Flowerlike Ceria Microspheres Materials for Bioethanol-H_2 Production and VOCs Decontaminatio

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ABSTRACT

Herein, we introduce a novel material of flowerlike mesoporous CeO_2 microspheres with nanointerspace, which was a kind of multifunctional material for both clean and renewable energy technologies. Catalyst of nickle oxide based on flowerlike cerium microspheres with high dispersion was made to achieve simultaneous dehydrogenation of ethanol and water molecules on multiactive sites. This special morphology catalyst represented novel stability more than 2000 h for hydrogen production at low temperature ethanol steam reforming. And, the molecules of poisonous volatile organic compounds (VOCs) such as benzene, HCN and so on could be adsorped chemically by this CeO_2 microspheres based materials easily at room temperature. And, carbon monoxide could be converted to carbon dioxide lower than 100°C by this CeO_2 microspheres based materials, without rare metals.

Keywords: Flowerlike ceira microspheres, bioethanol-H_2 production, steam reforming, VOCs Decontamination

1 INTRODUCTION

Energy and environment have been the most serious two problems all over the world. Hydrogen energy is now one of the important clean renewable energies in 21's century. More and more government and scientists become to fous on how to develop hydrogen production technology of high effciency and low energy consuming. There are many hydrogen production methods, such as catalytic reforming of alcohols, hydrocarbons and biomass, using solar energy to photolyse water, electrolyse water, and so on.

Biomass ethanol as a hydrogen source fuel has many advantages of that it is renewable, it operates in a closed carbon loop, thus it involves no net CO_2 emissions into the atmosphere. So, ethanol is safe and non-toxic as well as environmentally friendly. Furthermore, the infrastructure of petroleum transportation and gas station can be used by ethanol fuel [1,2].

We all know that rare earth metal oxides was of high alkaline and was favorable for dehydrogenation of alcohols. Reactions of ethanol over M/CeO_2 catalysts [2,3] have been studied. Ni/La_2O_3 catalyst had been previously found to exhibit good performance under conditions (800^oC) of reforming of methane with carbon dioxide, and to be very active and stable for the steam reforming of ethanol under certain operating conditions (above 300^oC) [4]. Nanocrystalline rare earth oxides had showed improved and size-dependent properties [6,7]. Actually, mesoporous ceria had shown great potential as versatile catalysts and catalyst supports due to their 3D surface and increased dispersion of active secondary components [8-10]. The work in this paper showed mesoporous flowerlike ceria microspheres did possess and advance the above advantages greatly.

2 EXPERIMENTAL

2.1 Catalyst preparation

In a typical synthesize experiment, glucose was dissolved into deionized water with magnetic stirring, which was followed by addition of acrylamide and hydrated cerium(III) nitrate to form a transparent solution. Then ammonia solution was added to the solution dropwise with stirring. This solution mixture was stirred for 5 h before being transferred into an autoclave. Then the autoclave was sealed and kept at 180^oC for 72 h in an electric oven. After that, the autoclave was cooled to room temperature naturally [10]. After abruption, washing, drying and calcination, the flowerlike CeO_2 microspheres were finally obtained. Nickel oxide was deposited from oxalate solutions on the active CeO_2 supports to form the NiO/ CeO_2 microspheres [4], then NiO/ CeO_2 microspheres were dipped on quartz ball carrier with 15.0 percent.

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2.2 Characterization of materials.

The phases and purity of the products were examined by X-ray powder diffraction (XRD) performed on Rigaku X-ray diffractometer with Cu Kα radiation (Japan, Rigaku, D/max-RB). The morphology of the products was observed by a scanning electron microscope (SEM, XL30s-FEG, 10 kV). TG-DSC-MS curves, on the flowerlike NiO/CeO_2 catalyst experience 1000h long-term stability test, were recorded by a NETZSCH STA 449 C instrument combined with a Balzers MID instrument, and a protective gas, Ar; range, 30/10(^oC/min)/800. Raman dispersion spectra was recorded on a Bruker SENTERRA spectrometer between 4500 ~ 20 cm^{-1}.

