

CO₂ REVERSE WATER-GAS SHIFT REACTION ON MESOPOROUS M-CEO₂ CATALYSTS

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Mesoporous M-CeO₂ (M = Ni, Co, Fe, Mn, and Cu) catalysts were prepared using the hard-template method and applied to investigate CO₂ reverse water-gas shift (RWGS) reaction. The physicochemical properties were studied using H₂-TPR, XRD, BET, CO₂-TPD, and H₂-TPD. Results show that the specific surface areas of the prepared Ni-CeO₂, Co-CeO₂, Fe-CeO₂, Mn-CeO₂, and Cu-CeO₂ catalysts exceed 120 m²/g. CO₂ RWGS reaction performances are affected by the *d*-orbital holes of transition metals. CO₂ RWGS reaction catalytic activities are ranked as follows: Ni-CeO₂ > Cu-CeO₂ > Co-CeO₂ > Fe-CeO₂ ≈ Mn-CeO₂. The Cu-CeO₂, Fe-CeO₂, and Mn-CeO₂ catalysts maintain 100 % CO selectivity at the studied temperature.

Keywords: mesoporous M/CeO₂ catalyst, carbon dioxide, RWGS reaction, carbon monoxide

INTRODUCTION

The rapid increase in the atmospheric concentration of the major greenhouse gas CO₂ accelerates global warming and triggers a series of serious environmental problems.^[1] This phenomenon has become increasingly severe and has been a global concern because of the large amount of fossil fuel combustion emissions. Therefore, reducing CO₂ emission levels is necessary. However, CO₂ is a cheap, non-toxic, and abundant C1 raw material.^[2] Thus, CO₂ utilization is a promising strategy to mitigate global warming.

Currently employed methods for CO₂ utilization include reverse water-gas shift (RWGS), MeOH synthesis, and methanation. However, a CO₂ molecule is linear with a double bond between the carbon and oxygen atoms (O=C=O), which results in high thermodynamic and chemical stability. Moreover, byproducts can be produced if CO₂ molecules directly react with H₂ to form methane and methanol.^[2] Thus, the CO₂ RWGS reaction is considered the most potential and promising method for CO₂ utilization. CO₂ can be converted into the more active CO via RWGS reaction. Syngas (CO + H₂) can be used to synthesize some important chemicals, such as alkanes, olefin, alcohols, dimethyl ether, gasoline, and acid, via the Fischer-Tropsch reaction.^[3,4,5] Meanwhile, CO₂ RWGS plays a vital role in many chemical processes, such as carbon neutral cycle.^[6,7,8] Thus, improving the efficiency of RWGS is essential.

CeO₂ is a typical rare earth metal oxide that features a face-centred cubic fluorite structure. The surface oxygen of CeO₂ can be reduced to form oxygen vacancies under reduction atmosphere. Oxygen vacancies are crucial in catalytic reactions, especially in the catalytic reduction reaction.^[9,10] Single CeO₂ usually shows a poor catalytic performance in the catalytic reaction. Many studies have also confirmed that the reducibility and forming ability of the oxygen vacancies of CeO₂ can be improved by introducing other metal elements.^[11,12] The introduction of other metal elements can also improve the catalytic activity and selectivity for the corresponding catalytic reaction.^[13] Transition metals (Ni, Co, Fe, Mn, and Cu) can dissolve into the CeO₂ lattice to form a solid solution

and generate oxygen vacancies.^[14] Transition metal oxides can interact with CeO₂ to promote the reducibility of catalyst precursors and improve the catalytic performance of Ce-based catalysts in the catalytic reaction.^[9,15] However, a homogeneous solid solution for the preparation of Ce-based composite oxides cannot be formed by traditional methods. This limitation affects the formation of oxygen vacancies and hinders the formed transition metal oxides from interacting with CeO₂. A homogeneous solid solution can be prepared using mesoporous silica as a sacrificial template.^[14] The hard-template method has been widely used to synthesize metal oxides and composite metal oxide catalysts with a high specific surface area and porous structure.^[16,17] However, few studies have used the hard-template method to prepare mesoporous Ni-CeO₂, Co-CeO₂, Fe-CeO₂, Mn-CeO₂, and Cu-CeO₂ catalysts for the CO₂ RWGS reaction. The goal of this work is to design a catalyst with high activity and selectivity for the CO₂ RWGS reaction.

Mesoporous Ni-CeO₂, Co-CeO₂, Fe-CeO₂, Mn-CeO₂, and Cu-CeO₂ catalysts were synthesized via the hard template method and applied to investigate the CO₂ RWGS reaction. The physical and chemical properties of the prepared mesoporous Ni-CeO₂, Co-CeO₂, Fe-CeO₂, Mn-CeO₂, and Cu-CeO₂ catalysts were investigated using X-ray diffraction (XRD), H₂-temperature programmed reduction (H₂-TPR), Brunauer-Emmett-Teller (BET) analysis, CO₂-temperature programmed desorption (TPD), and H₂-temperature programmed desorption (H₂-TPD).

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Can. J. Chem. Eng. 95:634–642, 2017

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DOI 10.1002/cjce.22730

Published online 21 November 2016 in Wiley Online Library (wileyonlinelibrary.com).

EXPERIMENTAL

Catalyst Preparation

Using the KIT-6 as template, the mesoporous Ni-CeO₂ (NiCE), Co-CeO₂ (CoCE), Fe-CeO₂ (FeCE), Mn-CeO₂ (MnCE), and Cu-CeO₂ (CuCE) catalysts were prepared by the hard-template method. The experimental process has been described in our previous report.^[15] Here, these details are not described. A certain amount of Ce(NO₃)₃ · 6H₂O and Cu(NO₃)₂ · 3H₂O (Ce/Cu mole ratio = 4) was dissolved in ethanol. The KIT-6 mesoporous silica was then added. The mixture was stirred at room temperature until a drying powder was obtained, followed by drying at 100 °C for 12.0 h. The powder was then slowly heated to 400 °C and calcined at that temperature for 2.0 h. The impregnation procedure was repeated once, followed by drying at 100 °C for 12.0 h and calcination at 500 °C for 3.0 h. The resulting sample was treated with NaOH to remove the silica template. Afterwards, the sample was centrifuged, washed several times with water, and then dried. The obtained product was denoted as CuCEO precursor. The CuCEO precursor was reduced by a high-purity H₂ stream at 400 °C for 2 h. The obtained product was denoted as the CuCE catalyst. The Cu(NO₃)₂ · 3H₂O was replaced by Ni(NO₃)₂ · 6H₂O, Co(NO₃)₃ · 5H₂O, Fe(NO₃)₃ · 9H₂O, or Mn(NO₃)₂ (aqueous solution of 50 %), respectively. The prepared process was repeated and the obtained precursors are NiCEO, CoCEO, FeCEO, and MnCEO. The precursors were reduced by high-purity H₂ stream at 400 °C for 2 h. The obtained products were denoted as the NiCE, CoCE, FeCE, and MnCE catalysts. The pure CeO₂ is also prepared by the hard-template method.

