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# $CO_2$ hydrogenation over acid-activated Attapulgite/ $Ce_{0.75}Zr_{0.25}O_2$ nanocomposite supported Cu-ZnO based catalysts

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#### ABSTRACT

A series of Cu-ZnO based catalysts supported on the Attapulgite/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> (ATP-CZO) nanocomposite prepared by different methods were synthesized using impregnation method for CO<sub>2</sub> hydrogenation to CO and methanol. The physicochemical properties and catalytic performance of these catalysts were investigated by N<sub>2</sub> adsorption/desorption, XRD, FE-SEM, TEM, N<sub>2</sub>O chemisorption, XPS, H<sub>2</sub>-TPR and CO<sub>2</sub>-TPD techniques. Results showed that the ATP-CZO-SC-P400 nanocomposite prepared by polyethylene glycol (PEG 400) modified solution combustion (SC) method owned the best dispersion of CZO particles on the ATP-CZO composite. Due to the dispersing effect of PEG 400, the intensity of Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> solid solution was enhanced, and the interaction between Ce-Zr-O oxides and ATP support was improved. Furthermore, the formation of strong basic sites and copper surface area of the catalyst were enhanced. As a result, the CZFK/ATP-CZO-SC-P400 catalyst showed the highest yield of methanol and CO from CO<sub>2</sub> hydrogenation. The intimate contact between metallic Cu sites and strong basic sites of ZnO, ATP-CZO composite and ZnO-CZO interfaces on the surface of catalyst was considered as an important factor. Attapulgite, with unique property, low cost and easy availability, is a potential catalyst support for CO<sub>2</sub> hydrogenation.

#### 1. Introduction

According to the Global Carbon Budget 2018, the global  $CO_2$  emissions are projected to go up in 2018 by more than 2% and reach to 37.1 Gt [1]. The increasing emissions bring a severe challenge for governments to achieve the goal of limiting global warming to below 2 °C by 2020. Carbon dioxide (CO<sub>2</sub>) catalytic hydrogenation to fuels or chemicals is considered as a feasible solution for reducing CO<sub>2</sub> emission [2]. The desired products from CO<sub>2</sub> hydrogenation include methanol which was mainly produced over Cu-based catalysts [3–9], hydrocarbons through combination of CO<sub>2</sub> reduction with the following Fischer–Tropsch (FT) reactions over modified Fe-and Co-based FT catalysts [10–13], and CO through reverse water-gas shift (RWGS) reaction over bimetallic or carbide catalysts [2,14]. Higher alcohols refers to  $C_{2+}$  alcohols ( $C_{2+}$ OH) can be also prepared from CO<sub>2</sub> hydrogenation over some multi-functional catalysts, like K/Cu-Zn-Fe catalysts [15], Mo-Co-K sulfide catalysts [16] and Pt/Co<sub>3</sub>O<sub>4</sub> catalysts [17]. Owing to

the fast hydrogenation of surface intermediates on catalyst surface with a high hydrogen/carbon ratio, methanol and CO are much easier to be produced than higher alcohols [18]. Unfortunately, because of the high thermodynamic stability and low reactivity of  $CO_2$  molecule, the  $CO_2$  conversion and aiming products selectivity are still hard to be improved.

Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst has been applied to produce methanol industrially from CO and CO<sub>2</sub> hydrogenation [19]. However, the undesired byproduct water molecule has a negative effect on the strong hydrophilic characteristic of alumina, thus leading to the rapid Cu sintering and serious catalyst deactivation [20]. In order to improve the catalytic activity of Cu-ZnO based catalyst, some oxide carriers like SiO<sub>2</sub> [21,22], TiO<sub>2</sub> [23], ZrO<sub>2</sub> [3,14,24,25], CeO<sub>2</sub> [26], or their combinations [27,28] have been used to modify the catalyst by substitution or addition. Especially, ZrO<sub>2</sub> can improve the Cu dispersion and surface basicity, thus increasing the catalytic activity and methanol selectivity of Cu/ZnO catalyst [29–32]. In compare to Cu/ZnO/ZrO<sub>2</sub> catalyst, the

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partial replacement of  $ZrO_2$  with  $CeO_2$  leaded to the further enhancement of  $CO_2$  hydrogenation properties over  $Cu/ZnO/Ce_{1-x}Zr_xO_2$  catalyst [28]. Therefore, the Ce-Zr-O oxide is a potential carrier for modifying Cu-ZnO based catalyst, but the high cost of ceria and zirconium materials brings a big challenge for its practical application.

Attapulgite (ATP, also known as palygorskite) is a natural hydrated magnesium aluminum silicate nonmetallic mineral, having 1-D nanorod-like crystal morphology and porous crystalline structure with tetrahedral layers [33]. Due to the structural properties of big surface area and pore volume and adjustable acid-base nature as well as thermal stability. ATP has been extensively used as catalyst or catalyst support in CO conversion [34-36], hydrogen production [37,38], biomass and platform chemicals conversion [39-42], etc. Our previous research [34] reported that the acid activation of ATP promoted the decomposition of intergranular sticking substance and carbonate impurity which increased the surface area and pore volume. The removal of octahedral cations  $(Mg^{2+}, Al^{3+} and Fe^{3+})$  and the formation of amorphous silica from the tetrahedral sheet were also enhanced which could improve the interaction between catalyst active components and ATP support [35]. Phongamwong et al. [21] found that a low amounts of silica, around 0.5-1.5 wt%, promoted the interdispersion of metal oxides components in CuO-ZnO-ZrO<sub>2</sub>-SiO<sub>2</sub> catalyst. Consequently, the metallic copper surfaces area and surface basicity were increased, and then the CO<sub>2</sub> conversion, methanol selectivity and catalyst stability were also improved. From this point of view, acid-activated ATP is also a promising CO<sub>2</sub> hydrogenation catalyst support because of geometric structural effect. Li et al. [43] prepared a series of ATP/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> nanocomposites by a homogeneous deposition method with hexamethylenetetramine as precipitator for the catalytic wet oxidation of methylene blue. ATP/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> showed the maximum degradation rate of methylene blue of 99% due to the significant interactions between Ce-Zr-O oxides and ATP support. Considering the low cost and better textural properties of ATP, it is valuable to try out ATP/  $Ce_{1-x}Zr_xO_2$  nanocomposite as the CO<sub>2</sub> hydrogenation catalyst support.