2.3 Ethanol steam reforming

Ethanol steam reforming test was carried out on a self-built system. Ethanol-water vapor mixtures were injected into a tube (with inner dia. 8 mm) through an electronically controlled sprayer-slide that sprayed small droplets onto the wall of the tube, preheated to 200^{o}C. This produced rapid vaporization, and that mixed solution to mixed vapor then to products exiting the catalyst bed in less than 36 ms.

Products were analyzed by a gas chromatography Angilent 7890A with 2 TCDs, with mass balance within 0.1%. All activity experiments were run for up to 80-100 h on a given catalyst, and then stability experiments were carried out after the activity tests.

3 RESULTS AND DISCUSSION

3.1 Catalysts characteristics

Fig. 1 (1) and (2) showed the XRD patterns of NiO based on flowerlike CeO_2 support and pure flowerlike CeO_2 microspheres respectively. The peaks labeled with the symbol "•" are corresponding to the diffraction of NiO, and peaks with symbol "○" are corresponding to the diffractions of CeO_2. There is no new peak appeared in the XRD patterns of NiO/CeO_2, meaning that the catalyst was just the mixture of nickel oxide and CeO_2 and no new phase was formed. From the diffraction peaks of NiO(111), CeO_2 (200), the crystal grain sizes of nickel oxide and CeO_2 of the catalyst, calculated with Scherrer formula, were 11.8 nm and 7.9 nm, respectively.

As Fig. 2 showed, the size and morphology of the support and supported catalyst were examined by FESEM. Fig. 2A and B showed CeO_2 particles are nearly monodisperse spherical particles with flowerlike texture. The average diameter of the microspheres is 2-4 µm, it can be seen that these flowerlike microspheres are composed of many nanosheets as the petals with an average thickness of about 20–30 nm and these nanosheets interweave together forming an open porous structure. Fig. 2C and D showed NiO particles are loaded dispersively on the flowerlike microspheres supports.

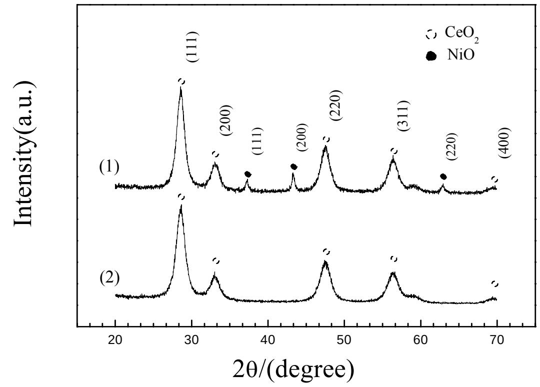

Figure 1: XRD of the sample of special flowerlike microsphere NiO/CeO_2 catalyst.

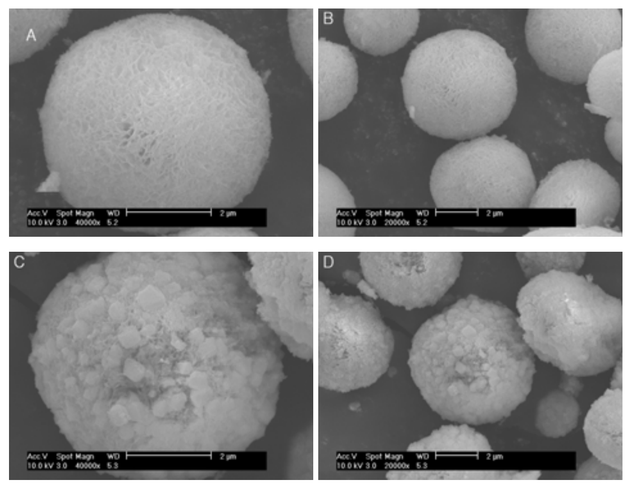

Figure 2: FESEM images of the flowerlike CeO_2 microspheres, and NiO/CeO_2 catalyst: (A, B) high and low magnification FESEM images of CeO2 flowerlike microspheres, respectively; (C, D) high and low magnification FESEM images of NiO particles supported on an individual CeO_2 microsphere, respectively.

3.2 Activity, selectivity and stability of ethanol steam reforming for H_2 production

Ethanol conversion (C_E) and product selectivity (S_P) weredefined as the same in literature [4]. Typical results of ethanol reforming stability on this special NiO–ceria catalyst were shown in Fig. 3, in which the selectivity of each product and the conversion of ethanol were shown as a function of reaction time of 2000 hours at 350^{o}C. These experiments were done at a mixed solution flow rate of 0.05 ml min^{-1} (total mixed vapor flow rate of 6.8 standard liters/min [gas hourly space velocity (GHSV)~1.0×10^5 h^{-1}]), with preheating to 200^{o}C.