Catalyst Characterization

H₂-TPR studies

Hydrogen temperature-programmed reduction (H₂-TPR) was carried out using a conventional apparatus equipped with a TCD detector. In the typical process, 30 mg of the precursor was placed in a U-type quartz tube (4.0 mm ID). Subsequently, TPR was performed by heating the samples from room temperature to 750 °C at the heating rate of 10 °C/min, in the presence of a 5 % H₂/Ar mixture (25 mL/min) flowing.

ICP-MS analysis

Elemental chemical analysis was performed using the inductively coupled plasma-optical (ICP) emission spectroscopy (ICP2060T).

XRD characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/Max-2500/PC diffractometer with a rotating anode using Ni filtered Cu-Kα as radiation source (λ = 0.154 18 nm) at 40 kV of tube voltage and 200 mA of tube current. The diffraction patterns were collected from 20 to 80° at the rate of 5°/min.

BET characterization

The adsorption-desorption isotherms of the samples were collected on a Micromeritic ASAP 2020 automatic analyzer at -196 °C. The samples were degassed under vacuum at 200 °C for 3.0 h prior to the measurement. Based on adsorption data, the Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area.

CO₂-TPD analysis

CO₂ temperature-programmed desorption (CO₂-TPD) was carried out using a conventional apparatus equipped with a TCD

detector. The catalyst (30 mg) was firstly pre-reduced with a 5 % H₂/Ar mixture (25 mL/min) at 400 °C for 1 h. After that, the catalyst was flushed with He flow (25 mL/min) at 400 °C for 30 min, then cooled to room temperature. The catalyst was saturated with 5 % CO₂/He (25 mL/min) at room temperature for 1 h, then flushed with He flow to remove all physical adsorbed molecules. Afterwards, the CO₂-TPD experiment was started from room temperature to 350 °C with a heating rate of 10 °C/min under He flow (25 mL/min) and the desorbed CO₂ was detected by TCD.

H₂-TPD analysis

H₂ temperature-programmed desorption (H₂-TPD) was carried out using a conventional apparatus equipped with a TCD detector. The catalyst (30 mg) was firstly pre-reduced with a 5 % H₂/Ar mixture (25 mL/min) at 400 °C for 1 h, then cooled to room temperature. After that, the catalyst was flushed with Ar flow (25 mL/min) to remove all physical adsorbed molecules. Afterward, the H₂-TPD experiment was started from room temperature to 400 °C with a heating rate of 10 °C/min under Ar flow (25 mL/min) and the desorbed H₂ was detected by TCD.

Catalytic Activity Tests

The CO₂ RWGS reaction was used to investigate catalytic performance of the prepared NiCE, CoCE, FeCE, MnCE, and CuCE catalysts. Before the RWGS reaction, the NiCE, CoCE, FeCE, MnCE, and CuCE catalyst precursors were reduced in situ in an high-purity H₂ stream at 400 °C for 2.0 h and at a heating ramp rate of 10 °C/min, followed by cooling under a H₂ flow to the given temperature. The RWGS catalytic tests of all catalysts were performed at atmospheric pressure in a continuous flow fixed-bed quartz tubular reactor (6 mm i.d.). The quartz tube reactor containing 50 mg catalyst was then placed inside the tubular furnace. The actual reduction and reaction temperatures were measured using a thermocouple which was directly inserted into the catalyst bed and were monitored by a temperature programmable controller (ÜGU, model 708P, China). The reaction temperature ranged from 260 to 400 °C. The feed gas mixture consisting of CO₂ (0.1 L/L), H₂ (0.4 L/L), and Ar (0.5 L/L) was passed through the catalysts at a flow rate of 50 mL/min, which is equivalent to a gas mass space velocity of 60 000 mL/g/h. The CO₂ conversion and production selectivity data were obtained and repeated at given temperature for 120 min. The gas products were analyzed using a packed TDX-01 column with an online gas chromatograph (GC 6890II) equipped with a thermal conductivity detector (TCD). The conversion of CO₂, CO selectivity, and CH₄ selectivity were calculated according to the following equations:

$$\text{CO}_2 \text{ Conversion} = \frac{[\text{CO}_2]_{\text{inlet}} - [\text{CO}_2]_{\text{outlet}}}{[\text{CO}_2]_{\text{inlet}}} \times 100 \% \quad (1)$$

$$\text{CO Selectivity} = \frac{[\text{CO}]_{\text{outlet}}}{[\text{CO}]_{\text{outlet}} + [\text{CH}_4]_{\text{outlet}}} \times 100 \% \quad (2)$$

$$\text{CH}_4 \text{ Selectivity} = \frac{[\text{CH}_4]_{\text{outlet}}}{[\text{CO}]_{\text{outlet}} + [\text{CH}_4]_{\text{outlet}}} \times 100 \% \quad (3)$$

The error bars in the CO₂ conversion and selectivities were calculated according to the standard deviation of the experimental data. It was shown that the results including conversions and selectivities were reproduced at error rates < 2 %.

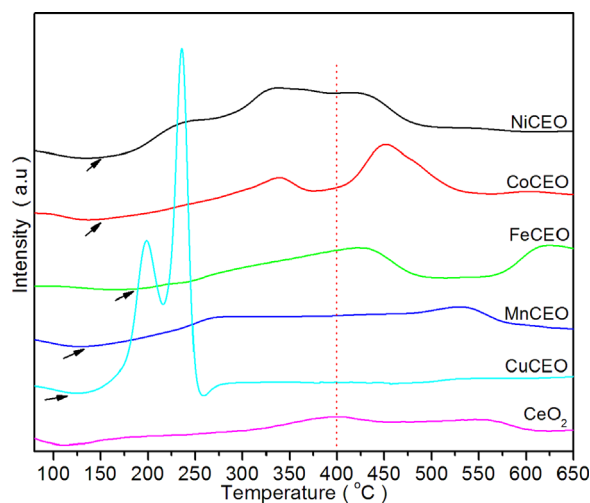


Figure 1. H₂-TPR profiles of the NiCEO, CoCEO, FeCEO, MnCEO, CuCEO precursors and CeO₂.