For Cu-ZnO based catalyst in CO<sub>2</sub> hydrogenation reaction, the mostly reported hydrogenation active sites are metallic copper (Cu<sup>0</sup>) and monovalent copper ion (Cu<sup>+</sup>) with a proper ratio [3,44]. The surface area and dispersion of copper species [45] or the metal-support interaction [26-28] or both of them [20,29,46] are crucial for affecting the catalytic behavior of Cu-ZnO based catalysts. Bonura et al. [24] proposed that an adequate balance between metal and oxide surface sites was important to develop a high-performance catalyst. Simultaneously, the dispersion and particle size of active components are extremely relevant to the textural properties of support material which can be largely affected by preparation method [47,48]. Therefore, the effects of preparation method on the textures and surface properties of  $ATP/Ce_{1-x}Zr_xO_2$  nanocomposites need to be investigated in detail. Besides catalyst support, some metallic promoters were adopted to improve these catalytic crucial factors, like La, Ce, Nd, Pr, Mg, Mn [49,50]. Our previous study [51] investigated the effect of K content in K/Cu-ZnO catalyst on CO2 hydrogenation performances and found that K<sub>2</sub>O played an important role in promoting Cu-ZnO interaction by adjusting the transfer of surface oxide species. Subsequently, we added medium concentration of Fe promoter into K/Cu-ZnO catalyst and found that Fe could promote the reduction of catalyst and increase the synergistic effect of Cu-FeCx dual-active sites for improving the selectivity of C2+ alcohols [15]. Therefore, Fe and K promoters are important components for modifying the Cu-ZnO based catalysts. In this work,  $ATP/Ce_{1-x}Zr_xO_2$  (x = 0.25) nanocomposite was prepared by different methods and used as the support of Cu-ZnO based catalyst for CO<sub>2</sub> hydrogenation. The textures and physicochemical properties of ATP/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> nanocomposite and these supported catalysts were characterized. In order to improve the dispersion of copper species and enhance the intimate contact of Cu-oxides dual sites, a modified solution combustion method using polyethylene glycol (PEG 400) as dispersing agent was adopted to promote the interaction between ATP particles and Ce-Zr-O oxides. The effects of addition amount of PEG 400 and probable  $\rm CO_2$  hydrogenation mechanism were also studied in detail.

# 2. Experimental

#### 2.1. Catalyst preparation

The ATP/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> nanocomposite (ATP-CZO, for short) was prepared by seven methods as showed in Supplementary material (Supplementary material, S1), including impregnation (IM), forward coprecipitation (FCP), backward coprecipitation (BCP), parallel-flow coprecipitation (PCP), hydrothermal (HT), Sol-Gel (SG) and solution combustion (SC). These ATP-CZO supported Cu-ZnO based catalysts with a molar ratio of Cu: Zn: Fe: K = 1:1:0.5:0.15 and Cu loading of 17.7 wt% were synthesized by impregnation method. Typically, the mixed aqueous solution containing Cu(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub> and  $K_2\text{CO}_3$  with a total metallic ions concentration of  $5.5\,\text{mol}\ \text{L}^{-1}$  was prepared according to the theoretical molar ratio by deducting the intrinsic iron and potassium components of ATP support [35]. Then, 8 g ATP-CZO powder (> 100 mesh) was added into the mixed solution. After impregnation for 4.5 h, the catalyst precursor was dried in air at 393 K overnight, and then calcined in air at 623 K for 5.5 h. These catalysts were named as CZFK/ATP-CZO and pelletized, crushed, and sieved to 60-80 mesh before use.

#### 2.2. Catalytic performances evaluation and product analysis

CO2 hydrogenation activity evaluation was carried out in a stainless steel tubular (internal diameter, 8 mm; length, 280 mm), continuousflow fixed-bed reactor [15]. Catalyst (60-80 mesh, 3g) mixed with quartz sand (40-60 mesh, 9g) was loaded in the middle of reactor, having a catalyst bed length of 100 mm. The reaction temperature was monitored by a thermocouple inserted into the middle of catalyst bed. Before CO<sub>2</sub> hydrogenation reaction, the catalyst was reduced at 573 K for 4 h with a stream of pure H<sub>2</sub> under pressure of 1.5 MPa. After reduction, the reactor was decreased to reaction temperature and then the reactant gas flow was introduced into the reactor. In order to reveal the relationship between the catalytic performances and reaction conditions, reaction temperature was increased from 503 K to 593 K by a temperature controller. Reaction pressure was adjusted from 4.0 MPa to 8.0 MPa with a backpressure regulator. The gas hourly space velocity (GHSV) was employed from 3000  $h^{-1}$  to 9000  $h^{-1}$  by changing the gas flow rate. The related catalytic performances were showed in the Supplementary material in detail. The gas and liquid products were separated by a cold trap and analyzed by off-line gas chromatograph (GC). The former was analyzed by a GC 9800 (Kechuang, Shanghai in China; column: TDX-01,  $1 \text{ m} \times 3 \text{ mm}$ ) equipped with a thermal conductivity detector (TCD). The latter was analyzed by a GC 9900 (Jiafen, Beijing in China; column: FFAP,  $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$ ) equipped with a hydrogen flame ionization detector (FID). The CO<sub>2</sub> conversion and products selectivity were calculated according to mass-balance method and three duplicate experiments were conducted to obtain the average with the error less than 5%. The space time yield (STY) and turnover frequency (TOF) of CH<sub>3</sub>OH and CO were calculated according to Dong et al. [3].

#### 2.3. Characterization

The detailed  $N_2$  adsorption/desorption, X-ray diffraction (XRD), Field emission scanning electron microscope (FESEM), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Vis-Raman spectra are showed in Supplementary material (Supplementary material, S2).

#### 2.3.1. Hydrogen-temperature programmed reduction (H<sub>2</sub>-TPR)

 $\rm H_2$ -TPR experiment was carried out in a U-tube quartz reactor using a ChemBET Pulsar-1 automated chemisorption analyzer (Quantachrome, US) with a 10 vol.%  $\rm H_2/Ar$  mixture as the reductive gas. The samples (120 mg) were pretreated with Ar at 393 K for 60 min, and then reduced from 323 K to 1073 K at a heating rate of 10 K min<sup>-1</sup>. The hydrogen consumption was monitored by a TCD and quantified by five pulses calibration.

#### 2.3.2. CO<sub>2</sub>-temperature programmed desorption (CO<sub>2</sub>-TPD)

CO<sub>2</sub>-TPD experiments were conducted in the same reactor as H<sub>2</sub>-TPR detection. The samples were reduced at 573 K for 1 h using 10 vol. % H<sub>2</sub>/Ar mixture with a flow rate of 30 mL/min. After cooling to 323 K, the catalysts were saturated in CO<sub>2</sub> flow at 323 K for 1 h and then flushed with Ar to remove the physical adsorbed molecules. Then, the desorption processes were performed with a heating rate of 10 K min<sup>-1</sup> under Ar flow up to 1073 K and the desorbed CO<sub>2</sub> were recorded by a mass spectrometer.

The number of surface metallic copper atoms of catalysts was determined by N<sub>2</sub>O oxidation at 323 K using the procedure described by Van Der Grift et al. [52]. Catalysts (105 mg) were first reduced for 2 h according to the H<sub>2</sub>-TPR procedure as mentioned above in a 10 vol.% H<sub>2</sub>/Ar flow (30 mL min<sup>-1</sup>) from 303 K to 573 K at 5 K min<sup>-1</sup>. The amount of hydrogen consumption in the first TPR process was denoted as *X*. And then, the reactor was purged with Ar to 303 K. A 20% N<sub>2</sub>O/N<sub>2</sub> flow (30 mL min<sup>-1</sup>) was introduced to oxidize surface copper atoms to Cu<sub>2</sub>O at 323 K for 1 h. Subsequently, the catalyst was flushed with Ar to remove the oxidant and cooled to 303 K. Finally another TPR experiment was performed as the same as the first reduction. Hydrogen consumption in the second TPR was denoted as *Y*. The surface area and dispersion of Cu were calculated according to equations reported by Van Der Grift et al. [52], as follows:

Reduction of all copper atoms:

 $CuO + H_2 \rightarrow Cu + H_2O$ , hydrogen consumption = X

Reduction of surface copper atoms only:

 $Cu_2O + H_2 \rightarrow 2Cu + H_2O$ , hydrogen consumption = Y

The dispersion of Cu and the area of surface Cu were calculated as:

 $D = (2 \times Y/X) \times 100\%$ S=2 × Y × N<sub>av</sub>/(X × M<sub>Cu</sub> × 1.46×10<sup>19</sup>) ≈ 1353 × Y/X (m<sup>2</sup>/g)

where  $N_{\rm av}$  = Avogadro's constant,  $M_{\rm Cu}$  = relative atomic mass of copper (63.456 g/mol), 1.46 × 10<sup>19</sup> is the number of copper atoms per square meter as the result of an average copper surface atom area of 0.0711 nm<sup>2</sup> [53].