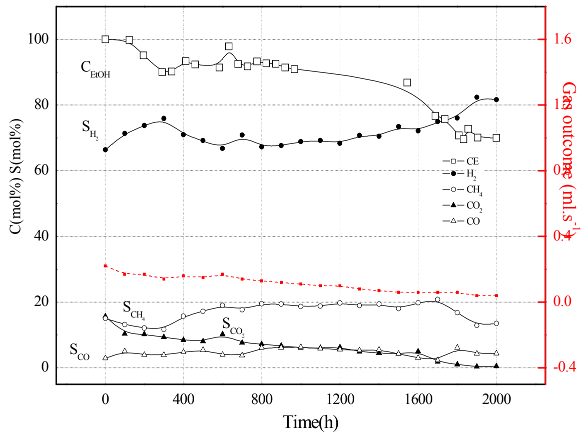

Figure 3: Typical curves of ethanol steam reforming on flowerlike NiO-ceria microsphere catalyst: Conversion of ethanol (C_{EtOH})and selectivity of products of H_2 (S_{H2}), CO (S_{CO}), CO_2 (S_{CO2}), and CH_4 (S_{CH4}) obtained over the special catalyst NiO/CeO_2 as function of time-on-stream. Experimental conditions: mass of catalyst 0.55 g, H_2O/ EtOH mol ratio R = 3:1, liquid flow rate 0.05 cm^3 min^{-1}, gas hourly space velocity (GHSV)~1.0×10^5 h^{-1}, P = 1 atm, keep T=350^{o}C.

When used in steam reforming of ethanol for producing H_2, these CeO_2 microspheres based NiO catalyst show excellent catalytic properties [11]. The stability of this special morphology catalyst NiO/CeO_2 with time-on-stream was examined at temperature of 350^{o}C considering to combine the WGS reaction with the steam reforming reactions to increase H_2 and eliminate CO selectivity.

It was really excited that the stability test of this special morphology catalyst exceed 2000 h stability test at 350^{o}C. The relationships of selectivity of each product and conversion of ethanol with time-onstream over catalyst NiO/CeO_2 were shown in Fig. 3. Under the experimental conditions, the conversion of ethanol was of 100 mol.% at the first 100 h, then decreased very slowly with an average ethanol conversion of 93.1 mol.% at the range of 100–1400 h, while decreased to 86.8 mol.% to 1600 h, the whole average value is 87.0 mol.% in 2000h.

The selectivity of H_2 was average above of 71.8 mol.% all over the 2000h. The selectivity of CO was much balanced and averaged at 4.7 mol.% during the whole stability test. The outlet velocity of products gas kept stable during the first 600 h and then slowly down (dash line as shown in Fig. 3). The above results means very good activity and stability of NiO/CeO_2 catalyst with flowerlike active support for ethanol steam reforming, which were much better than Ni/Al_2O_3 and common morphology nickle-lanthumum oxide [4] in low temperature domain (250–350^{o}C), and stability was also much better than the nano-sized ball like nickle–cerium. One important reason that enhanced catalytic activity and stability of the flowerlike Ni/CeO_2 catalyst for ethanol steam reforming should be the flowerlike supports beneficial for gas transport due to its open 3D porous structure and its double pore sizes distribution [10].

3.3 Ability to resist coke formation

This novel flowerlike Ni/CeO_2 catalyst also has outstanding ability to resist coke formation, which was proved by TG-DSC-MS test. As Figure 4 TG-DSC-MS curves showed, from MS curves, only found CO_x products during the tests indicated that the lost was C; TG curve showed when temperature incerased to 642^{o}C, the largest gravity lose, about 43.3% weight was lost, the carbon deposition was calculated as 0.655mg.g^{-1} cat.h^{-1}, which was much lower than other values reported; DSC curve showed different format carbon formed when the C deposition occurred on the catalyst.