RESULTS AND DISCUSSION

H₂-TPR Studies

Two obvious peaks can be observed for the NiCEO, CoCEO, FeCEO, MnCEO, and CuCEO precursors (Figure 1). Evident differences can be found in the peak positions, areas, and intensities of the two H₂ consumption peaks of the NiCEO, CoCEO, FeCEO, MnCEO, and CuCEO precursors. The NiCEO precursor shows two reduction peaks at 150–280 °C and 280–400 °C. In addition, a shoulder peak is observed at 400–550 °C. The H₂ consumption peak area of pure CeO₂ is far less than that of the NiCEO, CoCEO, FeCEO, MnCEO, and CuCEO precursors. And two weak H₂ consumption peaks can be observed for pure CeO₂ at about 400 and 560 °C, respectively. The amount of H₂ consumption is calculated by the integrating areas of H₂ consumption peaks and the data are given in Table 1. These results indicate that reducible oxygen species is very little and the reducibility is poor for the pure CeO₂. The excellent reducibility of composite metal oxides can be attributed to the introduction of transition metals. As a result, only a little CeO₂ reduction can be involved in the reduction process of introduced transition metal oxides. Meanwhile, considering the complexity of existence forms and reduction types for introduced transition metal oxides, it is difficult to be accurate in describing the CeO₂ reduction behaviour in the reduction process of the prepared composite oxides precursors. Therefore, these differences in the H₂ consumption peak can mainly be attributed to the different reduction processes of transition metal oxides.^[18] The peak at 232 °C of the NiCEO precursor can be assigned to the reduction of the adsorbed

oxygen.^[9] The peaks at 330 °C and 427 °C can be attributed to the stepwise reduction of NiO (NiO → Ni^{δ+} → Ni⁰) and the quick transition of Ni^{δ+} to Ni⁰. The H₂ consumption peak of the former is stronger than that of the latter, suggesting that NiO can be reduced to a greater degree during the first step.^[9] The peak at 197 °C of the CuCEO precursor can be attributed to the reduction of highly dispersed CuO at the CuO–CeO₂ interface, whereas the peak at 235 °C can correspond to the reduction of CuO in the lattice of CeO₂.^[19] The peaks at 335 °C and 451 °C of the CoCEO precursor can be attributed to the stepwise reduction of Co₃O₄ (i.e. Co₃O₄ → CoO → Co). The peaks at 426 °C and 623 °C of the FeCEO precursor can be assigned to the stepwise reduction of Fe₂O₃ (i.e. Fe₂O₃ → FeO → Fe).^[20] The peak at 266 °C for the MnCEO precursor can be attributed to the reduction of MnO₂/Mn₂O₃ into Mn₃O₄, whereas that at 535 °C can be assigned to the reduction of Mn₃O₄ into MnO.^[21] Hence, CuO species in CuCEO can be completely reduced by H₂ into Cu⁰ at 400 °C for 2 h. The Ni^{δ+} species in NiCEO can be effectively reduced by H₂ into Ni⁰ at 400 °C for 2 h. Partial CoO species in CoCEO can be reduced to Co⁰ by H₂ at 400 °C for 2 h. However, the transition metal oxides of the other precursors can only be reduced into low-valence metal oxide by H₂ at 400 °C for 2 h.

XRD Characterization

Figure 2a shows the XRD patterns of the NiCE, CoCE, FeCE, MnCE, CuCE, and CeO₂ catalysts. Figure 2b illustrates the partially enlarged XRD reflections of these catalysts. The typical eight peaks at 28.56°, 32.98°, 47.48°, 56.30°, 59.31°, 69.15°, 76.96°, and 79.09° are attributed to the *fcc* fluorite CeO₂ phase (JCPDS 34-0394) (Figure 2a). The diffraction peaks corresponding to Cu, Ni, Co, Mn, and Fe metal or oxides phase are not observed, which can be related to low content of transition metals as shown in Table 2 (< 0.15 g/g) or high dispersion. Maybe these species exist but lower than the XRD detection limit (< 0.05 g/g or < 4 nm). Moreover, the XRD peaks of the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts are obviously weaker, wider, and shift to a higher 2θ value compared with those of the CeO₂ catalyst as shown in Figure 2b and Table 2. The results suggest that a part of Ce⁴⁺ in the CeO₂ lattice can be replaced by transition metal ions to form a Ce-M-O solid solution. The extent of the shift of the XRD peaks obviously varies with the introduction of different transition metals. This phenomenon can be attributed to the five studied transition metals with different ionic radii (i.e. Ce⁴⁺ (0.101 nm) > Ni²⁺ (0.072 nm) > Cu²⁺ (0.070 nm) > Fe³⁺ (0.064 nm) > Co³⁺ (0.063 nm) > Mn^{x+} (Mn⁴⁺ = 0.054 nm, Mn³⁺ = 0.066 nm)).^[22] The ionic radius of the studied Mⁿ⁺ is smaller than that of Ce⁴⁺. The replacement of Ce⁴⁺ by Mⁿ⁺ results in unit cell shrinkage and consequently different reductions in the lattice parameters of pure CeO₂ as shown in Table 2. This process causes the

Table 1. Quantitative H₂-TPR, H₂-TPD, and CO₂-TPD analyses of the MCE catalysts and CeO₂

Samples	H ₂ consumption (mmol/g) and TPR peak position (temperature, °C)			CO ₂ desorption (mmol/g) and TPR peak position (temperature, °C)			H ₂ desorption (mmol/g) and TPR peak position (temperature, °C)	
NiCE	3.04 (232)	5.08 (330)	6.20 (427)	0.06 (72)	0.08 (103)	0.23 (143)	0.31 (77)	3.32 (160)
CoCE	3.50 (335)	—	7.16 (451)	0.09 (69)	0.12 (106)	0.44 (143)	—	2.41 (160)
FeCE	7.59 (426)	—	6.28 (623)	0.07 (73)	0.09 (103)	0.27 (143)	—	2.08 (141)
MnCE	4.77 (266)	—	4.71 (535)	0.08 (76)	0.10 (109)	0.37 (149)	—	2.01 (164)
CuCE	6.05 (197)	—	7.41 (235)	0.07 (65)	0.12 (96)	0.76 (150)	0.22 (99)	2.19 (150)
CeO ₂	2.38 (400)	—	1.25 (560)	0.07 (66)	0.10 (97)	0.29 (129)	—	1.98 (130)

