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Reverse water gas shift over In_2O_3–CeO_2 catalysts

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ABSTRACT

In_2O_3 has been predicted as an excellent catalyst for CO_2 conversion, for both hydrogenation to methanol at low temperature and reverse water gas shift (RWGS), whereas CeO_2 promotes RWGS. In the present work, the promotion effect of CeO_2 on RWGS over In_2O_3 was experimentally investigated. Characterizations show that the surface areas of the In_2O_3–CeO_2 catalysts increase from that of pure In_2O_3 whereas the size of the In_2O_3 particles in the In_2O_3–CeO_2 samples decreases as the fraction of CeO_2 increases. In addition, the presence of CeO_2 helps to create more, and stabilizes, oxygen vacancies, on which the dissociative hydrogen adsorption is enhanced and the amount of bicarbonate species resulting from activated CO_2 adsorption is increased. The synergistic effect between In_2O_3 and CeO_2 makes the In_2O_3–CeO_2 catalysts exhibit enhanced activity for RWGS over the pure In_2O_3.

1. Introduction

CO_2 utilization has attracted much attention worldwide nowadays [1,2]. Several reactions have been exploited for activation and conversion of CO_2 to valuable chemicals and fuel via various catalytic processes, including CO_2 hydrogenation [3,4], CO_2 reforming [5,6], and oxidation using CO_2 as an oxidant [7]. Recently, reverse water gas shift (RWGS) has been considered as a promising process for CO_2 utilization, which provides feedstock for the Fischer-Tropsch synthesis [8–11]. Noble metal-based catalysts are the most commonly used catalysts for RWGS. Continuous efforts have been made toward improving the catalytic activity and CO selectivity [10–12]. Based on the previous experimental and theoretical studies, RWGS reaction is believed to proceed through an oxygen exchange step, i.e., CO_2 is hydrogenated into formate species on the surface of catalyst and the formate species subsequently cleave one of the C=O bonds to form CO [8,12].

Reducible transition oxides can also catalyze hydrogenation of CO_2 and oxygen vacancies play a critical role by accommodating oxygen from C=O bond cleavage [12]. If these oxides are used as the supporting materials or promoters, they are expected to have a significant impact on the activation and conversion of CO_2. Furthermore, the use of metal oxides as catalysts has the potential to reduce, and even replace, the noble metals in catalysts for the reaction.

Recently, we studied the adsorption and conversion of CO_2 over the Al_2O_3, SiO_2, Ga_2O_3 and In_2O_3 based catalysts theoretically and experimentally [4,13–16]. Among those catalysts, In_2O_3 shows the best activity for RWGS. The adsorption of CO_2 on In_2O_3 has an adsorption energy of -1.25 eV, which is significantly more favorable than that on Ga_2O_3 [15]. The O—C—O angel of the adsorbed CO_2 is 126° and the lengths of two C—O bonds are 1.29 Å and 1.28 Å over In_2O_3. Those results indicate that the adsorbed CO_2 on In_2O_3 is significantly more distorted from its gas phase structure, and therefore, highly activated. Moreover, the selectivity of CO from RWGS over both In_2O_3 and Ga_2O_3 is 100% and no CH_4 is produced [16].

We also recently demonstrated that CeO_2 has a promotion effect on RWGS over a Ga_2O_3-based catalyst [17]. It has been shown that the presence of CeO_2 significantly enhances the generation of bicarbonate species during CO_2 adsorption. Furthermore, the presence of CeO_2 also increases the amount of oxygen vacancies on Ga_2O_3 so that more hydrogen can be dissociatively adsorbed and, subsequently, react with the adsorbed CO_2. In the present work, we aim to further improve and optimize the catalytic activities of In_2O_3-based catalysts for RWGS with CeO_2 as a promoter. Characterizations have been conducted to understand how CeO_2 promotes the activation and conversion of CO_2 on In_2O_3.

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2. Experimental

2.1. Catalyst preparation

The pure CeO_2 and In_2O_3 samples were obtained from calcination of cerium nitrate hydrate (99.0%, Kermel, China) and indium nitrate hydrate (99.999%, Alfa Aesar) at 500 °C for 3 h, respectively. To prepare In_2O_3–CeO_2 samples with different CeO_2/In_2O_3 ratios, the co-precipitation method was used. Firstly, a 10 mL solution of cerium nitrate and indium nitrate (20 wt% totally) and a 15 mL solution of Na_2CO_3 (25 wt%) were prepared. Secondly, the mixed nitrate solution was dropped at a rate of 20 drops/min in the three-necked flask with 50 mL deionized water while stirring continuously. At the same time, Na_2CO_3 solution was dropped into the flask to maintain a constant pH of 7 and solid precipitate was obtained. The flask was kept in a water bath at 70 °C. When the dropping was completed, the precipitate was aged for 12 h and then washed 5 times to remove residual Na ions before the precipitate being dried at 70 °C for 12 h and further calcined at 500 °C for 3 h. The In_2O_3–CeO_2 samples have In_2O_3–CeO_2 weight ratios of 75:25, 50:50, 25:75 and 10:90. These samples were designated as Samples A–D, as listed in Table 1. We also calculated the molar fractions of CeO_2 in the mixed oxide samples and present the results in Table 1.