### 3. Results and discussion

#### 3.1. Textural properties

The textural properties of these ATP-CZO nanocomposites are largely affected by the preparation method (Supplementary material, Table S1). For ATP-CZO-IM nanocomposite, the highest proportion of microporous surface area ( $S_{\text{Micro}}$ ) of 17.4% in BET surface area ( $S_{BET}$ ) was obtained. The highest proportion of microporous volume ( $V_{\text{Micro}}$ ) of 3.3% in total pore volume ( $V_{\text{total}}$ ) was achieved over ATP-CZO-SC-P400(3) nanocomposite. Differences in textures reflect differences in N<sub>2</sub> adsorption-desorption isotherms and BJH pore size distribution (Supplementary material, Fig. S1). The type IV isotherms with a different size of H3-type hysteresis loop are observed for all samples. Furthermore, the textural properties of these ATP-CZO nanocomposites supported Cu-ZnO based catalysts are shown in Table 1. It can be seen that the  $S_{BET}$  and  $V_{\text{total}}$  of those catalysts are much lower than them of ATP-CZO nanocomposites, implying the deposition of metallic oxides onto ATP-CZO nanocomposites. CZFK/ATP-CZO-IM catalyst shows the lowest  $S_{\rm BET}$  of 22.0 m<sup>2</sup>/g but the largest average pore diameter ( $D_{\rm P}$ ) of 24.1 nm, which is consistent with the lowest  $S_{\text{BET}}$  of ATP-CZO-IM nanocomposite. Though the  $S_{\text{BET}}$  and  $V_{\text{total}}$  of ATP-CZO-SC-P400(3) are not the highest in those ATP-CZO nanocomposites, CZFK/ATP-CZO-SC-P400(3) catalyst owns the highest  $S_{\text{BET}}$  of 65.0 m<sup>2</sup>/g and  $V_{\text{total}}$  of  $0.236 \text{ cm}^3/\text{g}$ . Due to the dispersing effect of PEG 400, the interaction between ATP and CZO particles in ATP-CZO-SC-P400(3) nanocomposite had been improved, and CZO particles were uniformly distributed on surface of ATP to enhance the orientation of ATP rodlike crystals (Supplementary material, Fig. S2). As a result, the cation interchange between ATP and metallic ions  $(Cu^{2+}, Zn^{2+} \text{ and } Fe^{3+})$  might be hindered, thus decreasing the entrance of metallic ions into ATP pores to generate bulk metallic oxides. N2O chemisorption was applied to detect the dispersion  $(D_{Cu})$  and surface area of metallic Cu  $(S_{Cu})$  on surface of CZFK/ATP-CZO-SC and CZFK/ATP-CZO-SC-P400(3) catalysts. The calculated  $D_{Cu}$  and  $S_{Cu}$  according to these equations reported by Van Der Grift et al. [52] increase from 4.4% and 30 m<sup>2</sup>/g-Cu to 13.3% and 90 m<sup>2</sup>/g-Cu, respectively. The results indicated that ATP-CZO-SC-P400(3) nanocomposite with specific textures and morphology is more beneficial for improving the dispersion of CuO than ATP-CZO-SC nanocomposite.

#### 3.2. XRD detection and morphology observation

The XRD patterns of these ATP-CZO nanocomposites supported Cu-ZnO based catalysts are shown in Fig. 1. The reflection peaks of palygorskite, quartz and Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> solid solution as showed in the XRD patterns of ATP-CZO nanocomposites (Supplementary material, Figs. S3 and S4) are still present with much lower peak intensity due to the deposition of metallic oxides onto ATP-CZO composite. As shown in Fig. 1, the diffraction peaks at  $2\theta = 35.7^\circ$ ,  $38.9^\circ$ ,  $49.0^\circ$  and  $2\theta = 31.8^\circ$ , 34.4°, 36.3°, 47.5°, 56.6°, 62.9° are corresponded to CuO (JCPDS, No. 45-0937) and ZnO (JCPDS, No. 65-3411), respectively. The calculated crystallite size of CuO and ZnO by Scherrer equation in Cu-ZnO based catalysts are shown in Table 1. CZFK/ATP-CZO-PCP catalyst shows the largest particle size of CuO, while CZFK/ATP-CZO-HT catalyst shows the smallest particle size of CuO, followed by CZFK/ATP-CZO-SC catalyst and CZFK/ATP-CZO-SC-P400(3) catalyst. The CZFK/ATP-CZO-IM catalyst has the largest particle size of CZO and ZnO (Table 1) which is ascribed to the agglormation of CZO oxide on surface of ATP (Supplementary material, Fig. S5). However, the larger particle size of CuO and ZnO for other catalysts is corresponded to the smaller particle size of CZO oxide, implying that CuO and ZnO might be well dispersed on ATP-CZO nanocomposite with much higher particle size of CZO oxide.

Furthermore, the diffraction peaks at  $2\theta$  of  $33.2^{\circ}$ ,  $35.7^{\circ}$ ,  $54.2^{\circ}$  and weak diffraction peaks at 2 $\theta$  of 35.5°, 62.7° are ascribed to  $Fe_2O_3$ (JCPDS, No. 84-0307) and CuFe<sub>2</sub>O<sub>4</sub> (JCPDS, No. 77-0010), respectively. The formation of CuFe<sub>2</sub>O<sub>4</sub> phase indicates the improvement of Cu-Fe interaction, which played an important role in synthesizing higher alcohols over binary Cu-Fe-based catalyst [35]. These fresh CZFK/ATP-CZO catalysts were also observed by FE-SEM as shown in Fig. 2. Most samples show similar block-like morphology with some agglomeration. According to the particle size of CuO, ZnO and CZO oxides (Table 1), these big blocks might be assigned to the aggregation of ZnO. Since the metallic components are complex in these catalysts, the dispersion position of metallic oxides is difficult to be clarified. However, comparing to FE-SEM image of CZFK/ATP-CZO-SC catalyst (Fig. 2g), CZFK/ATP-CZO-SC-P400(3) catalyst showed more uniform pore structure. The agglomeration of metallic oxides (Fig. 2h) was also relieved because of the dispersion effect of PEG 400. The detailed active elements distribution of CZFK/ATP-CZO-SC and CZFK/ATP-CZO-SC-P400(3) catalysts are displayed in Fig. 3. The distribution of Cu, Zn and Fe is isolated each other on CZFK/ATP-CZO-SC catalyst, while Cu is well distributed overlapping with the distribution of Zn and Fe on