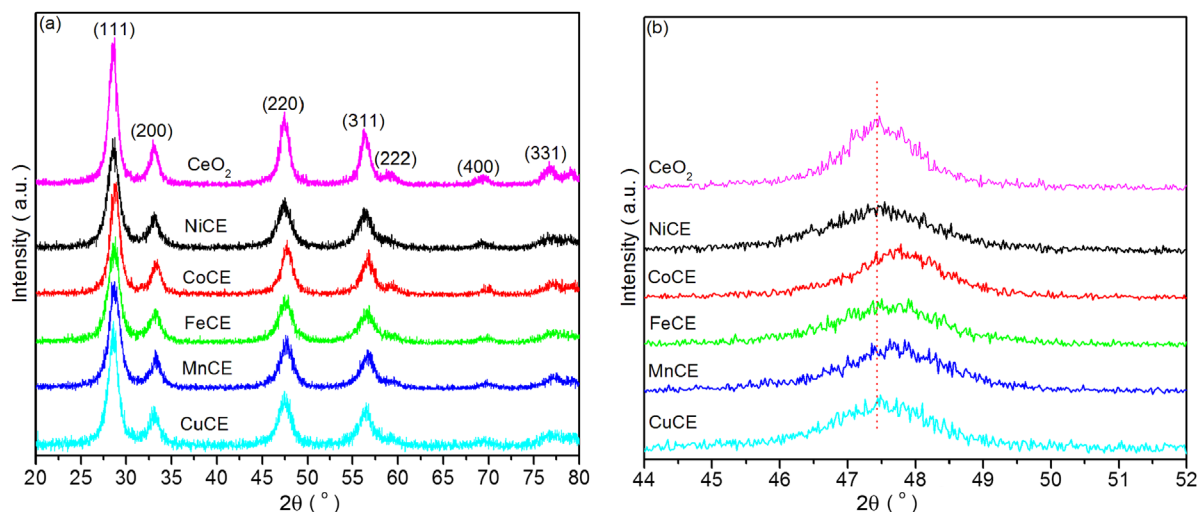


Figure 2. (a) XRD patterns and (b) enlarged XRD reflections of the NiCE, CoCE, FeCE, MnCE, CuCE, and CeO₂ catalysts.

different shifts to higher 2θ values for the formed NiCE, CoCE, FeCE, MnCE, and CuCE catalysts. Ni²⁺ and Cu²⁺ have similar ionic radii and are smaller than that of Ce⁴⁺. The replacement of Ce⁴⁺ by Ni²⁺ or Cu²⁺ results in small unit cell shrinkage, leading to the small incremental shift of the XRD peaks for the formed NiCE and CuCE catalysts. The replacement of Ce⁴⁺ by Co³⁺ results in the large unit cell shrinkage and the large incremental shift in the XRD peak for the formed CoCE catalyst, which can be attributed to the far smaller ionic radius of Co³⁺ compared with that of Ce⁴⁺. The XRD peak of the MnCE catalyst shows less incremental shift compared with that of the CoCE catalyst, which can be attributed to Mn³⁺ replacing a portion of the Ce⁴⁺, except for Mn⁴⁺.^[18] A large amount of the Ce-M-O solid solution is formed by the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts, resulting in charge imbalance in structure and lattice distortion such that the corresponding crystal defects of the catalysts increase. The existence of crystal defects is conducive to reactant molecule adsorption and activation on the corresponding catalysts, effectively improving the catalytic performance of the corresponding NiCE, CoCE, FeCE, MnCE, and CuCE catalysts.

BET Characterization

The nitrogen adsorption-desorption isotherms of the prepared NiCE, CoCE, FeCE, MnCE, and CuCE catalysts shown in Figure 3 are typical type IV with a type-H3 hysteresis loop, suggesting a mesoporous structure. The formation of a hysteresis loop can be attributed to the capillary condensation of the adsorbed N₂

molecules in the mesoporous structure of the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts.^[17] The NiCE and MnCE catalysts have similar adsorption-desorption isotherms. When P/P_0 ranges from 0.50 to 0.75, the adsorption isotherm is convex-shaped and starts to deviate from the desorption isotherm, whereas capillary condensation is obvious at $P/P_0 = 0.75$ –1.00. The FeCE and CuCE catalysts have similar adsorption-desorption isotherms, which are convex-shaped and start to deviate from the desorption isotherm at $P/P_0 = 0.65$ –0.80. Capillary condensation is observed at $P/P_0 = 0.80$ –0.95. The adsorption isotherm of the CoCE catalysts shows a convex shape and starts to deviate from the desorption isotherm at $P/P_0 = 0.70$ –0.80, whereas capillary condensation occurs with $P/P_0 = 0.80$ –1.00. Figure 3b shows the pore size distribution curves of MCE catalysts from the desorption branch of isotherm. The MCE catalysts have a mesoporous structure from the pore size data shown in Figure 3b. Only one narrow peak is observed for each curve, suggesting that the prepared mesoporous MCE catalysts have uniform pore size. The specific surface areas of the NiCE, CoCE, FeCE, MnCE, CuCE, and CeO₂ catalysts, which were obtained using the BET equation, are 146.5, 125.5, 136.1, 149.7, 138.6, and 144.9 m²/g, respectively. The result shows that all samples have large specific surface areas. A large specific surface area can be conducive to reactant molecule adsorption and activation on the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts to improve catalytic reaction. Therefore, the differences in specific surface areas can result in the various catalytic performances of the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts.

Table 2. Metal compositions and physical properties of the MCE catalysts and CeO₂ catalyst

Samples	$n_{\text{Ce}}/n_{\text{M}}$		M content ^a (g/g)	$2\theta_{\text{CeO}_2}$ (°)			Crystallite size ^c (Å)	Lattice parameter (Å)
	Theoretical values	Actual values ^b		(111)	(200)	(220)		
CeO ₂	—	—	—	28.53	32.98	47.39	73	5.7398
NiCE	4	1.86	0.15	28.56	33.17	47.47	48	5.7381
CoCE	4	3.01	0.10	28.88	33.36	47.85	58	5.7015
FeCE	4	2.17	0.12	28.73	33.24	47.65	49	5.7229
MnCE	4	2.55	0.10	28.68	33.28	47.70	49	5.7091
CuCE	4	2.44	0.13	28.62	33.13	47.55	50	5.7304

a and b, values measured by ICP; c, calculation from CeO₂(220) in the XRD pattern using the Scherrere equation

