Revised supporting information

A sol-gel auto-combustion method to prepare Cu/ZnO catalysts for low-temperature methanol synthesis

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Supporting Information

1. Experimental

1.1 Preparation of Catalysts

According to the principle of propellant chemistry [1], the valences of the elements C, H, and O were 4^+, 1^+, and 2^- respectively. Nitrogen had a valence of zero because N_2 was assumed to be liberated during the combustion process. The net oxidizing valence of $Cu(NO_3)_2$ and $Zn(NO_3)_2$ was worked out to be 10^-, whereas the net reducing valence of citric acid was 18^+. For the stoichiometric redox reaction between the fuel and the oxidant, the reaction between citric acid and metal nitrates was presented as Eq. (1).

$$9Cu(NO_3)_2 + 9Zn(NO_3)_2 + 10C_6H_8O_7 = 9CuO + 9ZnO + 60CO_2 + 18N_2 + 40H_2O \quad (1)$$

1.2 Characterization Techniques

Micro-Raman analysis of specimen was performed on a multichannel bench Renishaw InVia Reflex spectrometer coupled with a Peltier-cooled charge-coupled device detector. The instrument was equipped with a 514 nm diode laser for excitation, with a maximum output power of 100 mW. The power of the laser could be decreased to 10% of the maximum output power. The spectrum was centered to 520.00 cm^{-1} over a timeframe of 1 s, with diffraction grating of 1200 grooves/mm. The sample was scanned from 800 to 1900 cm^{-1} because this spectra region provided the most valuable data on the microstructure of carbon and carbonates. All samples were duplicated five times to check the reproducibility of the spectrum and to enhance the accuracy by accumulation.

1.3 Catalytic Activity Tests

In hydrogenation of CO and CO_2 over Cu catalysts, CO and CO_2 could be interconverted each other during the reaction. So CO and CO_2 conv. did not indicate "conversion" of each reactant. Only the conversion and TOF of total carbon defined made sense. TOF was the total carbon turnover frequency:

$$\text{TOF (batch reaction)} = [(85 - 40) \times 50 \times (33\% + 5.23\%) \times \text{total carbon conv.} \times 6.02 \times 10^{23}]/(3600 \times 1000 \times 22.4 \times S_{Cu} \times \text{catalysts weight} \times \text{reaction hours} \times 1.4 \times 10^{19}) \ldots\ldots (2)$$

$$\text{TOF (flow batch reaction)} = [\text{velocity of flow (20 ml/min)} \times 60 \times (33\% + 5.23\%) \times \text{total carbon conv.} \times 6.02 \times 10^{23}]/(3600 \times 1000 \times 22.4 \times S_{Cu} \times \text{catalysts weight} \times 1.4 \times 10^{19}) \ldots\ldots (3)$$

where the number of Cu atoms in one square meter was 1.4×10^{19}.

2. Results and discussion

2.1 Raman analysis of the burnt catalysts with different M/CA mole ratios

The Raman spectra of the burnt catalysts after 10 h reduction by 5% hydrogen were compared in Fig. 1 in the region from 800 to 1900 cm^{-1}. The curves in Figs. 1a-1c were assigned to the burnt catalysts $C_{0.5}$, $C_{1.4}$, and $C_{1.8}$. Fig. 1d displayed the spectrum of the precursor with M/CA = 1/1 burnt in argon without further reduction.

Two relatively broad Raman bands at about 1340 and 1590 cm^{-1}, which corresponded to the D (disordered) and G (graphitic) bands of the amorphous carbon [2-5], were exhibited in Fig. 1d. The bands at about 1110 cm^{-1} were attributed to the $(CO_3)_2^-$ symmetric stretching vibration in the carbonates [6-8]. The Raman spectrum of the $(CO_3)_2^-$ symmetric stretching modes in pure carbonates was commonly in the region from 1050 to 1110 cm^{-1} [9].

In Figs. 1a-1c, only one broad band at about 1110 cm^{-1} assigned to the carbonates was presented. No bands were attributed to the amorphous carbon, proving that the amorphous carbon derived from the decomposition of the citric acid in the argon atmosphere (as compared in Fig. 1d) was oxidized in air. The second exothermic peak in the DTA curves in Figs. 1c and 1d arose from the amorphous carbon oxidation. By increasing the citric acid content, the band at about 1110 cm^{-1} gradually increased. Thus, more carbonates were left in the burnt catalyst with the increase of citric acid content in the precursors. This result was also supported by TG-DTA and FT-IR analysis.

2.2 XRD analysis of the precursor with M/CA = 1/1

The XRD patterns of the precursor with M/CA = 1/1 after drying at 393 K for 40 h were presented in Fig. 2. The characteristic peaks were attributed to NH_4NO_3 only.

2.3 *Activity of the burnt catalysts without the help of citric acid*

The reaction result of the referent, which was prepared without citric acid, was displayed in Table 1. Analytical-grade $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ with the mole ratio of Cu/Zn = 1/1 were first dissolved in the distilled water, denoted as C_0, followed by stirring and refluxing at 353 K for 4 h. Subsequently, the neutralized solution was evaporated at 343 K on a hot plate by continuous stirring until dark blue viscous xerogels was formed. Thereafter, the gels were dried at 393 K for 40 h and were loaded in a muffle oven. The temperature was increased to about 723 K at a heating rate of 2 K/min and maintained for 3 h. The burnt catalysts were reduced by a flow of 5% hydrogen in nitrogen at 523 K for 10 h and successively passivated by 1% oxygen diluted by nitrogen.

