CeO₂ Nanorods-Supported Transition Metal Catalysts for CO Oxidation

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A catalytically active oxide support in combination with metal catalysts is required in order to achieve better low temperature activity and selectivity. Here, we report that CeO₂ nanorods with a superior surface oxygen release/storage capability were used as an active support of transition metal (TM) catalysts (Mn, Fe, Co, Ni, Cu) for CO oxidation reaction. The as-prepared CeO₂ nanorods supported 10 wt% TM catalysts were highly active for CO oxidation at low temperature, except for the Fe sample. It is found that the 10 %Cu-CeO₂ catalyst performed best, and it provided a lower light-off temperature with T50 (50 % conversion) at 75 °C and T100 (100 % conversion) of CO to CO₂ at 194 °C. The atomic level surface structure of CeO₂ nanorods was investigated in order to understand the improved low temperature catalytic activity. The richness of surface roughness and various defects (voids, lattice distortion, bending, steps, twinning) on CeO₂ nanorods could facilitate oxygen release and storage. According to XRD and Raman analysis, copper species migrate into the bulk CeO₂ nanorods to a greater degree. Since CO adsorbed over the surface of the catalyst/support is detrimental to its catalytic activity, the surface defects on the CeO₂ nanorods and CeO₂-TM interactions were critical to the enhanced activity.

Introduction

In oxide-supported metal heterogeneous catalysts, it has been recognized that metal catalysts supported on different oxides have different catalytic properties, depending on the reducibility of the oxide,¹ the surface acidity and basicity of the oxide,² and the metal-oxide interaction/reaction.³ Charge transfer or redox reactions are essential steps for the catalytic reaction at elevated temperatures, therefore the reducible oxide support presents a potential advantage compared to the conventional non-reducible oxide support, e.g. silica (SiO₂) and alumina (Al₂O₃). Reducible metal oxides are solid state compounds exhibiting variable valence or oxidation states of the metal, such as CeO₂, TiO₂, VO_x, FeO_x, CoO_x, MnO_x, HfO_x, PrO_x, TbO_x, and SmO_x. Many transition and lanthanide metals in oxides possess variable oxidation states because of the variable occupancy of 3d and 4f orbitals, respectively.

Among the reducible oxides, cerium exhibits two possible oxidation states – Ce³⁺ and Ce⁴⁺ – and several types of coordination in the cubic fluorite structure CeO₂, cubic Ce₂O₃ structure (C-Ce₂O₃) and hexagonal Ce₂O₃ structure (A-Ce₂O₃) (Figure 1). Ceria (CeO₂) can release lattice oxygen under oxygen lean conditions and store oxygen under oxygen rich conditions, mainly accommodated by a reversible valence change of cerium ions (Ce⁴⁺ + e⁻ ↔ Ce³⁺ or O²⁻ + 2Ce⁴⁺ ↔ 2Ce³⁺ + 1/2O₂(g)) with formation or elimination of oxygen vacancies (in Kröger-Wink notation: O_O^x + 2Ce_{Ce}^x → V_O^{••} + 2Ce_{Ce}[•] + 1/2O₂(g)), shown in Figure 1. For the two Ce₂O₃ sesquioxides, hexagonal Ce₂O₃ (A-Ce₂O₃) is formed after high temperature treatment above 1100 °C under a reducing atmosphere, and it is a stable phase that does not store oxygen; cubic Ce₂O₃ (C-Ce₂O₃) or CeO_{2-x} (0 < x ≤ 0.5) is only stable at high temperatures below 1100 °C under a reducing atmosphere. The reduced Ce₂O₃ will be reoxidized to CeO₂ at low temperatures and/or high oxygen partial pressures.^{4,5}

Metal nanoparticle catalysts (Pt/Au/Ni/Cu/Ag) used for CO oxidation can be promoted by a reducible CeO₂ support.⁶⁻¹⁰ CeO₂ supports are shown to have superior oxygen mobility via an easy redox reaction (4CeO₂ ↔ 2Ce₂O₃ + O₂), which enhances catalyst activity. The role of CeO₂ is believed to involve the adsorption and

interaction of CO on the surface of CeO₂ and at the metal/CeO₂ interface. CeO₂ nanorods have been reported to present low temperature surface reducibility due to either two {100} and two {110} faces on the crystal surface^{11,12} or oxygen vacancy clusters on the surfaces.¹³ In this study, we report the synthesis and characterization of CeO₂ nanorod-supported TM catalysts and aim to understand the role of CeO₂ support shape/surface defects for CO oxidation.

