size might promote the coke formation in dry reforming process. As elucidated in XRD patterns, average particles size of Cu species in $\text{SiO}_2\text{-Cu@CeO}_2$ was larger than that of Ni species in $\text{SiO}_2\text{-Ni@CeO}_2$. The coke residuals mainly originated from the cracking of methane ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) and/or Boudard reaction ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$). However, $\text{SiO}_2\text{-Ni@CeO}_2$ still maintained the relatively stable performance during the whole testing period suggesting its better stability.

Raman spectra were recorded to evaluate the type of the formed coke over the used catalysts. As shown in Figure 6a, two main peaks typically corresponding to sp^2 bonded carbon species were noted. The characteristic peak at ca.1347 cm^{-1} was ascribed to the amorphous coke with disordered network (D band). On the other hand, another peak at ca.1587 cm^{-1} was indexed to the graphic carbon with high crystallinity and symmetry (G band). Typically, I_D/I_G was used to measure the crystallinity degree of the coke. In fact, the I_D/I_G ratio for $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst (0.77) was higher than that of $\text{SiO}_2\text{-Cu@CeO}_2$

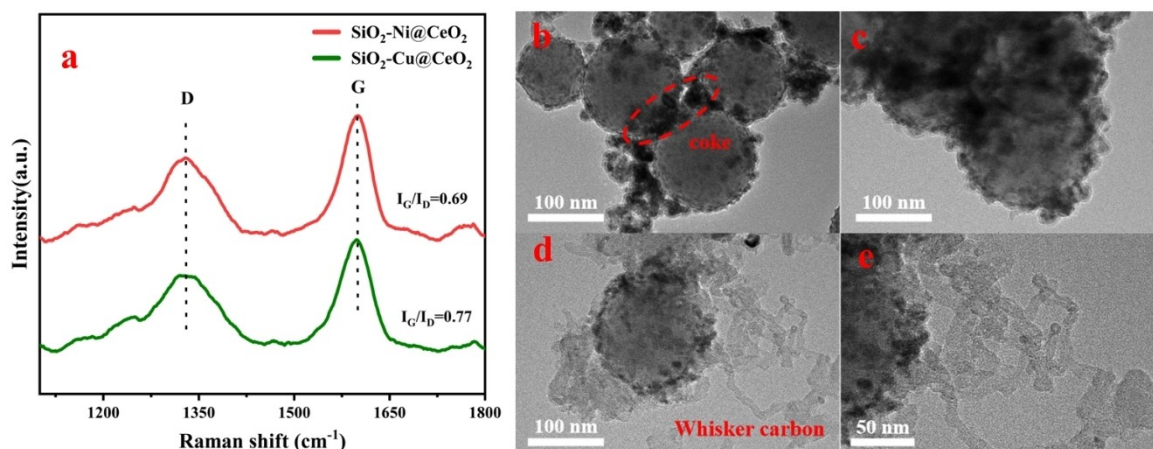


Figure 6. (a) Raman spectra of the spent catalysts; TEM images of the spent catalysts. (b, c) $\text{SiO}_2\text{-Cu@CeO}_2$ (20 h tests); (d, e) $\text{SiO}_2\text{-Ni@CeO}_2$ (50 h tests).

(0.69), reflecting the less graphitization degree. As elucidated by Mattos et al.,^[28] the formation of the amorphous coke was not fatal to the catalytic activity. This might explain the relatively higher stability of $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst.

TEM images of the used $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst after stability tests at 550°C are presented in Figure 6(d, e). It clearly depicted the formation of filamentous type coke. Considering its approximately stability, it could be concluded that the whisker coke deposition might barely result in deactivation. Indeed, the active metallic nanoparticles could still contact with the reactant gas and further maintain the occurrence of catalytic cycle. On the contrary, the spent $\text{SiO}_2\text{-Cu@CeO}_2$ catalyst were obviously encapsulated by carbon which might inhibit the intimate contact of reactants with active sites, thereby leading to the deactivation. This type of coke possessed the high crystallinity and was detrimental for catalytic activity. This finding was in coincidence with Raman results. TG analysis was employed to elucidate the amount of coke formation over the used catalysts. As depicted in Figure S3, the slight mass decrease at below 100°C might be assigned to the adsorbed water. Moreover, the slightly positive change of mass was attributed to the re-oxidation of active metal (Cu, Ni) particles.^[29] In case of the used $\text{SiO}_2\text{-Cu@CeO}_2$ (20 h tests), what followed was the two-step mass decrease (8.63 % and 5.84 %, respectively), corresponding to the elimination of coke with various degree of graphitization. However, the used $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst after the longer time tests (50 h) exhibited the smaller mass decline, suggesting the less carbon deposition. The formation rates of carbon for $\text{SiO}_2\text{-Ni@CeO}_2$ was $0.15\text{ mg/g}_{\text{cat}}/\text{h}$ while the value for $\text{SiO}_2\text{-Cu@CeO}_2$ was as high as $0.74\text{ mg/g}_{\text{cat}}/\text{h}$. The good anti-coke capacity of $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst might be indexed with smaller Ni particles sizes as illustrated in TEM and XRD.