#### Table 1

Structural	parameters	of	CZFK/ATP-CZO	catalysts.
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Sample	$S_{\rm BET}$ (m <sup>2</sup> /g)	$V_{\rm total}~({\rm cm^3/g})$	$D_{\rm P}$ (nm)	XRD – Crystallite size (nm) <sup>a</sup>			
				CZO	CuO	ZnO	
CZFK/ATP-CZO-IM	22.0	0.133	24.1	6.1	21.8	545.1	
CZFK/ATP-CZO-FCP	47.9	0.193	16.1	4.0	24.6	257.0	
CZFK/ATP-CZO-BCP	55.4	0.175	12.7	3.0	28.6	316.0	
CZFK/ATP-CZO-PCP	55.3	0.181	13.1	2.9	31.2	328.5	
CZFK/ATP-CZO-HT	37.7	0.206	21.8	4.3	18.2	235.1	
CZFK/ATP-CZO-SG	30.5	0.137	18.0	3.8	23.3	304.3	
CZFK/ATP-CZO-SC	24.6	0.124	20.1	4.1	20.4	216.6	
CZFK/ATP-CZO-SC-P400(3)	65.0	0.236	14.5	4.0	21.0	222.4	

<sup>a</sup> Calculated using Scherrer equation based on the reflection of (220) lattice plane at  $2\theta = 48.0^{\circ}$  for CZO, (111) lattice plane at  $2\theta = 38.9^{\circ}$  for CuO and (101) lattice plane at  $2\theta = 36.3^{\circ}$  for ZnO.



Fig. 1. XRD patterns of ATP-CZO nanocomposites supported Cu-ZnO based catalysts. (a) IM, (b) FCP, (c) BCP, (d) PCP, (e) HT, (f) SG, (g) SC and (h) SC-P400(3).

CZFK/ATP-CZO-SC-P400(3) catalyst. As suggested above, ZnO seems to act as a physical support for dispersing CuO species [54], thus improving the  $D_{Cu}$  and  $S_{Cu}$  on CZFK/ATP-CZO-SC-P400(3) catalyst.

#### 3.3. XPS analysis

XPS patterns of Cu  $2p_{3/2}$ , Zn 2p and Fe  $2p_{3/2}$  on fresh CZFK/ATP-CZO-SC and CZFK/ATP-CZO-SC-P400(3) catalysts are shown in Fig. 4. There are two peaks at 930  $\degree$  938 eV assigned to the binding energy (BE) of Cu  $(2p_{3/2})$ , which are derived from the spin-obit doublet of Cu 2p [55]. Simultaneously, a couple of satellite peaks at higher BE of 938  $\degree$  948 eV is also observed. They are resulted from the shake-up transitions by ligand-to-metal 3d charge transform [56]. The lower copper BE of 932  $\degree$  934 eV is indicative of the Cu<sub>A</sub><sup>2+</sup> in tetrahedral CuO (A) species [57], and the higher copper BE of 934  $\degree$  937 eV is distributed to the Cu<sub>B</sub><sup>2+</sup> in octahedral composite metal oxides (B) [35]. The composite copper oxide has also been detected by XRD with different intensity. From Fig. 4, it is evident that the tetrahedral and octahedral Cu<sup>2+</sup> cations are concomitant in these catalysts. From the high resolution scan of Fe  $2p_{3/2}$  on fresh CZFK/ATP-CZO-SC and CZFK/ATP-CZO-SC-P400(3) catalysts as shown in Fig. 4, these peaks at BE of 710–712 eV



Fig. 2. FESEM images of Cu-ZnO based catalysts supported on ATP-CZO nanocomposites prepared from different method. (a) IM, (b) FCP, (c) BCP, (d) PCP, (e) HT, (f) SG, (g) SC and (h) SC-P400(3).



Fig. 3. EDS mapping of Cu, Zn, Fe and K on (a) ATP-CZO-SC and (b) ATP-CZO-SC-P400(3) nanocomposites supported Cu-ZnO based catalysts.

and 712–714 eV are assigned to  $Fe_A^{3+}$  in  $Fe_2O_3$  phase and  $Fe_B^{3+}$  in composite metal oxide phase (such as  $CuFe_2O_4$  spinel), respectively [35]. The BE of  $Fe_A^{3+}$  shows an increase by 0.5 eV, which is similar with the BE increase of  $Cu_A^{2+}$  on CZFK/ATP-CZO-SC-P400(3) catalyst. For Zn 2p spectra, the BE of Zn  $(2p_{3/2})$  is 1022.3 eV and Zn  $(2p_{1/2})$  is 1045.3 eV, which is the characteristic of ZnO [58]. The peak position and peak intensity on CZFK/ATP-CZO-SC-P400(3) catalyst show a slight increase relative to CZFK/ATP-CZO-SC catalyst. These results implied that the shift of  $Cu_A^{2+}$  on CZFK/ATP-CZO-SC-P400(3) catalyst to higher BE was related to the coordination of copper in the CuFe<sub>2</sub>O<sub>4</sub> spinel and the stronger interaction between CuO and Fe<sub>2</sub>O<sub>3</sub>. Furthermore, the interaction between CuO and ZnO was also enhanced due to the increase of  $D_{Cu}$  and  $S_{Cu}$ . The preparation method of ATP-CZO composite has a large effect on the BE of Cu  $2p_{3/2}$ , Zn 2p and Fe  $2p_{3/2}$  and the proportion of  $Cu_A^{2+}/Cu_B^{2+}$  and  $Fe_A^{3+}/Fe_B^{3+}$  (Supplementary

material, Fig. S6). CZFK/ATP-CZO-PCP catalyst shows the highest proportion of  $\text{Cu}_{A}^{2+}/\text{Cu}_{B}^{2+}$ , indicating the presence of a large amount of dispersed CuO phase. CZFK/ATP-CZO-HT catalyst has the highest proportion of  $\text{Fe}_{B}^{3+}/\text{Fe}_{A}^{3+}$ . This might be caused by different dispersion, location and size of metallic oxides on the ATP-CZO structure, and the interactions between metallic oxides and ATP-CZO nanocomposite.

# 3.4. The reducibility of the catalysts

The investigation of the reduction behavior of the heterogeneous catalyst is beneficial for the identification of active sites and the metalsupport interaction (MSI). TPR experiment of the ATP-CZO nanocomposite supported Cu-ZnO based catalysts was performed. As shown in Fig. 5 and Table 2, two types of peaks are present on these reduction curves, which located on the range of 540  $\degree$  590 K (low-temperature)



Fig. 4. XPS patterns of Cu-ZnO based catalysts supported on ATP-CZO nanocomposites prepared from different method: (a) SC and (b) SC-P400(3).

and 698  $\degree$  1029 K (high-temperature), respectively. Since ZnO and Ce-Zr-O oxides are not reduced within this temperature range [46,59], the low-temperature reduction peak is assigned to the reduction of highly

dispersed CuO to Cu:  $CuO + H_2 \rightarrow Cu + H_2O$  [35,51]. CZFK/ATP-CZO-PCP catalyst shows the highest reduction temperature of dispersed CuO (586 K) with the maximum fraction (72%), which is related with its



Fig. 5. H<sub>2</sub>-TPR profiles of Cu-ZnO based catalysts supported on ATP-CZO nanocomposites prepared from different method. (a) IM, (b) PCP, (c) HT, (d) SG, (e) SC and (f) SC-P400(3).