Figure 1. Structural change during redox process in ceria (CeO₂).

Experimental

Catalyst Preparation

CeO₂ nanorods were prepared by a hydrothermal method at temperatures in the range of 50-130 °C under different NaOH concentrations, using Ce(NO₃)₃·6H₂O as the cerium source. The cerium precursors were 99.99 % purity for cerium (III) nitrate hexahydrate and purchased from Alfa Aesar. Sodium hydroxide pellets were >98% purity and obtained from Sigma-Aldrich. Typically 0.1M Ce(NO₃)₃·6H₂O and 6M NaOH mixtures were heated to 50~130

°C and held for 24 hrs in a sealed 25 mL Teflon-lined autoclave (~50 % fill). Afterwards the autoclave was cooled to room temperature before the solid products were recovered by suction filtration. The materials were washed thoroughly with distilled water to remove any co-precipitated salts, then washed with ethanol to avoid hard agglomeration in the nanoparticles, and dried in air at 50 °C for 12 hrs. Metals (Mn/Fe/Co/Ni/Cu) were loaded onto the CeO₂ nanorod supports using an incipient wetness technique (impregnation method). Mn(NO₃)₂·4H₂O, Fe(NO₃)₃, Co(NO₃)₂·6H₂O, Ni(CH₃CO₂)₂·4H₂O, and Cu₂CO₃ for metal additives of Mn, Fe, Co, Ni, Cu, respectively, were used as the starting materials. The loading amount of added metal additives were adjusted to be 10 wt%. The co-precipitates were dried at 100 °C for 12 hrs and then calcined in air at 400 °C for 5 hrs. The resultant powders were obtained after a reduction treatment in 5vol%H₂/95vol%He atmosphere at 600 °C for 5 hrs.

Catalyst Characterization

Powder X-ray diffraction (XRD) analysis was performed on a Rigaku Miniflex II diffractometer using Cu K α radiation with a wavelength of 1.5408 Å. The samples were loaded on an aluminum plate and the data was collected over a 2 θ range of 5°-90° with a step size of 0.5°/min. The recorded patterns were analyzed using JADE software to determine peak positions, lattice constant, and average crystalline sizes by use of Scherer's formula.

Raman scattering was performed in a Horiba iHR 320 Raman Spectrometer with a 532 nm laser module and 10~40 second exposure time. All peak intensities and positions were obtained by Lorentzian fitting. The Raman scattering in the 100-3200 cm⁻¹ region was collected.

Single point BET surface area analysis of the catalysts was determined by N₂ adsorption/desorption isotherms at liquid nitrogen temperature. Hydrogen temperature programmed reduction (H₂-TPR) study of the as-prepared catalysts were examined using hydrogen chemisorption on a Micromeritics AutoChem™ II 2920 chemisorption analyzer instrument to explore how much hydrogen adsorbs and consumes onto the catalyst as a function of temperature. No pretreatment was performed before H₂-TPR. The powder samples were heated at a rate of 10 °C/min from room temperature to 900 °C. The gas mixture (5% H₂ and 95%He) was passed through the catalyst sample (80~100 mg) at a rate of 50 mL/min. A cold trap filled with a mixture of isopropanol, KCl, and ice was placed in the gas line upstream of the thermal conductivity detector (TCD) to remove any water moisture. A thermal conductivity detector continuously monitored the H₂ concentration. A cuprous oxide sample (Cu₂O) was used to calibrate the TPR profile peak area allowing consumption of H₂ to be calculated.

A JEOL 2100 transmission electron microscope (TEM) was used for structural and chemical analysis of the nanocrystals at the atomic level, operated at 200 kV and equipped with an EDAX detector for chemical composition analysis and an annular dark-field detector. High resolution transmission electron microscopy (HRTEM) was used to determine the exposed crystal facets in individual CeO₂ nanocrystals. TEM samples were prepared by using dilute suspensions of the nanopowder samples. These solutions were obtained by ultrasonication particles in ethanol for 5 min then dropping the suspension of the sample powders onto an ultrathin

carbon film/holey carbon, 400 mesh copper grid (from Ted Pella) and letting it air dry for several hours.

