Nanocrystalline Ceria-based Catalysts for Water-gas Shift

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Introduction:

Water-gas-shift is a mature industrial process, which is applied in the production of hydrogen for ammonia synthesis and for adjusting the CO/H_2 ratio for the subsequent synthesis of methanol. Presently, there is a renewed interest in the water gas shift reaction because of its potential use in conjunction with fuel cell power generation. Advanced catalysts for the water-gas shift reaction are being actively sought by the developers of fuel cells.

From the review of the water-gas shift reaction literature, cerium oxide-based catalysts are singled out as very promising for both low- and high-temperature application. Cerium oxide can supply its surface oxygen, thus catalyzing a variety of oxidation reactions, including WGS. Nanocrystalline ceria is much more reducible than well-crystallized materials [1]. The addition of platinum metals, gold and base metal oxides, such as copper oxide, can significantly enhance the reducibility and WGS activity of ceria [2-5]. Dopants such as La or Zr oxides are added to ceria to suppress its crystal growth at high temperatures, and to also increase its reducibility.

Preparation, characterization, and catalytic properties of Cu_xO- or Au- ceria catalysts prepared as nanostructured materials are reported in this paper. Catalysts were characterized by XRD, XPS, STEM/EDS, HREM, TPR, and oxygen storage capacity (OSC) measurements.

Experimental:

Catalyst preparation Bulk doped or undoped ceria and Cu_xO-ceria were synthesized by the urea gelation/coprecipitation method (UGC), as described in detail elsewhere [3]. The cerium salt used in UGC is $(NH_4)_2Ce(NO_3)_6$. In brief, aqueous metal nitrate solutions were mixed with urea and heated to 100 ^oC under vigorous stirring and addition of deionized water. The resulting gel was aged for 8 hours at 100 ^oC; after aging, the precipitate was filtered and washed. Further, the precipitate was dried at 100-120 ^oC and calcined in static air at 400 ^oC for 10 h or 650 oC for 4 h. A slow heating rate, 2 ^oC/min, was used to reach the desired calcination temperature. In all preparation methods used in this work, the same heat treatment procedure was followed.

Gold-ceria samples were prepared by coprecipitation (CP) and by deposition precipitation (DP) of gold on ceria made by the above UGC method. The CP method involves mixing an aqueous solution of $HAuCl_4$, cerium (III) nitrate and lanthanum nitrate with $(NH_4)_2CO_3$ at 60-70 ^oC, keeping a constant pH value of 8 and aging the precipitate at 60-70 ^oC for 1h. Deposition-precipitation took place by adding the desired amount of $HAuCl_4$ dropwise into an aqueous slurry of the prepared ceria. The pH of the aqueous slurry had already been adjusted to the value of 8 using $(NH_4)_2CO_3$. The resulting precipitate was aged at room temperature for 1h. A few gold-ceria samples were prepared by UGC, following the procedure described above.

Catalyst characterization The total sample surface area was measured by single-point BET N_2 adsorption/desorption on a Micromeritics Pulse ChemiSorb 2705.

X-ray powder diffraction (XRD) analysis of the samples was performed on a Rigaku 300 X-ray Diffractometer with Rotating Anode Generators and a monochromatic detector. Copper K_a radiation was used. High-resolution transmission electron microscopy (HREM) performed on a JEOL 2010 instrument with an ultimate point-to-point resolution of 1.9 Å and lattice resolution of 1.4 Å. A Kratos AXIS Ultra Imaging X-ray Photoelectron Spectrometer with a resolution of 0.1 eV was used to determine the atomic metal ratios of the surface region and the metal oxidation state of selected catalysts.

Activity tests Water-gas shift reaction tests were performed in a quartz-tube flow reactor. A simulated reformate feed gas mixture was used containing 11% CO, 11% CO_2, 26 % H_2, and 26 % H_2O in helium. The reactant and product gas streams were analyzed using a HP-6890 gas chromatograph equipped with a thermal conductivity detector (TCD).