smallest CZO size and the second largest ZnO size (Table 1). On the contrary, CZFK/ATP-CZO-SC-P400(3) catalyst shows the lowest reduction temperature of CuO (540 K) with the minimum fraction (41%). which are also lower than them of CZFK/ATP-CZO-SC catalyst. FESEM. XRD, XPS and N<sub>2</sub>O-adsorption results have proved that the dispersion of CuO can be improved by using the PEG 400 modified ATP-CZO-SC composite as catalyst support. In order to investigate the effects of addition amount of PEG 400 on morphology and structure of ATP-CZO-SC supported Cu-ZnO based catalyst, these CZFK/ATP-CZO-SC-P400(x) catalysts were observed by TEM. As shown in Fig. 6, CuO particles are dispersed onto the surface of ZnO and the Cu-ZnO interface is formed in all catalysts. However, much more ZnO sheet are exposed on CZFK/ ATP-CZO-SC-P400(0) catalyst. The dispersion of metallic oxides was improved by increasing x from 1 to 7. Combining with the above  $N_2$ adsorption-desorption, XRD, SEM and XPS detections, the improvement of dispersed CuO reduction on CZFK/ATP-CZO-SC-P400 catalyst can be ascribed to the following three points: (1) the decrease of interaction

between CuO and ATP; (2) the intimate contact between CuO and other oxides (Ce-Zr-O solid solution, ZnO and Fe<sub>2</sub>O<sub>3</sub>) for increased interactions; (3) the improved dispersion of CuO upon ZnO sheets to form much more Cu-ZnO interface. However, when x is 10, CuO particles seem not to be closely connected with ZnO sheets on ATP-CZO-SC-P400(10) nanocomposite but show much smaller crystallite size. This is because the mechanical strength and intensity of Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> solid solution in ATP-CZO-SC-P400(10) nanocomposites, which can be due to the strong heat release and more gases released in the combustion process of PEG 400 [46].

Furthermore, apart from CZFK/ATP-CZO-IM and CZFK/ATP-CZO-PCP catalysts, other catalysts display a shoulder peak at 608  $\degree$  618 K accompanying with the reduction peak of dispersed CuO. XPS results have shown that Fe<sub>B</sub><sup>3+</sup> in composite metal oxide phase is present in all catalysts (Fig. 4 and Fig. S6 in Supplementary material), thereby the shoulder reduction peak can be assigned to the reduction of bulk CuO

#### Table 2

Reduction	peak	temperature	and hvd	lrogen	consumption	over	CZFK/ATP-	CZO	catalysts.
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Sample	Peak I		Peak II		Peaks III, IV, V, VI, VII	Total Con. <sub>H2</sub> (µmol $g_{cat.}^{-1}$ )	
	Tem. (K) <sup>a</sup>	$Con{H2}$ (%) <sup>b</sup>	Tem. (K) <sup>a</sup>	$Con{H2}$ (%) <sup>b</sup>	Tem. (K) <sup>a</sup>	$Con{H2}$ (%) <sup>b</sup>	
CZFK/ATP-CZO-IM	583	3356(66%)	-	-	735, 789, 971	1679(34%)	5035
CZFK/ATP-CZO-PCP	586	4467(72%)	-	-	769, 882	1698(28%)	6165
CZFK/ATP-CZO-HT	568	2633(50%)	618	658(12%)	718, 790, 830, 964	1996(38%)	5287
CZFK/ATP-CZO-SG	576	3355(59%)	616	640(11%)	743, 792, 846, 968	1706(30%)	5701
CZFK/ATP-CZO-SC	570	3153(58%)	608	437(8%)	725, 784, 840, 973, 1029	1868(34%)	5458
CZFK/ATP-CZO-SC-P400(3)	540	2107(41%)	611	1148(22%)	698, 791, 844, 971	1947(37%)	5202

<sup>a</sup> Peak temperature.

<sup>b</sup> Relative proportion of hydrogen consumption.



Fig. 6. TEM images of Cu-ZnO based catalysts supported on ATP-CZO-SC-P400(x) nanocomposites. (a) x = 0, (b) x = 1, (c) x = 3, (d) x = 5, (e) x = 7 and (f) x = 10.

and composite copper oxide (such as CuFe<sub>2</sub>O<sub>4</sub> reduction to Cu and Fe<sub>2</sub>O<sub>3</sub> [35,60]). N<sub>2</sub> adsorption-desorption and SEM results (Table 1 and Fig. S5 in Supplementary material) showed that the formation of bulk metallic oxides were hindered due to the uniformly distribution of CZO upon ATP support in CZFK/ATP-CZO-SC-P400 catalyst. As a result, the obvious increase of H<sub>2</sub> consumption involved in the shoulder peak in contrast to CZFK/ATP-CZO-SC catalyst was caused by composite copper oxides due to the improvement of interactions between CuO and other metallic oxides. In addition, a high-temperature reduction peak at 698 ^ 1029 K can be found on the reduction curves of all catalysts, which is ascribed to the consecutive reduction of  $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$  [60]. CZFK/ATP-CZO-HT catalyst shows the highest H<sub>2</sub> consumption of Fe<sub>2</sub>O<sub>3</sub> reduction, and then is CZFK/ATP-CZO-SC-P400(3) catalyst. Taken together, CZFK/ATP-CZO-SC-P400(3) catalyst is the sole sample of which the H<sub>2</sub> consumption of CuFe<sub>2</sub>O<sub>4</sub> composite and subsequent Fe<sub>2</sub>O<sub>3</sub> is much higher than that of dispersed CuO, indicating the formation of more  $CuFe_2O_4$  and the enhancement of Cu-ZnO interaction.

#### 3.5. Surface adsorption behavior of the catalysts

In order to examine the basicity site of fresh CZFK/ATP-CZO-SC and CZFK/ATP-CZO-SC-P400(3) catalysts, CO<sub>2</sub>-TPD was performed to investigate the surface adsorption behavior of CO<sub>2</sub> on these two catalysts. For comparison, ATP-CZO-SC-P400(3) support was also studied. As shown in Fig. 7, two broad CO<sub>2</sub> desorption bands ranging from 353 and 573 K to 523 and 923 K (labeled as LT and HT peaks, respectively) can be observed. The LT peak ( $\alpha$  peak) of ATP-CZO-SC-P400(3) support centered at 400 K is assigned to the interaction of CO<sub>2</sub> with weakly



Fig. 7. CO<sub>2</sub>-TPD profiles of (a) ATP-CZO-SC-P400 nanocomposite, (b) CZFK/ ATP-CZO-SC catalyst and (c) CZFK/ATP-CZO-SC-P400(3) catalyst.

basic hydroxyl groups on the ATP and Ce-Zr-O oxide [3,61]. The HT peak is constituted by a symmetrical peak at 695 K ( $\beta_1$  peak) containing a feeble shoulder peak at 734 K ( $\beta_2$  peak). Qu et al. [61] found that the CO<sub>2</sub> desorption peak at 473  $\degree$  673 K was corresponded to the bidentate carbonate species which formed on the moderate basic sites of Ce-Zr mixed oxides. Another HT peak at 823  $\degree$  973 K was attributed to the adsorption of CO<sub>2</sub> on the strong basic sites (low-coordination oxygen