Measurement of Catalytic Activity for CO Oxidation

The catalytic oxidation of CO was conducted using a fixed bed plug flow reactor system. 1vol%CO/20vol%O₂/79vol%He with a 70 mL/min flow rate was supplied by a mass flow controller and passed through the catalyst bed. The catalyst (~30 mg) was mixed with quartz wool (coarse, 9 μ m) and filled in the quartz tube reactor. The reaction temperature was programmed between 30 °C and 350 °C and monitored by a thermocouple. The reactant CO and product CO₂ were analyzed by using an on-line gas chromatograph (SRI multiple gas analyzer GC, 8610C chassis) system. The catalytic activity or CO conversion was calculated with the following equation: %_{CO} = $\left[\frac{Area_{CO}}{Area_{CO} + Area_{CO_2}} \right] \times 100\%$.

Results and Discussion

Characterization of CeO₂ Nanorods Support

The length as well as the diameters of the CeO₂ nanorods may be manipulated by adjusting the temperature of the hydrothermal reaction as well as the dwell time as indicated by our previous report.¹⁴ The length and diameter of the nanorods increase with both hydrothermal temperature and dwell time, however, at temperatures above 110 °C the formation of CeO₂ nanocubes was observed. In this study, the CeO₂ nanorods were synthesized at 90 °C with a dwell time of 24 hrs. Figure 2 shows the X-ray diffraction pattern, Raman spectrum, low magnification TEM image, H₂-TPR profile, and high resolution TEM image (HRTEM) of the CeO₂ nanorods. The XRD pattern in Figure 2 (a) reveals that the structure of the as-synthesized sample is in agreement with a face centered cubic CeO₂ phase (JCPDS-34-0394). The Raman analysis of CeO₂ nanorods depicted in Figure 2 (b), shows the main peaks at 262, 461 and 602 cm⁻¹. The 461 cm⁻¹ vibration is ascribed to the CeO₈ vibrational unit in cubic CeO₂, which is only first order Raman active. The 262 and 602 cm⁻¹ vibrations are assigned to the oxygen sublattice disorder and/or oxygen vacancies¹⁵ suggesting a significant amount of oxygen vacancies or disorder in the as prepared CeO₂ nanorods.

Figure 2. X-ray diffraction pattern (a), Raman spectrum (b), TEM image (c), H_2 -TPR profile (d), and HRTEM images (diffractogram inserted) (e) of as-prepared CeO_2 nanorods.

Figure 2 (c) represents a low magnification TEM image of the as-synthesized CeO_2 nanorods, which are typically 50-100 nm in length and 5-20 nm in diameter. Confirmed by the high resolution TEM analysis as shown in Figure 2 (e), a significant lattice distortion and surface roughness (steps, voids, twinning, bending) were observed consistent with the Raman analysis shown in Figure 2 (b). The H_2 -TPR profile data in Figure 2 (d) shows two reduction peaks for the surface and bulk reductions, respectively, with a great higher surface reduction peak at 502 °C. This indicates significantly improved low-temperature surface reduction of the as-synthesized CeO_2 nanorods, compared with other morphological CeO_2 , i.e. ceria nanooctahedra with dominant {111} surfaces.¹⁶ The reduction temperature and distribution between the surface and bulk peak areas are good indicators of the overall performance of the material as an oxidation-reduction catalyst. The higher mobility of the surface oxygen ions in less stable crystal planes helps in the removal of lattice oxygen during reduction processes.¹⁷⁻²⁰ It must be noted that, shown in Figure 2 (e), the HRTEM images clearly suggest a {111} termination surface with a significant amount of defects, including steps, voids, lattice distortion, twinning, and bending. The data thus obtained are inconsistent with the those available in the literature,¹¹⁻¹² claiming a rod geometry with two {001} and two {011} surfaces, although the {001} surface was occasionally observed in

the present study. By exposing these more “defected” crystal planes, CeO_2 nanorods have a much higher surface reduction percentage than their conventional octahedrally shaped counterparts with {111} crystal planes. Additionally, a larger percentage of the reduction takes place in the lower temperature surface reduction area.