2.2. Thermal gravimetric analysis (TGA)

The TGA analysis for all samples was carried out under a flow of mixed gas (total flow: 25 mL/min, O_2:N_2 = 1:4) at a constant heating rate of 10 °C/min in a Netzsch STA 449 F3 system. The sample (approximately 10 mg) was loaded into an alumina crucible and heated from room temperature to 1000 °C.

2.3. X-ray diffraction (XRD)

The XRD patterns of the samples were recorded on a Rigaku D/Max-2500 diffractometer at a scanning speed of 4°/min over the 2θ range of 10–90°. The diffractometer was equipped with a Ni-filtered Cu Kα radiation source (λ = 1.54056 Å). The phase identification was made by comparing the diffraction patterns with the Joint Committee on Powder Diffraction Standards (JCPDSs).

2.4. High resolution transmission electron microscope (HR-TEM)

HR-TEM measurements were performed on a Philips Tecnai G^2F20 system operated at 200 kV. The sample was suspended into ethanol and dispersed ultrasonically for 15 min. A drop of the suspension was deposited on a copper grid coated with carbon to prepare the sample for TEM analysis.

2.5. Field emission scanning electron microscope (FESEM)

The morphology of the sample was characterized using FESEM (FEI Nanosem430).

2.6. N_2 adsorption–desorption measurements

The measurement was carried out with an Autosorb-1 analyzer from Quantachrome Instruments (AUTOSORB-1-C) using nitrogen adsorption at liquid-nitrogen temperature (77 K). The sample was degassed in situ at 200 °C for 3 h before nitrogen adsorption measurement. The multi-point Brumauer–Emmett–Teller (BET) method was employed to calculate the specific surface areas. The pore size distributions were derived from the isotherms using the BJH model.

2.7. Raman spectra

Raman spectra were acquired using a Renishaw inVia reflex spectrometer with a 532 nm wavelength He–Ne laser and a full-range grating. The beam power is 5 mW and the integration time is 10 s.

2.8. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra were recorded using a BRUKE Tensor-27 spectrometer with a resolution of 4 cm^{-1}. During the FTIR study, the sample was held in an IR cell with CaF_2 windows. The sample was heated in flowing Ar (20 mL/min) over the temperature range from room temperature to 300 °C at a heating rate of 10 °C/min. The sample was held at 300 °C for 1 h and then cooled down to 50 °C before the flowing gas was switched to CO_2 and H_2 (20 mL/min, CO_2:H_2 = 1:1) from Ar for 30 min, and back to Ar (20 mL/min) for 30 min. The entire process was performed under the atmospheric pressure.

2.9. Catalytic activity test

RWGS was conducted under atmospheric pressure in a quartz-tube fixed-bed reactor (i.d. = 4 mm). A catalyst sample of 50 mg was packed into the quartz tube. The reaction started in a gaseous mixture of Ar, CO_2 and H_2 with a volume ratio of 2:1:1 (total flow rate = 40 mL/min) over a temperature range of 250–500 °C. The effluent was analyzed online by a gas chromatograph (Agilent 6890D) equipped with a TDX01 column and a thermal conductivity detector (TCD).

3. Results and discussion

3.1. Catalytic activity

Fig. 1 shows the conversions of CO_2 and H_2 over the pure In_2O_3, the mixed In_2O_3–CeO_2 samples A–D and the pure CeO_2 for RWGS. Obviously, the conversion of CO_2 and H_2 on all samples increases with increasing temperature. Among these samples, pure CeO_2 exhibits no activity until 450 °C. In contrast, there is a significant conversion at the temperature as low as 300 °C on pure In_2O_3. These results are consistent with our previous work [16]. As shown in Fig. 1, conversions of CO_2 and H_2 on Samples A and B are higher

Table 1
Weight ratios, mole ratios and particle sizes according to XRD patterns of all samples.

Sample	Weight ratio (In_2O_3:CeO_2)	Mole fraction of CeO_2 (%)	Particle size (nm)	
			In_2O_3	CeO_2
Pure In_2O_3	1:0	0	28.0	–
Sample A	3:1	21.2	13.8	14.3
Sample B	1:1	44.6	13.3	13.9
Sample C	1:3	70.9	–	12.1
Sample D	1:9	87.7	–	12.3
Pure CeO_2	0:1	100	–	10.4