anions) [62]. Because of the interaction between Ce-Zr-O oxide particles and ATP on ATP-CZO-SC-P400(3) support, the bidentate carbonate species is desorbed at much higher temperature. The strong basic sites were decreased due to the loss of oxygen vacancies. As for CZFK/ATP-CZO-SC and CZFK/ATP-CZO-SC-P400(3) catalysts, the weakly basic hydroxyl groups was strongly diminished during the calcination process of the catalyst, leading to the obvious decrease of desorption peak intensity. However, the peak temperature was much higher which might be related with the inner hydroxyl groups of the ATP support. In addition, the introduction of CZFK metallic particles did not affect obviously on the desorption peak temperature and intensity of moderate basic sites on ATP-CZO-SC-P400(3) composite. It was amazing that a newly generated HT peak at 774 K on CZFK/ATP-CZO-SC catalyst (v peak) can be observed, which may be caused by the enhancement of interaction between ZnO and Ce-Zr-O oxide [32]. As shown in Fig. 7, CZFK/ATP-CZO-SC-P400(3) catalyst showed much higher desorption peak temperature and intensity of y peak than CZFK/ATP-CZO-SC catalyst, implying the higher strength of ZnO-CZO interfaces active sites for CO<sub>2</sub> adsorption and conversion. Since they have the same catalyst composition, the improvement of total CO<sub>2</sub> adsorbed can be attributed to the enhancement of the interdispersion of mixed metal oxides (Figs. S7 and S8 in Supplementary material). Simultaneously, the interaction between metallic Cu and other metal oxides (ZnO, Fe<sub>2</sub>O<sub>3</sub> and Ce0.75Zr0.25O2 solid solution) after H2 reduction was also improved, which have been confirmed by BET, SEM, TEM, XPS and H2-TPR as mentioned above. Combining with these characterization results, it can be concluded that the formed ZnO-CZO interfaces are the active sites for CO<sub>2</sub> adsorption and conversion, while metallic Cu is the hydrogenation active site to adsorb H2 and facilitate H2 dissociation to produce methanol [32].

### 3.6. Catalyst performances

# 3.6.1. Evaluation of CO<sub>2</sub> hydrogenation over different catalysts

CO<sub>2</sub> hydrogenation performances over those Cu-ZnO based catalysts supported on ATP-CZO composite prepared from different methods were evaluated. As shown in Fig. 8, the preparation method of ATP-CZO composite has an important influence on catalytic performances. CZFK/ATP-CZO-PCP catalyst showed the lowest CO2 conversion of 10.5%, which was associated with its H2-TPR behavior (the highest reduction temperature of dispersed CuO and no reduction peak of composite copper oxide), which implied the importance of Cu species for improving catalytic activity. It's well known that CO<sub>2</sub> is thermodynamically stable and difficult to be activated. The dispersed Cu species are responsible for CO2 hydrogenation activity over Cu-ZnO based catalysts [46]. Though the dispersion of CuO over CZFK/ATP-CZO-SC-P400(3) catalyst was improved in contrast to CZFK/ATP-CZO-SC catalyst, which had been demonstrated by  $N_2O$  adsorption, SEM, TPR, TEM and XPS measurements, its catalytic activity is just a little lower than that of CZFK/ATP-CZO-SC catalyst with the highest  $\mathrm{CO}_2$ conversion of 18.2%. Therefore, the  $S_{Cu}$  and  $D_{Cu}$  of Cu-ZnO based catalyst was not the sole factor for determining CO<sub>2</sub> hydrogenation activity. Some other factors, like the intimate contact between CuO and other oxides (Ce-Zr-O solid solution, ZnO and Fe<sub>2</sub>O<sub>3</sub>) for increased interactions, and the improved dispersion of CuO upon ZnO sheet to form much more Cu-ZnO interface should be taken into account for improving the catalytic activity [63,64].

The products selectivity was also affected by the preparation method of ATP-CZO composite (Fig. 8a). It can be seen that CO was the dominant product of CO<sub>2</sub> hydrogenation over all catalysts under 593 K via RWGS reaction (CO<sub>2</sub> + H<sub>2</sub>  $\rightarrow$  CO + H<sub>2</sub>O), an endothermic reaction [2]. At the same time, CH<sub>4</sub> also was generated with different levels by direct CO<sub>2</sub> hydrogenation (CO<sub>2</sub> + 4H<sub>2</sub>  $\rightarrow$  CH<sub>4</sub> + 2H<sub>2</sub>O) due to the presence of FT element-Fe in the catalyst, which is called the methanation of CO<sub>2</sub> [65]. Mixed alcohols (marked as ROH, including methanol-C<sub>1</sub>OH and higher alcohols-C<sub>2</sub>+OH) cannot be only formed by the

direct CO<sub>2</sub> hydrogenation, but also generated by the hydrogenation of CO intermediate [66]. CZFK/ATP-CZO-SG catalyst showed the highest CH4 (non-desired product) selectivity of 30.3% while the lowest ROH selectivity of 7.8%. The highest CO selectivity of 55.8% was obtained over CZFK/ATP-CZO-HT catalyst, indicating that the lowest CuO particle size (Table 1) and the highest H<sub>2</sub> consumption of Fe<sub>2</sub>O<sub>3</sub> reduction (Table 2) play a decisive role in producing CO. For these ATP-CZO composite without PEG 400 modification supported Cu-ZnO based catalysts, the ROH selectivity over CZFK/ATP-CZO-FCP catalyst was the maximum of 23.3%, and then was CZFK/ATP-CZO-BCP catalyst of 20.7% and CZFK/ATP-CZO-PCP catalyst of 18.7%. The downtrend was consistent with the gradual decrease of crystallite size of CZO particles but opposite to the increase of crystallite size of CuO and ZnO particles (Table 1). However, other catalysts did not conform to the law. CZFK/ ATP-CZO-SC catalyst showed a smaller CuO particle size of 20.4 nm, while the ROH selectivity was only 8.8% companying with the formation of 37.2% other oxygenates (marked as HOC). It was amazing that the ROH selectivity was obviously increased to 17.5% over CZFK/ATP-CZO-SC-P400(3) catalyst at the expense of the sharply decrease of HOC selectivity. Since they have similar crystallite size of CuO, ZnO and CZO particles, the increase of ROH selectivity can be due to much higher  $S_{Cu}$ and D<sub>Cu</sub> for H<sub>2</sub> dissociation adsorption (Fig. 5 and Table 2) and higher strength of ZnO-CZO interfaces active sites for CO2 adsorption and conversion. At the same time, the proportion of methanol in mixed alcohols was high up to 97.6% and the STY of methanol and CO also showed the maxima over CZFK/ATP-CZO-SC-P400(3) catalyst (Fig. 8b). In sum, on the purpose of improving the CO<sub>2</sub> conversion and production ability of methanol and CO over ATP-CZO composite supported Cu-ZnO based catalysts, PEG 400 modified SC method is better choice for the preparation of ATP-CZO carrier.

The effects of addition amount of PEG 400 on catalytic CO<sub>2</sub> hydrogenation performance over ATP-CZO-SC-P400(x) nanocomposites supported Cu-ZnO based catalysts were also investigated. As shown in Table 3, the  $CO_2$  conversion shows a gradual increase. However, the selectivity of CH<sub>4</sub> and ROH shows an opposite change which reflects the competitive reaction route of CO<sub>2</sub> hydrogenation. Moreover, CO selectivity shows a consecutive decrease which seems like to contribute to the increase of HOC selectivity. From the effects of the addition amount of PEG 400 on the STY of methanol and CO formation over CZFK/ATP-CZO-SC-P400(x) catalysts as shown in Fig. 9, the competitive production of methanol and CO was present. With the increase of addition amount of PEG 400, the D<sub>Cu</sub> increased firstly and then decreased. According to the relationship between STY and  $D_{Cu}$ , the yield of methanol was directly related with D<sub>Cu</sub> and the CZFK/ATP-CZO-SC-P400(5) catalyst showed the highest methanol yield due to the highest  $D_{Cu}$ . This further proved that metallic Cu is the hydrogenation active site for adsorbing H<sub>2</sub> and facilitating H<sub>2</sub> dissociation to produce methanol. Raman detection results showed that the intensity of Ce-Zr-O oxide increased with the increase of x from 0 to 7 and then showed an obvious decrease when x was 10 (Fig. S9 in Supplementary material). CO<sub>2</sub>-TPD results showed that a higher strength of ZnO-CZO interfaces active sites was generated in CZFK/ATP-CZO-SC-P400(3) catalyst. Therefore, the increase of Ce-Zr-O oxide intensity is beneficial for improving the strength of ZnO-CZO interfaces active sites for CO<sub>2</sub> adsorption and conversion. Consequently, CO<sub>2</sub> conversion shows a gradual increase with the increase of addition amount of PEG400 from x = 1 to x = 7, but continuously increases when x = 10 which might be due to much smaller CuO crystallite size (Fig. 6).