Structural Description of CeO_2 Nanorods-Supported TM Catalysts

The XRD patterns of the CeO_2 nanorods supported TM catalysts are shown in Figure 3. All the samples, after loading the metals, exhibited a cubic fluorite structure of CeO_2 , which was identified using standard data (JCPDS file no. 34-0394). CeO_2 crystal structure did not undergo changes after the 10wt% loading of metals, whereas the morphology of CeO_2 rods changed slightly based on the TEM analysis. The nanorods have a lower length-to-diameter ratio due to the thermal treatments (oxidation at 400 °C for 5 hrs and reduction at 600 °C for 5 hrs). Diffraction peaks corresponding to metal species were observed only in the samples of Cu- CeO_2 , Ni- CeO_2 , and Co- CeO_2 . In other words, the patterns consist of metallic Cu or Ni or Co and CeO_2 phases in these samples. A trace amount of CuO was detected from the Cu- CeO_2 sample, identified at 2θ of 35.6 °C and 38.7 °C in the XRD pattern. Whereas the XRD patterns of Fe- CeO_2 and Mn- CeO_2 samples show the characteristic peaks of Fe_2O_3 (γ - Fe_2O_3 , JCPDS file no. 89-5892) and cubic MnO (JCPDS file no. 07-0230) phases, indicating an incomplete reduction in these two samples. Among these samples, it was also observed that the XRD patterns of Cu species is sharper indicating a larger size of Cu, and a more crystalline nature of the Cu that was deposited on the CeO_2 nanorods. Also a shift of the CeO_2 peaks to lower 2θ values indicated the formation of a solid solution particularly much more profound for the Cu sample, shown by the dashed lines along the (200) peak in Figure 3. Additionally, this observation is consistent with Raman analysis.

Figure 3. XRD patterns of CeO_2 nanorods supported TM catalysts.

In Figure 4 (a), the Raman spectrum of 10%Mn- CeO_2 shows one main band for CeO_2 at 454 cm^{-1} attributed to the stretching mode of the Ce-O lattice due to a vibration mode of $F2g$ symmetry. It also reveals a main band for MnO at 643 cm^{-1} attributed to the stretching mode of the Mn-O lattice.²¹ The two Raman bands observed for the

10%Fe-CeO₂ sample at 325 and 629 cm⁻¹ are due to γ -Fe₂O₃ species.²² Several Raman bands related to cobalt oxides were identified using Raman spectroscopy shown in Figure 4 (c), which could not be directly detected from XRD measurement in the 10%Co-CeO₂ sample. They can be assigned to the cobalt oxides according to the literature,²³ suggesting the existence of small well dispersed CoO_x on CeO₂. Similarly, the bands at 229, 547, and 629 were assigned to the NiO species for the 10%Ni-CeO₂ sample in Figure 4 (d). No new Raman band was observed for the 10%Cu-CeO₂ sample except for the peak shift. This peak shift may result from the formation of solid solution of Cu-CeO₂, as shown in the XRD measurements with an evidence of diffraction peak shifting to low angles. It is important to note that several TM oxides were not detected from XRD analysis, but they show a relatively strong oxide Raman band, indicating the existence of small well dispersive TM oxides on the CeO₂ nanorods. Due to the larger contact area with the CeO₂ support, these small species could significantly contribute to the reduction processes in H₂-TPR of CeO₂ and in CO oxidation reaction.

Figure 4. Raman spectra of CeO₂ nanorods supported TM catalysts.

H₂-TPR Characterization of CeO₂ Nanorods-Supported TM Catalysts

After the addition of the transition metals onto the CeO₂ support, the reducibility or H₂ consumption of the CeO₂ nanorod supported TM catalysts was determined by H₂-TPR. For the pure CeO₂ nanorod sample, H₂-TPR shows two distinctive reduction peaks, corresponding to surface reduction at 502 °C and bulk reduction at 836 °C, shown in Figure 2 (d). Figure 5 clearly indicates that the reduction temperature was lowered significantly for all the CeO₂ nanorods supported TM catalyst samples as compared to pure CeO₂. All the peaks are relatively weak in the 10%Mn-CeO₂ and 10%Fe-CeO₂ samples indicating low H₂ consumption. For the 10%Mn-CeO₂ sample, XRD shows a mixture of CeO₂ and cubic MnO phases. Manganese oxides undergo successive reduction steps during the H₂-TPR experiment: $Mn_2O_3 \xrightarrow{350\text{ }^\circ\text{C}} Mn_3O_4 \xrightarrow{470\text{ }^\circ\text{C}} MnO$.²⁴ It was reported that detectable H₂ consumption is not observed for MnO up to 617 °C from a H₂-TPR study.²⁵ As a consequence, the reduction peaks in Figure 5 at 197 °C and 328 °C should be attributed to the formation of MnO modified CeO₂ or CeO₂-MnO solid solution. It was