To be concluded, the mesoporous structure of CeO_2 shell in $\text{SiO}_2\text{-Ni@CeO}_2$ sample as depicted in BET findings could facilitate the ethanol decomposition and CO_2 reduction via transferring the reactant gas to the active sites and promote the elimination of carbon by active O species via removing the formed CO (Figure 7). Hence, the improvement of mass transfer for reactants and products might enhance the catalytic activity/stability. More oxygen defects associated with Ce^{3+} species as elucidated by XPS profiles were favorable for the adsorption/activation of CO_2 . The generated active oxygen species could greatly accelerate the oxidation of carbon deposits, thereby preventing the coke accumulation. Meanwhile, the stronger interaction between Ni and ceria shell was also correlated with the coke-resistance capacity and anti-sintering feature. The particle size of Ni species calculated from XRD pattern of the spent $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst was 4.63 nm which was less than that of Cu species (8.05 nm). The relatively high dispersion of active Ni species could maintain its good activity. The above positive factors contributed to the high performance of $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst in EDR reaction.

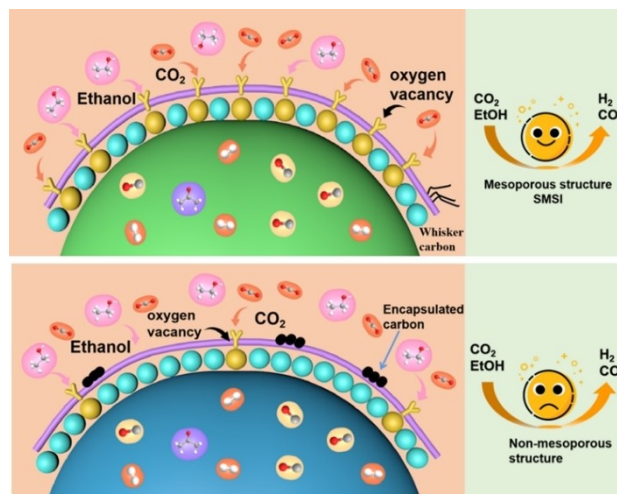


Figure 7. The proposed reaction mechanism of ethanol dry reforming.

Conclusions

In summary, transition metal-based $\text{SiO}_2\text{-Cu@CeO}_2$ and $\text{SiO}_2\text{-Ni@CeO}_2$ catalysts with core@shell structure were synthesized by a facile electrostatic adsorption method and applied for ethanol dry reforming. Herein, $\text{SiO}_2\text{-Ni@CeO}_2$ sample exhibited the better catalytic activity in comparison with $\text{SiO}_2\text{-Cu@CeO}_2$ catalyst. Indeed, 99.3 % of ethanol conversion could be achieved with a H_2/CO ratio of 1.1 which was closed to the theoretical value. Meanwhile, Ni-based catalyst also possessed the relatively good stability. The observed higher catalytic performance for $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst might be ascribed to several positive factors, including the efficient mass transfer for reactant/product gas due to mesoporous structure, the strong synergistic Ni-Ce interaction and the high Ni dispersion which could enhance the activation of reactants and increase the carbon-resistance capacity and sintering-free feature. Hence, $\text{SiO}_2\text{-Ni@CeO}_2$ catalyst could possess the potential application in other heterogeneous reactions involving metal aggregation and coke deposition challenges.

Experimental Section

Chemicals

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are selected as precursors. $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, ethanol, ammonia solution, $\text{C}_6\text{H}_{12}\text{N}_4$ (99 %), Tetraethyl orthosilicate are purchased from Aladdin Chemical company. Herein, these chemicals are analytical grades and directly applied.

Preparation of $\text{SiO}_2\text{-Cu}$ and $\text{SiO}_2\text{-Ni}$

Firstly, a mixture of TEOS (2 mL) and ethanol (70 mL) was added to another mixture of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (2 mL) and deionized water (12.5 mL). After stirring at room temperature for 24 h, 0.8 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added and further stirred for 5 h at 70°C . Subsequently, the achieved precipitate was centrifuged and washed. After dried at 60°C overnight, the precipitate was calcined at 550°C for 3.5 h. The achieved product was labeled as $\text{SiO}_2\text{-Cu}$. Another $\text{SiO}_2\text{-Ni}$ sample

was prepared by the same method, with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as nickel precursors

Preparation of $\text{SiO}_2\text{-Cu@CeO}_2$ and $\text{SiO}_2\text{-Ni@CeO}_2$

1.2 g $\text{SiO}_2\text{-Cu}$ and 1.13 g $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ were dissolved in 200 mL of ethanol. After the addition of $\text{C}_6\text{H}_{12}\text{N}_4$ (20 g), the mixture was stirred at 70 °C. Finally, the precipitate was calcined at 550 °C for 3.5 h ($\text{SiO}_2\text{-Cu@CeO}_2$). Indeed, the $\text{SiO}_2\text{-Ni@CeO}_2$ sample was synthesized by the same processes in which $\text{SiO}_2\text{-Cu}$ was replaced by $\text{SiO}_2\text{-Ni}$.

Characterization of the catalysts

The catalyst structure was examined by TEM and SEM technique. The reducibility was explored by $\text{H}_2\text{-TPR}$. The crystallinity and specific surface area of the catalyst was determined by XRD and N_2 adsorption-desorption isotherms, respectively. The coke types were analyzed using Raman profiles. The surface chemical states of the catalysts were probed by XPS technique. Thermogravimetry (TG) of the spent catalysts were conducted on a thermogravimetric analyzer TGA-8000. The detailed characterization information might be observed in Supporting Information.

Catalytic activity test

The catalytic performance was tested in a conventional fixed-bed reactor. 100 mg of catalysts were insitu reduced and then CO_2 reforming with ethanol was carried out. The product gas was online determined by a GC equipped with FID and TCD detectors. The calculation of ethanol conversion and the outlet gas composition could be achieved in Supporting Information.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Dry reforming · Syngas · Transition-metal based catalysts · Core-shell

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