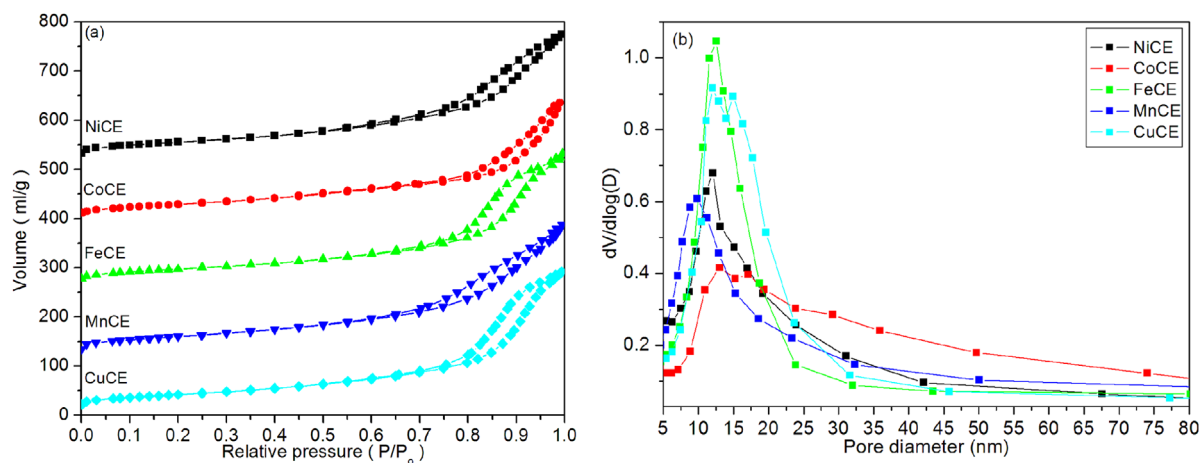


Figure 3. N₂ adsorption-desorption isotherms of the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts.

CO₂-TPD Analysis

Figure 4 shows the CO₂-TPD curves of the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts. Three obvious CO₂ desorption peaks can be observed at 36–90 °C (denoted as α peak), 90–123 °C (denoted as β peak), and 123–300 °C (denoted as γ peak) for the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts. The CO₂ desorption peaks exhibit differences for the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts. The α peaks of the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts appear at 72, 69, 73, 76, and 65 °C, respectively. The α peaks of NiCE and FeCE show smaller peak areas and weaker peak intensities, whereas the CuCE catalyst shows a lower CO₂ desorption temperature. The β peaks of the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts appear at 103, 106, 103, 109, and 96 °C, respectively. The CuCE catalyst shows the largest CO₂ desorption peak area among all the prepared catalysts and a low desorption peak temperature. The γ peaks for the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts are observed at 143, 143, 143, 149, and 150 °C, respectively. For the γ peak, the NiCE catalyst shows the weakest peak intensity and the smallest peak area, whereas the CuCE catalyst displays the largest CO₂ desorption peak area among all of the prepared catalysts. And, the CO₂-TPD profile of pure CeO₂ is also shown in Figure 4 and three CO₂ desorption peaks at about 40–240 °C are observed.

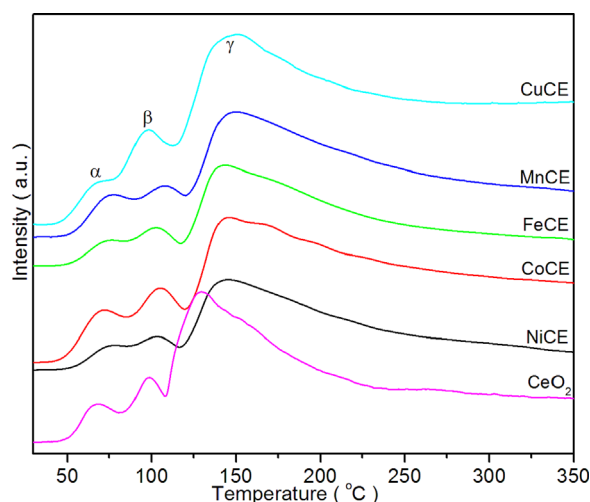


Figure 4. CO₂-TPD curves of NiCE, CoCE, FeCE, MnCE, CuCE, and CeO₂ catalysts.

Information on the type and number of CO₂ adsorption active sites on the surface of the catalysts can be obtained through CO₂-TPD analysis. Three CO₂ desorption peaks can be observed in all CO₂-TPD curves, indicating that the CO₂ adsorption active sites on the surface of the investigated catalysts have three types. CO₂ desorption peaks α , β , and γ can be ascribed to the weak, moderate, and strong adsorption active sites for the CO₂ molecules on the surface of the catalysts, respectively.^[23] As can be seen in Figure 4, CO₂ desorption peaks of pure CeO₂ obviously shift to a lower temperature than that of MCE catalysts, indicating that the introduction of transition metals (Ni, Co, Fe, Mn, or Cu) can improve the adsorption performance of corresponding catalysts for CO₂ molecules. The adsorption ability of the catalysts for reactant CO₂ molecules can affect the catalytic performance of the corresponding catalyst. The adsorption is too weak or strong, which is not conducive to CO₂ activation or suppression in the chemical reaction. The adsorption ability of the catalysts for CO₂ can be changed to different extents by introducing diverse transition metals (Figure 4). Improving the catalytic performance of the corresponding catalysts is important. The adsorption ability of the catalysts for gas species can be identified by the initial desorption temperature and desorption peak temperature of the adsorbed gas species on the catalyst. Catalysts with high initial desorption temperatures and desorption peak temperatures have strong adsorption abilities for the corresponding gas species. The desorption peak temperatures of the low-temperature desorption peak α exhibit the following order: MnCE > FeCE > NiCE > CoCE > CuCE > CeO₂. These results suggest that introducing Mn enhances the adsorption ability of weak adsorption active sites for CO₂ molecules on the surface of the studied catalysts. However, this adsorption ability can be obviously weakened by introducing Cu. Similar rules are followed by the desorption peaks β and γ . Thus, introducing Mn can enhance CO₂ adsorption ability for the MnCE catalyst. However, the strong adsorption ability for CO₂ may result in competitive adsorption between reactants CO₂ and H₂ molecules. Moreover, the adsorption and activation of H₂ can be inhibited on the surface of the catalysts to suppress the CO₂ catalytic hydrogenated reduction reaction. The CO₂ desorption peak areas are always related to the amount of adsorbed CO₂, which can indirectly indicate the number of CO₂ adsorption active sites on the surface of the corresponding catalyst. The amount of adsorbed CO₂ was calculated by integrating peak areas and the results are shown in Table 1. Figure 4 and Table 1 show that introducing Co and Mn