Temperature-programmed reduction (TPR) Temperature-programmed reduction (TPR) of the as-prepared catalysts in fine powder form was carried out in a Micromeritics Pulse ChemiSorb 2705 instrument. The gas streams were monitored by TCD for H_2-TPR, while a mass-spectrometer (MKS-model RS-1) is used in CO-TPR. A 20% H_2/N_2 or 10%CO/He gas mixture (50 cm^3/min (NTP)) was used as reducing gas. The sample was heated at a rate of 5 °C/min from room temperature to 900 °C.

Oxygen storage capacity (OSC) measurements Oxygen storage capacity measurements were carried out in a flow reactor system, equipped with a switching valve for rapid introduction of step changes in gas streams of CO/He, He, and O_2/He. A total gas flow rate of 50 cm^3/min (NTP) was used. The sample was exposed to 10% CO/He and 10% O_2/He step changes at the desired test temperature. The steady-state signals of CO, CO_2 and O_2 were detected by mass spectrometry.

Results and Discussion:

The backbone of the catalyst is ceria, while the metal or metal oxide is the minor phase. The amount of La or Zr oxide used as dopant in ceria, was varied from 10 to 30 at. %. Physical properties of some materials are listed in **Table 1**.

As shown in **Table 1**, the ceria lattice parameter α increases with La content, while it decreases when Zr is used as dopant. The addition of copper oxide also decreased the lattice parameter of ceria.

Table 1. Physical properties of as-prepared materials

(Prepared by urea coprecipitation/gelation method, calcined at 400 ^oC)

Sample	BET S. A. (m^2/g)	CeO_2 lattice parameters α (Å)	CeO_2 particle size (nm)	
			<111>	<200>
CeO_2	140.5	5.417	6.2	5.5
$Ce(10La)O_x$	161.6	5.435	5.1	4.8
$Ce(30La)O_x$	175.0	5.461	4.3	3.9
$Ce(30Zr)O_x$	169.1	5.364	4.1	3.7
$10CuCeO_x$	177.7	5.417	4.8	4.5
$10CuCe(10La)O_x$	200.3	5.419	4.0	3.5
$10CuCe(30La)O_x$	176.1	5.422	4.3	3.3
$10CuCe(30Zr)O_x$	168.0	5.352	4.2	3.9
$0.5AuCe(10La)O_x$	--	5.432	4.2	3.8
$5AuCe(10La)O_x$	--	5.438	4.5	4.1
$10AuCe(10La)O_x$	158.1	5.439	4.5	4.4

The surface oxygen of ceria is substantially weakened by gold or copper oxide as found by H_2-TPR, **Figure 1**. OSC measurements using step pulses of CO were in agreement with the TPR results; the presence of gold or copper oxide greatly enhances the OSC of ceria, **Figure 2**. Carbon-containing species left on the

surface after the CO step, can be fully removed with O_2 or partially removed with H_2O [5].

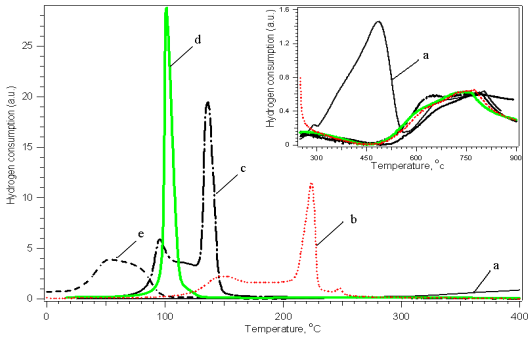

Figure 1. (a) CL (UGC) (b) 5Cu-CL (UGC); (c) 10Cu-CL (UGC); (d) 8Au-CL (UGC); (e) 4.5Au-CL(DP); all materials calcined at 400 °C, 10 h