reported that the incorporation of small amounts of manganese oxide (15 mol%) in CeO₂ led to the formation of homogeneous solid solutions with a cubic structure of CeO₂,²¹ resulting in an improved low temperature reducibility of the material. This is consistent with the observation of peak shifting to the low diffraction angle of the XRD pattern of 10%Mn-CeO₂ sample in Figure 3 (a). For the 10%Fe-CeO₂ sample, XRD shows a mixture of CeO₂ and γ -Fe₂O₃ phases in Figure 3 (b). Iron oxides undergo successive reduction steps during the H₂-TPR experiment: $Fe_2O_3 \xrightarrow{379\text{ }^\circ\text{C}} Fe_3O_4 \xrightarrow{592\text{ }^\circ\text{C}} Fe \text{ or } FeO + Fe$.²⁶ In accordance with these reduction steps, the low-temperature peaks at 197 °C and 328 °C can be assigned to the reduction of Fe₂O₃ to Fe₃O₄ and Fe₃O₄ to Fe or Fe and FeO, respectively, while the high-temperature peak at 657 °C is due to the reduction of CeO₂-rich solid solution phase. In comparison with other samples, the 10%Mn-CeO₂ and 10%Fe-CeO₂ samples have low H₂ consumption below 350 °C. This would also explain their poor behavior in CO oxidation shown later.

Figure 5. H₂-TPR profiles of CeO₂ nanorods supported TM catalysts.

Both 10%Co-CeO₂ and 10%Ni-CeO₂ samples show a lower reduction peak at 270 °C and 210 °C, respectively. This can be explained by the presence of Co and Ni on the CeO₂ nanorod surface, which acts as a catalyst in the CeO₂ reduction leading to a shift of the H₂ consumption peaks to lower temperatures.^{27,28} The 10%Cu-CeO₂ sample shows three consecutive peaks at 135 °C, 154 °C, and 180 °C. From the XRD pattern in Figure 3 (e), only trace amounts of the CuO phase were detected after the reduction treatment at 600 °C under a 5%H₂/95%He gas atmosphere, so these low temperature peaks (Figure 5 (e)) should mainly be associated with the synergistic effect of copper species and CeO₂ support.²⁹ For the CuO-CeO₂ catalysts, the literature states these low temperature TPR peaks were attributed to finely dispersed CuO interacting with CeO₂ and larger CuO particles, respectively.³⁰⁻³³ Although only a trace amount of CuO was detected from the XRD analysis shown in Figure 3 (e), the presence of CuO on CeO₂ significantly changes the reducibility of the catalyst. The strong metal-support interaction (SMSI) between CuO and CeO₂ are believed to change the reduction temperature. The TPR results indicate that the CeO₂ nanorods

supported Cu catalyst had a superior temperature reducibility and H₂ consumption than the other TM-CeO₂ catalysts studied.

The BET surface area of the CeO₂ nanorod-supported metal catalysts is in the range of 10-55 m²/g, as shown in Table 1. From the H₂-TPR results in Figure 5, it could be concluded that the order of the first reduction temperature, reflecting the feasibility of oxygen activation, was established: Cu-CeO₂<Mn-CeO₂<Ni-CeO₂<Co-CeO₂<Fe-CeO₂. Meanwhile, the H₂ consumption order below 500 °C, corresponding to the amount of oxygen reacted, was identified as: Cu-CeO₂>Co-CeO₂>Ni-CeO₂>Fe-CeO₂>Mn-CeO₂, shown in Table 1.

Table 1. BET surface area and H₂ consumption during the H₂-TPR experiments of CeO₂ nanorods supported TM catalysts.

	Sample Mass (mg)	BET surface area (m ² /g)	Peak area (RT~500°C)	H ₂ consumption (RT~500°C) (μmol/g)
10%Mn-CeO ₂	98.1	51.6	5.34	1187.8
10%Fe-CeO ₂	94.5	10.4	6.18	1427.0
10%Co-CeO ₂	97.5	27.2	7.51	1680.7
10%Ni-CeO ₂	96.5	37.6	6.78	1533.0
10%Cu-CeO ₂	84.0	36.0	9.12	2369.0