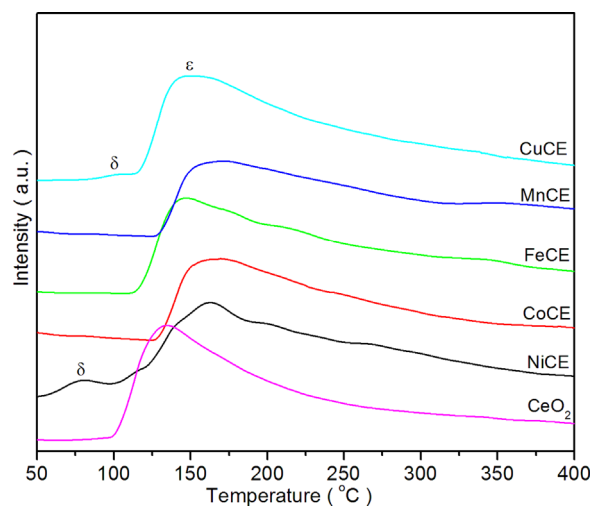


Figure 5. H₂-TPD curves of NiCE, CoCE, FeCE, MnCE, CuCE, and CeO₂ catalysts.

can promote the formation of CO₂ weak adsorption active sites of the corresponding catalysts. By contrast, introducing Cu and Co can be obviously conducive to the formation of CO₂ moderate adsorption active sites of the corresponding catalysts. A large CO₂ desorption peak γ is observed for all catalysts, indicating a large amount of CO₂ strong adsorption active sites on the catalysts. These results indicate that Co and Cu species can obviously increase the number of CO₂ adsorption active sites. This phenomenon is conducive to the adsorption and activation of CO₂ molecules to improve the participation of CO₂ molecules in the catalytic hydrogenated reduction reaction.

H₂-TPD Analysis

Figure 5 shows the H₂-TPD curves of the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts. A wide and strong H₂ desorption peak (denoted as ϵ peak) is observed at 110–400 °C for the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts. Different H₂ desorption peaks appear after the introduction of the different transition metals to the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts. A weak desorption peak (denoted as δ peak) is observed at 55–99 °C and 75–112 °C for the NiCE and CuCE catalysts, respectively. The initial desorption temperatures of ϵ peaks appear at 100, 125, 111, 125, and 111 °C for the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts, respectively. As a comparison, the H₂-TPD profile of

pure CeO₂ is also shown in Figure 5. A large H₂ desorption peak appears at about 97–300 °C, which obviously shifts to a lower temperature than that of MCE catalysts. This phenomenon suggests that pure CeO₂ has a weak adsorption ability for H₂ molecules.

The δ and ϵ peaks can be attributed to the desorption of two adsorption states of H species on the catalyst surface. The δ peak represents the desorption of chemical adsorption state H₂ molecules, whereas the ϵ peak can be assigned to the desorption of dissociated H species.^[23] In addition, obvious δ peaks are observed only in the H₂-TPD curves of the NiCE and CuCE catalysts. This phenomenon can be attributed to the presence of Ni⁰ and Cu⁰ active species in the NiCE and CuCE catalysts, respectively. Moreover, the NiCE catalyst shows a low δ desorption peak temperature, indicating the weak adsorption intensity for the chemical adsorption state H₂ molecules on the surface of the NiCE catalyst. For the ϵ peak, the initial desorption peak temperatures of the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts exhibit the following order: CoCE $\approx$ MnCE > FeCE = CuCE > NiCE > CeO₂. This result suggests that the NiCE catalyst has a weak adsorption ability for dissociated H species. The CoCE and MnCE catalysts have strong adsorption abilities for dissociated H species. The strong adsorption ability of these catalysts for H species can induce reactant H₂ and CO₂ molecules to generate competitive adsorption. This phenomenon is not conducive to the adsorption and activation of reactant CO₂ molecules on the catalysts and affects the catalytic performance of the corresponding catalysts. The desorption peak area of chemical adsorption state H₂ molecules for the NiCE catalyst is larger than that for the CuCE catalyst. This result indicates that the NiCE catalyst has a higher adsorption performance for H₂ molecules than the CuCE catalyst. The H₂ desorption quantitative data obtained from the integrated peak areas are listed in Table 1. The H₂ desorption amounts for the corresponding ϵ peaks show the following order: NiCE > CoCE > CuCE > FeCE > MnCE. This result indicates that the NiCE catalyst has a high adsorption ability for dissociated H species. The high adsorption performance of the catalyst for H species can be conducive to generate more active H species to promote the hydrogenation reaction.

Catalytic Activity Test

Figure 6a shows that CO₂ conversion increases with increasing reaction temperature on the NiCE, CoCE, FeCE, MnCE, CuCE, and CeO₂ catalysts. The CO₂ conversions on the NiCE, CoCE, FeCE,

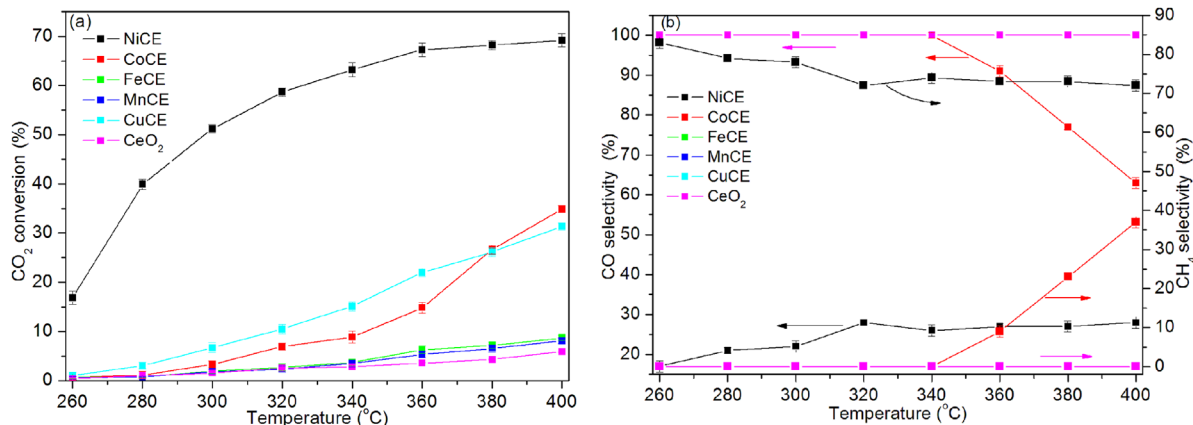


Figure 6. (a) CO₂ conversion and (b) CO and CH₄ selectivity on the prepared NiCE, CoCE, FeCE, MnCE, CuCE, and CeO₂ catalysts.