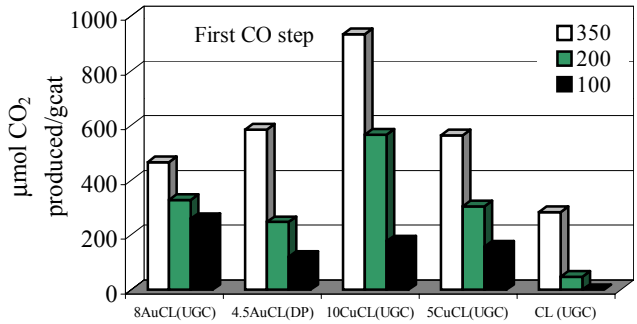

Figure 2. OSC of ceria-based catalysts at three different temperatures 350 °C, 200 °C and 100 °C; 10%CO/He, 10%O_2/He, 50cm^3/min (NTP), all materials calcined at 400 °C, 10 h;
CL: Ce(10La)O_x

The amount of CO_2 produced during the CO and O_2 steps in OSC is a strong function of the type of dopant used in ceria. This is shown in **Figure 3**.

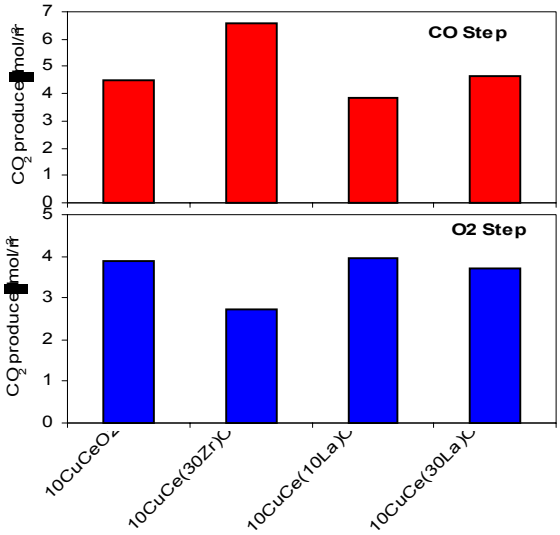

Figure 3. OSC of ceria-based catalysts with different dopants at 350 °C; 10%CO/He, 10%O_2/He, 50cm^3/min (NTP), all materials calcined at 400 °C, 10 h.

WGS rate measurements were conducted with simulated reformate gas mixtures. In 11%CO-7%CO_2-26%H_2O-26%H_2-He gas mixture, at 250 °C, the rate over 5-8%Au-ceria(La)O_x catalysts is 6-9 µmol/gcat*sec, while that over 10%CuCe(La)O_x is 3.2 µmol/gcat*sec. At 350 °C, the WGS reaction rate over the same gold and copper-ceria catalysts is 22-47.5 and 31 µmol/gcat*sec, respectively, **Figure4.**

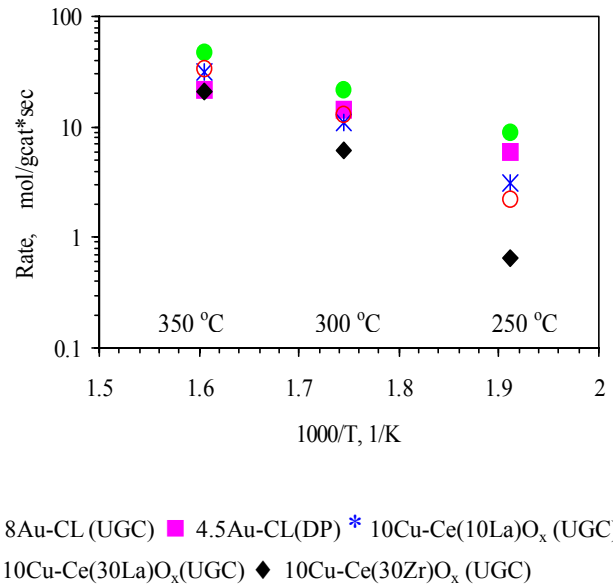

Figure 4 WGS rate over various ceria-based materials calcined at 400 °C, 10h; Simulated reformate gas mixture: 11% CO /7% CO_2/ 26% H_2 /26% H_2O /He

Conclusions:

Nanocrystalline ceria-based materials are active water-gas shift catalysts. Activity and reducibility greatly depend on the structural properties of these materials.

Acknowledgement:

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