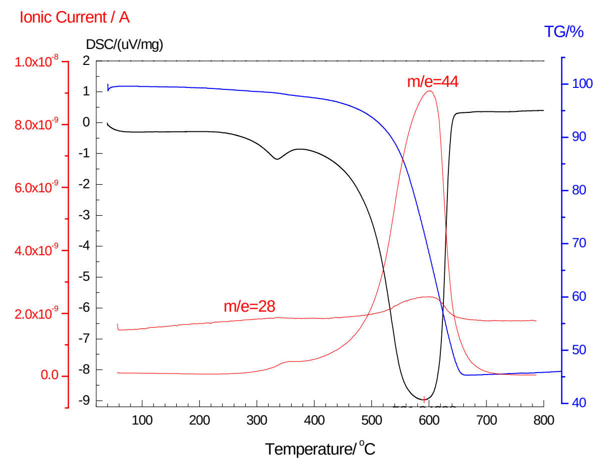

Figure 4: TG-DSC-MS curves, on the flowerlike NiO/CeO_2 catalyst experience 1000h long-term stability test. Protective gas, Ar; range, 30/10(^{o}C/min)/800.

3.4 Ability to VOCs' Decontamination

Ceria (CeO_2) has earned intensive interest in the past decade because it plays a vital role in emerging technologies for environmental and energy-related applications. It is widely used as a promotor in three-way catalysts (TWC) for the elimination of toxic auto-exhaust gases, low-temperature water-gas shift reaction, fuel cells, oxygen sensors, and oxygen permeation membrane systems. Nanaocrystalline CeO_2 has showed improved and size-dependent properties. In particular, nanocrystalline CeO_2 with high surface area and open mesoporous structure is desired for above applications in view of their potential kinetic advantages. Actually, mesoporous ceria has shown great potential as versatile catalysts and catalyst supports due to its high surface area and increased dispersion of active secondary components.

When NiO nanoparticles was loaded and dispersed equably in the petals of this special ceria microsphere, the potential of this catalyst was really advanced strongly. The molecules of poisonous volatile organic compounds (VOCs) such as benzene, hydrocyanic acid and so on could be adsorped chemically by this CeO_2 microspheres based materials easily at room temperature, whereas this chemical adsorption were not observed on the common morphologic ceria particles. Furthermore, carbon monoxide could be converted to carbon dioxide lower than 100°C by this CeO_2 microspheres based materials, without rare metals. In Fig.5, C_6H_6 peak was found obviously at about 1000cm^{-1} in the raman dispersion spectrum of 20-4500cm^{-1}.

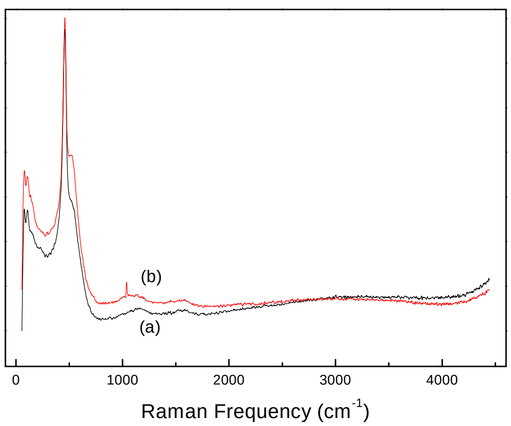

Figure 5: Raman dispersion curves, (a) background ; (b) the pattern of flowerlike NiO/CeO_2 catalyst exposed to saturated C_6H_6 vapor for 10min then desorpted in air for 15min at room temperature.

4 CONCLUSION

Fast and efficient renewable fuel reforming is one of the critical steps in producing H_2 for the hydrogen energy. Ethanol is now the most available and economical renewable fuel. As reported in this paper, the special flowerlike microspheres CeO_2 based catalysts had novel low temperature activation for ethanol steam reforming reactions with high H_2 selectivity, CO elimination, outstanding coke resisted ability and high stability more than 2000 h at 350^{o}C, which make them practical catalysts to be used in ethanol steam reforming processors for many application, such as hydrogen sources for fuel cells, distributed hydrogen station, hydrogen sources for satellitic ground station, and so on.

So, this mesoporous flowerlike ceria microspheres materail possesses huge potential to be a multifunctional material for environment decontamination and hydrogen energy technology. Its application in other aspects was still in research.

ACKNOWLEDGEMENT

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