MnCE, CuCE, and CeO₂ catalysts reach 69.21, 34.91, 8.69, 8.12, 31.34, and 5.91 %, respectively, when the reaction temperature increases from 260 °C to 400 °C. The NiCE catalyst clearly exhibits the highest CO₂ conversion among the studied catalysts in the range of 260–400 °C. The CoCE catalyst obviously shows a higher CO₂ conversion than the CuCE catalyst when the reaction temperature exceeds 380 °C. The FeCE and MnCE catalysts show similar CO₂ conversions of less than 10 %. Figure 6b shows that the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts present different selectivities in the studied temperature range. The FeCE, MnCE, and CuCE catalysts show 100 % CO selectivity. However, aside from the CO products, the byproduct CH₄ is also detected with the NiCE and CoCE catalysts. The CO selectivity over the NiCE catalyst remains less than 28 % (the rest is the byproduct CH₄). CO selectivity is 100 % at temperatures below 340 °C for the CoCE catalyst, whereas the byproduct CH₄ is detected with exceeding 340 °C and the selectivities of CO and CH₄ are 63 % and 37 % at 400 °C, respectively. Thus, the CuCE catalyst not only has a high CO₂ conversion but also maintains 100 % CO selectivity in the studied temperature range. The results indicate that the CuCE catalyst is a promising catalyst for the CO₂ RWGS reaction.

The CO₂ RWGS reaction is a reversible thermodynamic endothermic reaction (i.e. $\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$, $\Delta H_{298\text{ K}} = 41.19\text{ kJ/mol}$). On the basis of the thermodynamic equilibrium, increasing the temperature is conducive to the balance movement in the direction of generating CO to improve CO₂ conversion. Collision theory states that the amount and movement velocity of activated molecules can increase with increasing reaction temperature. This phenomenon increases the effective collision probability between active molecules and accelerates the reaction to promote CO₂ conversion. Therefore, CO₂ conversion over the NiCE, CoCE, FeCE, MnCE, CuCE, and CeO₂ catalysts increases with increasing reaction temperature.

CO₂ RWGS is a typical heterogeneous catalytic reaction. This process involves the diffusion, adsorption, and surface reaction of reactants, as well as the desorption and diffusion of products. The adsorption and activation of reactant molecules on the surface of the catalysts are important steps for the CO₂ RWGS reaction. The adsorption and activation abilities of the catalysts for the reactant molecules play a decisive role on the CO₂ RWGS reaction. The structure and specific surface area of the catalysts affect the adsorption and activation abilities of the catalysts for reactant molecules. As can be seen in Figure 6a, pure CeO₂ has the lowest CO₂ conversion compared with the MCE catalyst. This can be attributed to the CeO₂ with the large crystallite size, the poor adsorption ability for reactant molecules, as confirmed by the XRD, CO₂-TPD, and H₂-TPD results. These also reveal that the introduction of transition metals (Ni, Co, Fe, Mn, or Cu) can improve the catalytic performance of the corresponding catalyst for the CO₂ RWGS reaction. The catalytic performance for the CO₂ RWGS reaction can be changed to different extents by introducing diverse transition metals. XRD and BET results show that the Ce-M-O solid solution is formed in the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts and that all of the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts have mesoporous structures and large specific surface areas. Therefore, the different structures and specific surface areas of the catalysts may not be the main factor that causes the activity differences in the CO₂ RWGS reaction for the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts. In addition, the adsorption performance of the reactant molecules and the number of surface active sites can play important roles in the adsorption and activation of the reactant molecules. H₂-TPD results show that the NiCE catalyst has a strong adsorption performance for H₂

molecules and can effectively activate H₂ molecules to form a large number of active H species to promote CO₂ molecule hydrogenation. Thus, the NiCE catalyst shows the highest CO₂ catalytic hydrogenation reaction activity, and CO₂ conversion can reach 69.21 %. CO₂-TPD results show that the CuCE catalyst has a strong CO₂ molecule adsorption performance, which is conducive to the adsorption and activation of CO₂ molecules on the catalyst to promote the catalytic hydrogenation of CO₂ molecules. H₂-TPR and H₂-TPD results show that CuO in the CuCEO precursor can be completely reduced to form Cu⁰. The formed active Cu⁰ species is conducive to H₂ molecule adsorption to form chemically adsorbed H₂. The chemically adsorbed H₂ is easily dissociated to form active H species, thereby promoting the catalytic hydrogenation of CO₂ molecules. Therefore, CuCE shows a high catalytic activity for the CO₂ RWGS reaction. CO₂-TPD and H₂-TPD results show that the CoCE catalyst has a strong adsorption ability for CO₂ and H₂ molecules, which results in the competitive adsorption of reactant H₂ and CO₂ molecules. This phenomenon is not conducive to CO₂ and/or H₂ adsorption and activation, which exerts an adverse effect on the catalytic hydrogenation of CO₂ molecules. The MnCE catalyst has a strong CO₂ adsorption performance, which hinders the desorption of the adsorption state CO₂ and results in the strong adsorption of CO₂ to form stable carbonate compounds that poison the catalyst, thereby inhibiting the catalytic reaction. Consequently, the MnCE catalyst shows a low CO₂ catalytic hydrogenation activity. CO₂-TPD results show that the FeCE catalyst has a poor CO₂ adsorption performance, which is not conducive for CO₂ molecule activation on the catalyst. This characteristic is unfavourable for CO₂ catalytic hydrogenation. Therefore, the FeCE catalyst presents a poor CO₂ RWGS reaction catalytic activity. The CO₂ RWGS catalytic reaction activities of the catalysts exhibit the following order: NiCE > CuCE > CoCE > FeCE = MnCE.