Catalyst Activity Test for CO Oxidation

The catalytic activity for the CO oxidation of the different TM (Cu/Ni/Co/Fe/Mn) supported on CeO₂ nanorods was tested at different temperatures up to 350 °C, as shown in Figure 6. It was observed that the 10%Cu-CeO₂ catalyst performed best. It provided a lower light-off temperature, and a 100% conversion of CO to CO₂ at 194°C. 10%Co-CeO₂ catalyst shows a slightly better performance compared to the 10%Ni or the 10%Mn-CeO₂ catalysts. On the other hand, 10%Fe-CeO₂ sample appeared to be less active when compared to other samples. This may be due to the incomplete reduction of Fe₂O₃. Another possibility for the low activity of 10%Fe-CeO₂ sample could be due to more severe agglomeration after the impregnation of Fe, since the agglomerated powder sample of Fe was very hard to grind to a fine powder. Figure 7 shows the TEM image and EDX spectrum of 10% Fe-CeO₂ nanorods sample, indicating a significant agglomeration of particles. The activities of the catalysts are compared as follows based on the T50 and T100 (the temperatures where 50% and 100% CO conversion are achieved): CuT50 (75 °C)<CoT50 (141 °C)<MnT50 (173 °C)<NiT50 (176 °C)<FeT50 (264 °C); CuT100 (194 °C)<CoT100 (236 °C)<NiT100 (273 °C)< MnT100 (289 °C)<FeT100 (N/A). The highest CO conversion for the 10%Fe-CeO₂ catalyst was about 60% up to 350 °C. All samples clearly present superior catalytic activity to the previously reported CeO₂ particle supported TM catalyst.³⁴⁻³⁶ This may be due to the CeO₂ support effect. Based on the H₂-TPR study, CeO₂ nanorods typically show better low temperature reducibility compared to the CeO₂ nanocubes and nanoctahedra.

Figure 6. CO conversion of CeO₂ nanorods supported TM catalysts.

Table 2. CO conversion of CeO₂ nanorods supported TM catalysts.

	Mass (mg)	BET surface area (m ² /g)	T50 (°C)	T100 (°C)
10%Mn-CeO ₂	28.3	51.6	173	289
10%Fe-CeO ₂	28.0	10.4	264	-
10%Co-CeO ₂	28.5	27.2	141	236
10%Ni-CeO ₂	28.9	37.6	176	273
10%Cu-CeO ₂	28.6	36.0	75	194

(a) TEM image

(b) EDX spectrum

Figure 7. TEM image (a) and EDX spectrum (b) of 10% Fe-CeO₂ nanorods.

TEM Analysis

The segregation of Cu species (Cu or CuO_x) from the CeO_2 nanorods are clearly observed in the TEM images of 10%Cu- CeO_2 sample shown in Figure 8 (a) and (b). The rod structure of CeO_2 did not collapse after the impregnation of copper and heat treatments (oxidation at 400 °C for 5 hrs and reduction at 600 °C for 5 hrs), however, the rods become shorter. According to HRTEM analysis based on the lattice fringe measurement, it is important to note that the CeO_2 nanorods expose the {111} surfaces (Figure 8 (c)), conforming to the $d_{(111)}=3.12\text{\AA}$ in the JCPDS 34-5134 database. This observation is different from previously reported results that nanorods are elongated along the <110> direction and expose two {011} and two {001} surfaces.¹¹⁻¹² In addition, although some single crystalline nanorods were found, the majority of the nanorods exhibited relatively rough surfaces with significant surface defects (Figure 2 (e) and Figure 8 (d)). For gas adsorption and the metal-oxide support interaction, it is much more efficient if the rough and “defected” surface is used instead of a smooth one. In addition to a higher surface area, the rough surface of CeO_2 nanorod support also leads to more catalytic sites and thus to higher activity. This might be a critical reason for the improved low temperature performance of CeO_2 nanorods-supported TM catalyst.

Figure 8. TEM and HRTEM images of 10%Cu- CeO_2 nanorods catalysts

Conclusions

The support shape and surface defects of the CeO_2 in TM- CeO_2 catalysts have a dramatic effect on its ability to oxidize CO to CO_2 . All CeO_2 nanorods supported TM catalyst show a significantly improved low temperature catalytic activity for CO oxidation. The Cu- CeO_2 sample performed best for both H_2 consumption and CO oxidation.

Based on the Raman analysis and high resolution TEM study, the two possible reasons to explain the enhanced activity were identified: (a) creation of oxygen vacancies and CO adsorption sites through defected surfaces on CeO_2 nanorods and (b) formation of a solid solution at the metal-oxide interface, resulting in increased oxygen mobility.

Acknowledgements

This work is supported by the National Science Foundation (NSF CHE-1362251) and the American Chemical Society Petroleum Research Fund (#52323). We thank Samuel Mutinda for the help of the TPR experiment. And the use of TEM facilities at the Center of Excellence in Materials Science and Engineering at Youngstown State University are gratefully acknowledged.

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