To compare the catalytic efficiency produced by a unit site of a copper atom on the surface of a catalyst, the turnover frequency (TOF) which represents the number of CO and methanol produced on a unit site per second ( $s^{-1}$ ), was calculated from the  $S_{Cu}$  for various catalysts. Results from Fig. 9 showed that the TOF of methanol increased with increased addition amount of PEG 400 until it reached the same maximum for CZFK/ATP-CZO-SC-P400(5) and CZFK/ATP-CZO-SC-P400(7) catalyst; then, a decrease occurred with further increase in PEG 400



Fig. 8.  $CO_2$  hydrogenation properties comparison of Cu-ZnO based catalysts supported on ATP-CZO nanocomposites prepared from different method. Reaction conditions: T = 593 K, P = 6.0 MPa,  $n(H_2):nCO_2 = 3:1$  and GHSV = 5000 h<sup>-1</sup>.

content. A maximum TOF<sub>Methanol</sub> of  $1.3 \times 10^{-3}$  is obtained with a minimum TOF<sub>CO</sub> of  $1.9 \times 10^{-3}$ . Gao et al. [31] found that the CO<sub>2</sub> conversion over Cu/Zn/Al/Zr catalysts is related to the exposed Cu surface area and the dispersion of Cu, while the CH<sub>3</sub>OH selectivity is related to the distribution of basic sites on the catalyst surface. In this work, the CO<sub>2</sub> conversion over CZFK/ATP-CZO-SC-P400(x) catalysts did not show the same change trend with  $D_{Cu}$  and  $S_{Cu}$  due to some other parameters as mentioned below.

#### 3.6.2. Structure-properties-catalytic performance correlations

 $CO_2$  hydrogenation to methanol has been extensively studied over Cu-ZnO based catalysts, including different metallic oxides (Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, etc.) or their composites supported and modified solid-state catalysts. Some crucial factors for active sites, like a Cu step with a nearby Zn serving as adsorption site for oxygen-bound intermediates [19], a synergy of Cu and ZnO at the interface [67,68], and an adequate balance between metal (Cu<sup>0</sup>) and oxide surface sites (ZnO and ZrO<sub>2</sub>)

#### Table 3

Latalytic performance for CO <sub>2</sub> hydrogenation or	er ATP-CZO-SC-P400(x) nanocomposites supported Cu-ZnC	) based catalysts <sup>a</sup> .
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Catalyts	CO <sub>2</sub> conversion	Products selectivity (C-mol%)				Alcohols distribution (wt%)		
	(%)	CH <sub>4</sub>	CO	ROH <sup>b</sup>	HOC <sup>c</sup>	C <sub>1</sub> OH	C <sub>2+</sub> OH	
CZFK/ATP-CZO-SC-P400(1)	12.4	25.7	62.2	7.4	4.7	92.3	7.7	
CZFK/ATP-CZO-SC-P400(3)	13.9	14.4	44.6	17.3	23.7	96.3	3.7	
CZFK/ATP-CZO-SC-P400(5)	14.0	10.2	36.4	25.3	28.1	97.0	3.0	
CZFK/ATP-CZO-SC-P400(7)	15.7	11.5	36.5	21.4	30.6	97.0	3.0	
CZFK/ATP-CZO-SC-P400(10)	17.7	16.6	33.0	12.6	37.8	90.2	9.8	

<sup>a</sup> Reaction condition: T = 593 K, P = 6.0 MPa,  $n(H_2):nCO_2 = 3:1$  and GHSV = 5000 h<sup>-1</sup>.

<sup>b</sup> ROH stands for mixed alcohols.

<sup>c</sup> HOC stands for other oxygenates.



**Fig. 9.** Effect of the addition amount of PEG 400 in CZFK/ATP-CZO-SC-P400(x) catalysts on the dispersion of Cu ( $D_{Cu}$ ) and STY of methanol and CO (a) and surface area of Cu ( $S_{Cu}$ ) and TOF of methanol and CO (b). Reaction conditions: T=593 K, P=6.0 MPa,  $n(H_2):nCO_2=3:1$  and GHSV= $5000h^{-1}$ .

[24], were proposed to form and stabilize the intermediates for methanol synthesis. Metallic copper species acts as the crucial role for H<sub>2</sub> activation, of which the exposed surface area [46], dispersion, particle size [69] and the ratio of  $Cu^0/Cu^+$  [3] can control the  $CO_2$  conversion and methanol selectivity. Oxides carriers plays the most important role in adsorbing and activating  $CO_2$ , of which the crystalline form [70] and basic sites [21,26,27] can control catalyst texture and exposed metal surface, also affecting adsorption properties and catalyst functionality of the Cu-ZnO system [28]. According to the mechanism of  $CO_2$  hydrogenation to methanol, the larger exposed copper surface area is favorable to provide the large interfacial contact between copper and metal oxides [21], thus enhancing the formation and transformation of formate intermediate species. Therefore, a metal-oxide dual site nature on metal/oxides interface is crucial for the efficient synthesis of methanol from  $CO_2$  hydrogenation.

For the  $CO_2$  hydrogenation to CO by RWGS reaction,  $CeO_2$  is commonly used to support active-metal because of its reducibility and

high intrinsic activity toward  $CO_2$  adsorption [2]. Two major reaction mechanisms have been proposed for RWGS to CO. One is surface redox mechanism which claimed that  $CO_2$  is directly reduced into CO on the surface of metallic copper [21,51]. The other is the formate decomposition mechanism, in which  $CO_2$  is first hydrogenated into formate on the metal site, followed by cleavage of the C=O bond to generate CO on the metal/oxides interface site [2,71]. From this point of view, the estimate contact between metallic copper and oxides is very important, which is similar to the synthesis of methanol.