CO₂ molecules not only can facilitate the RWGS reaction on the catalysts but also induce the side reaction methanation. Figure 6b shows that the FeCE, MnCE, and CuCE catalysts retain 100 % CO selectivity in the RWGS reaction in the range of the used reaction temperature. However, the NiCE catalyst has a poor CO selectivity in the used reaction temperature range. The CoCE catalyst has 100 % CO selectivity at less than or equal to 340 °C, and CO selectivity sharply decreases at temperatures above 340 °C. Transition metals can accept electrons from the outside and adsorb reactant species because of the existence of *d*-orbital holes; these metals can also bond with the adsorbed species. These characteristics exhibit an important effect on the catalytic performance of the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts in the CO₂ RWGS reaction. Transition metals generally display more *d*-orbital holes, i.e. unoccupied *d* orbitals in the *d* energy band, strong adsorption abilities for reactants, and bond forming abilities.^[24] The values of the *d*-orbital holes of Ni and Co are 0.6 and 1.7, respectively. The corresponding transition metal has a strong adsorption ability for reactants and the bonding ability is attributed to the unoccupied *d* orbitals in the *d* energy band, which can promote the absorption and activation of H₂ molecules to form active hydrogen species. Consequently, deep hydrogenation of CO₂ molecules is promoted to generate CH₄ (i.e. $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$), and the generated CO molecules can also facilitate hydrogenation reaction on the active centres of the corresponding catalyst to form CH₄ molecules (i.e. $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$).^[25] H₂-TPR results show that the Ni^{δ+} species in the NiCEO precursor can be effectively reduced to generate Ni⁰ species, but completely reducing the Co^{δ+} species in the CoCEO precursor to form Co⁰ species by H₂ at 400 °C for 2 h is

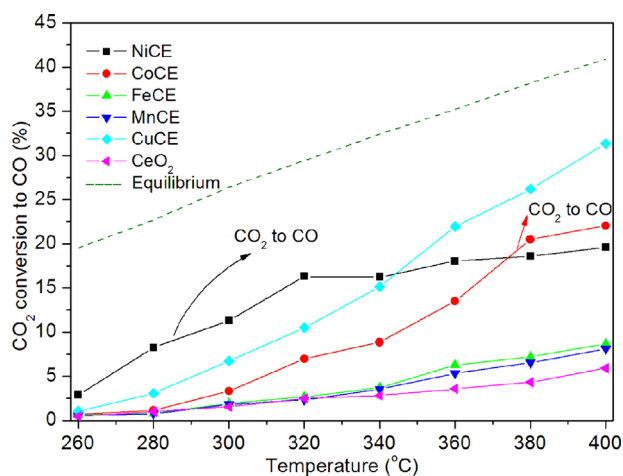


Figure 7. Equilibrium conversion of RWGS reaction and the RWGS reaction activities of the MCE catalysts CeO₂.

difficult. A large amount of Ni⁰ species in the NiCE catalyst is conducive to the side reaction of methanation and results in the CO₂ RWGS reaction with a poor CO selectivity and a high byproduct CH₄ selectivity. Only a small amount of Co⁰ species exists in the CoCE catalyst, and the *d* energy band of Co has a large amount of unoccupied *d* orbitals. These characteristics confer the CoCE catalyst with a strong H species adsorption ability and bonding ability. The strong adsorbed H species is hard to desorb at low reaction temperatures, which is not conducive to activating H species for methanation. Therefore, the CoCE catalyst has 100 % CO selectivity at low reaction temperatures. However, the strong adsorbed H species can be desorbed to form active H species for methanation at high reaction temperatures. Consequently, a large amount of the byproduct CH₄ can be generated at high temperatures. The CuCE catalyst has a large amount of Cu⁰ species. However, Cu has no *d*-orbital holes, that is, the *d* orbits of Cu are completely occupied, which is not conducive to the adsorption and bonding of H species. By contrast, the O of CO₂ has lone-pair electrons, which can pair with the *d* electrons of Cu⁰. This characteristic can be conducive to the adsorption and activation of CO₂ molecules. CO₂-TPD results also confirm that the CuCE catalyst has a high CO₂ molecule adsorption performance. This characteristic can be used to elucidate the high CO₂ conversion and CO selectivity of the CuCE catalyst. H₂-TPR results show that transition metal oxides in the FeCE and MnCE precursors can only be reduced to form low-value metal oxides by H₂ at 400 °C for 2 h. That is, pure transition metals cannot be generated under the used experimental conditions, which are not conducive to the adsorption and activation of H species and inhibit CO₂ hydrogenation reduction. This phenomenon may be the main reason for the low CO₂ conversion and 100 % CO selectivity of the FeCE and MnCE catalysts at the used reaction temperature. Based on the above analyses, the CuCE catalyst with the high CO₂ conversion and 100 % selectivity of CO is the optimal catalyst for the CO₂ RWGS reaction among the studied catalysts.

In order to well understand the RWGS catalytic reaction behaviours of all the catalysts, the RWGS reaction activities of the studied catalysts and the equilibrium conversion of the RWGS reaction are shown in Figure 7. The equilibrium conversion of the CO₂ RWGS reaction is obtained from the literature.^[26] For RWGS reaction as an equilibrium reaction, it can be found that all the catalysts show less CO₂ conversion compared to the

thermodynamic equilibrium. Obviously, the CO₂ conversion of the CuCE catalyst is the closest to the thermodynamic equilibrium with increasing the reaction temperature among these catalysts. And, the CuCE catalyst can maintain 100 % CO selectivity at the studied temperature range as shown in Figure 6b. In contrast, the CO₂ conversions of the NiCE and CoCE catalysts are away from the thermodynamic equilibrium with increasing reaction temperature, which can be attributed to the formation of CH₄ as shown in Figure 6b. The FeCE, MnCE, and CeO₂ catalysts show a similar activity trend. And, the CO₂ conversions of the FeCE, MnCE, and CeO₂ catalysts are obviously far less active than the thermodynamic equilibrium.

CONCLUSIONS

XRD results indicate that transition metal ion Mⁿ⁺ can replace the Ce⁴⁺ of CeO₂ to form a Ce-O-M solid solution via the hard-template method. BET results show that the prepared NiCE, CoCE, FeCE, MnCE, and CuCE catalysts have mesoporous structures and large specific surface areas. The CO₂ conversions on the NiCE, CoCE, FeCE, MnCE, and CuCE catalysts reach 69.21, 34.91, 8.69, 8.12, and 31.34 % at 400 °C, respectively. The CO selectivities of the corresponding catalysts are 28, 63, 100, 100, and 100 %, respectively. The CuCE catalyst not only has a high CO₂ conversion but also exhibits 100 % CO selectivity. The high CO₂ RWGS reaction catalytic activity of the CuCE catalyst can be attributed to the existence of the active species Cu⁰ and the excellent CO₂ molecule absorption performance, as confirmed by the H₂-TPR and CO₂-TPD results. Thus, the CuCE catalyst is a promising catalyst for the RWGS reaction.

ACKNOWLEDGEMENT

This research is funded by Chongqing Research Program of Basic Research and Frontier Technology (No. cstc2014jcyjA90019).

NOMENCLATURE

ΔH enthalpy variation (kJ/mol)
P pressure (Pa)

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Manuscript received February 25, 2016; revised manuscript received August 4, 2016; accepted for publication August 9, 2016.