In this study, the acid-activated ATP was combined with Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> solid solution to produce ATP-CZO composite by different methods. Characterization results show that the preparation method of ATP-CZO composite has an important effect on its textures and the characters of CZO nanoparticles which differ obviously in texture, size and dispersion. In comparison, the ATP-CZO composite produced by PEG 400 modified SC method showed much better dispersion of CZO particles and directionally arranged ATP rodlike crystals

(Figs. S2 and S5 in Supplementary material). The interaction between Ce-Zr-O oxides and ATP support was effectively enhanced [43], thus alleviating the cation interchange between ATP and metallic ions (Cu<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>3+</sup>). Then the crystallite size and intensity of Ce-Zr-O oxides could be adjusted by changing the addition amount of PEG 400 (Figs. S4 and S9 in Supplementary material). Furthermore, as shown in Fig. 3, ZnO and Fe<sub>2</sub>O<sub>3</sub> were integrated with large crystallite size on the surface of ATP-CZO composite. As a result, CuO was intimately contacted and uniformly distributed upon ZnO-Fe<sub>2</sub>O<sub>3</sub> aggregate to form CuO-ZnO interface and CuFe<sub>2</sub>O<sub>4</sub> composite according to XRD, XPS and H<sub>2</sub>-TPR detections, implying the enhancement of interactions between CuO and other oxides (ZnO and Fe<sub>2</sub>O<sub>2</sub>). Moreover, the exposed copper surface area was also increased to provide much more active sites for H<sub>2</sub> adsorption and activation (Figs. 5 and 9). Bonura et al. [28] investigated the effects of ZnO promoter on the structure and CO<sub>2</sub>-hydrogenation functionality of Cu/CeO<sub>2</sub>, Cu/ZrO<sub>2</sub> and  $Cu/Ce_{(1-x)}Zr_xO_2$  ( $0 \le x \le 1$ ) catalysts. ZnO acted as a promoter of both structural and catalytic functionality of the metal copper phase. The  $CuZnO/Ce_{(1-x)}Zr_xO_2$  catalyst with a Ce/Zr ratio of 1/6 showed the highest catalytic activity and the increase of CeO<sub>2</sub> substitution by ZrO<sub>2</sub> was beneficial to increase the methanol yield. That's why the present catalyst supported on the ATP/Ce0.75Zr0.25O2 nanocomposite with a Ce/Zr ratio of 3/1 showed a lower catalytic activity and a higher CO selectivity. In future, the ATP/Ce $_{(1-x)}$ Zr $_x$ O $_2$  nanocomposite prepared from PEG 400 modified SC method with much lower Ce/Zr ratio is a promising carrier for supporting Cu-ZnO based catalysts to produce methanol from CO<sub>2</sub> hydrogenation.

As displayed in Fig. 10, CO and methanol could be simultaneously synthesized depending on the structural properties of CZFK/ATP-CZO-SC-P400 catalyst. On one hand, according to XRD (Fig. 1), XPS (Fig. 4) and  $CO_2$ -TPD result (Fig. 7), ZnO acted as a physical support for dispersing CuO species. The FT element-Fe further improved the

interdispersion of mixed metal oxides and the interactions between metallic Cu and other metal oxides (ZnO, Fe<sub>2</sub>O<sub>3</sub> and Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> solid solution) after H<sub>2</sub> reduction. The formation of CuFe<sub>2</sub>O<sub>4</sub> phase could relieve agglomeration of Cu species to maintain lower particle size of metallic Cu where more dissociative adsorbed H<sub>2</sub> provides a source of atomic hydrogen for spillover onto these intimately contacted ZnO, Ce-Zr-O solid solution and ZnO-CZO interfaces (Fig. 3) [3,67,70]. On the other hand, the strong basic sites on ZnO, ATP-CZO composite and ZnO-CZO interfaces could serve as the active sites for CO<sub>2</sub> adsorption, activation and conversion into carbonate species, bicarbonate species and formate species. The interactions between metallic Cu and ZnO. ATP-CZO composite and ZnO-CZO interfaces favored to stabilize the intermediates for further hydrogenation to produce methanol [21]. Therefore, ZnO acted as a structural promoter for improving the dispersion of metallic copper in the present catalyst and provided catalytic basic site for CO<sub>2</sub> adsorption and activation. However, as exhibited in catalytic performances, the CZFK/ATP-CZO-SC-P400 catalyst showed better formation ability for CO by RWGS reaction than methanol. This can be due to the promotion of C=O bond scission by reducible CeO<sub>2</sub> and proved later in a long-term stability study of catalyst.

#### 3.6.3. Catalysts stability

The stability of CZFK/ATP-CZO-SC-P400(3) catalyst for CO<sub>2</sub> hydrogenation at 593 K, 6.0 MPa and 5000 h<sup>-1</sup> is shown in Fig. 11. It can be found that the CO<sub>2</sub> conversion decreases slightly from 16.8% to 15%. The products selectivity showed an obvious change. In the initial reaction period of 8 h, the selectivity of HOC/ROH decays sharply to increase the selectivity of CO and CH<sub>4</sub>, which indicating the side reaction for HOC production was restrained. Subsequently, the selectivity of HOC/ROH decreases by 21.6% in following 22 h reaction which contributes to the selectivity increase of CO by 17.5% and CH<sub>4</sub> by 4.1%. The further increase of reaction time to 60 h did not change obviously



Fig. 10. Diagram of CO<sub>2</sub> hydrogenation to CO and methanol over CZFK/ATP-CZO-SC-P400 catalyst.



Fig. 11. Catalytic stability test of CZFK/ATP-CZO-SC-P400(3) catalyst for CO<sub>2</sub> hydrogenation. Reaction conditions: T = 593K, P = 6.0 MPa,  $n(H_2):nCO_2 = 3:1$ and  $GHSV = 5000h^{-1}$ .

the catalytic performances. Throughout the process of stability evaluation, the slight decay of CO<sub>2</sub> conversion may be due to the little agglomeration of active Cu species. CO and methanol are competitively produced from CO<sub>2</sub> hydrogenation with much higher CO selectivity over CZFK/ATP-CZO-SC-P400(3) catalyst. Moreover, the pathway that methanol was decomposed into CO also can explain the increase of CO selectivity to some extent. In sum, though CO was mainly produced over the present catalyst (Table 3, Figs. 8 and S10 in Supplementary material), the ATP-CZO nanocomposite can be adopted as a promising catalyst support for CO<sub>2</sub> hydrogenation.

# 4. Conclusions

A series of Cu-ZnO based catalysts supported on the ATP/ Ce0.75Zr0.25O2 nanocomposite prepared by different methods were synthesized for CO<sub>2</sub> hydrogenation to CO and methanol. The preparation method of ATP-CZO nanocomposite has a significant effect on the physicochemical properties and catalytic performance. Some conclusions can be drawn as follows:

- (1) The PEG 400 modified solution combustion method can improve effectively the formation and dispersion of CZO particles, enhance the orientation of ATP rodlike crystals and adjust the intensity of Ce-Zr-O oxides, thus leading to the increase of interaction between Ce-Zr-O oxides and ATP support and the formation of strong basic sites.
- (2) Exposed copper surface area of ATP-CZO nanocomposite supported Cu-ZnO based catalysts can be obviously increased due to the dispersion effect of PEG 400, but not the sole factor for determining the CO<sub>2</sub> hydrogenation activity. ZnO acted as a structural promoter for improving the dispersion of metallic copper and provided catalytic basic site for CO<sub>2</sub> adsorption and activation. Iron promoter has promoted the interaction between Cu species and other metal oxides (ZnO, Fe<sub>2</sub>O<sub>3</sub> and Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> solid solution) which can control the products selectivity.
- (3) The catalytic performances data revealed that CO and methanol can be produced simultaneously and competitively from CO<sub>2</sub> hydrogenation depending on the intimate contact of strong basic sites on ZnO, ATP-CZO composite and ZnO-CZO interfaces (mainly responsible for CO<sub>2</sub> adsorption, activation and conversion) and metallic Cu sites (mainly responsible for H<sub>2</sub> adsorption and dissociation to produce methanol) on the surface of catalyst.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110499.

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