The combustion process in air was a redox process which was strongly influenced by the mole ratio of oxidant to reductant. The greater reductant content in the redox reaction made the redox process much milder. Nitrate ions and O_2 in air acted as oxidant, while citric acid acted as reductant. For C_0, the catalyst preparation process of C_0 was only the decomposition of nitrate. No reductant participated in the reaction and the fierceness degree could not be controlled. By increasing the citric acid content in the catalysts precursors from $C_{0.5}$ to $C_{0.7}$, the combustion process was more violet than that of C_0, because deficient reductant made the redox process more severe. By continually increasing the content of citric acid from $C_{0.8}$ to $C_{1.4}$, the combustion process was gradually milder. Meanwhile, the decomposition of citric acid was an endothermic process accompanied by the releasing of H_2O and CO_2, which improved heat diffusion and heat adsorption. The combustion process was well identified by TG-DTA analysis in Fig. 2 (manuscript). However, by superfluously increasing the citric acid content from $C_{1.5}$ to $C_{1.8}$, excessive citric acid could lead to much more organic residues, which might cause a more severe pyrolysis process. Therefore, there was a balanced point between the citric acid content and metal nitrates, through which the whole process took place in a less severe way. The crystalline sizes of Cu were closely influenced by the temperature of combustion and pyrolysis processes. With the help of citric acid, the catalyst preparation process could be controlled and homogenous catalysts with smaller Cu crystalline sizes could be obtained.

References

1 S. R. Jain, K.C. Adiga and V. R. Pai Verneker, *Combust. Flame*, 1981, **40**, 71.

2 K. H. Kwok and W. K. S. Chiu, *Carbon*, 2003, **41**, 673.

3 A. Kromka, J. Breza, M. Kadlečíková, J. Janík and F. Balon, *Carbon*, 2005, **43**, 425.

4 U. Ritter, P. Scharff, C. Siegmund, O. P. Dmytrenko, N. P. Kulish, Y. I. Prylutskyy, N. M. Belyi, V. A. Gubanov, L. I. Komarova, S. V. Lizunova, V. G. Poroshin, V. V. Shlapatskaya and H. Bernas, *Carbon*, 2006, **44**, 2694.

5 M. Veres, S. Tóth, M. Füle, M. Koós and J. Non-Cryst. *Solids*, 2006, **352**, 1348.

6 R. L. Frost and M. Dickfos, *Polyhedron*, 2007, **26**, 4503.

7 S. K. Sharma, A. K. Misra, P. G. Lucey and R. C. F. Lentz, *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.*, 2009, **73**, 468.

8 S. M. dePaula, M. F. G. Huila, K. Araki and H. E. Toma, Micron, 2010, **41**, 983.

9 W. Kaabara, S. Botta, R. Devonshirea, *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.*, 2011, **78**, 136.

Figure Captions

Fig. 1. Raman analysis of the burnt catalysts (a) $C_{0.5}$, (b) $C_{1.4}$, (c) $C_{1.8}$, and (d) the precursor with M/CA = 1/1 burnt in argon without further reduction.

Fig. 2. XRD patterns of the precursor with M/CA = 1/1 after drying at 393 K for 40 h (●, NH_4NO_3).

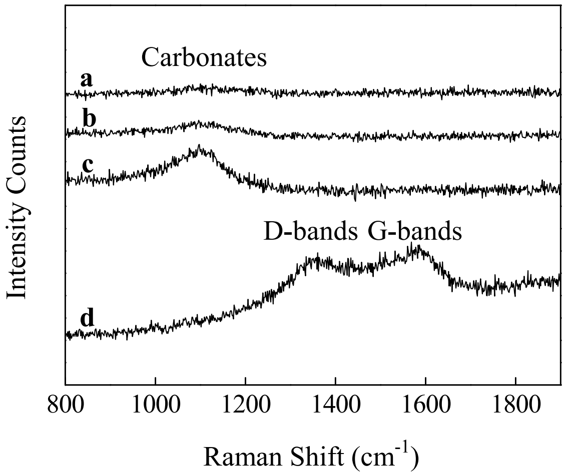

Fig. 1. Shi et al.

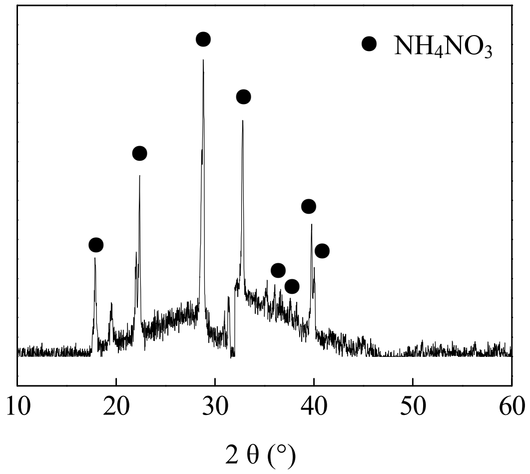

Fig. 2. Shi et al.

Table 1 Characterization results and the batch activity records for low-temperature methanol synthesis using the bunt Cu/ZnO catalysts without the help of citric acid.

Catalysts	S_{BET}[a] (m^2/g)	S_{Cu}[b] (m^2/g)	Cu[c]	Conversion %	TOF[d]	Selectivity %	
				C_{total}	($10^{-3}s^{-1}$)	CH_3OH	HCOOR[e]
C_0	9.32	3.6	59.0	33.0	5.1	40.5	59.5

Reaction conditions: T = 443 K, P = 5.0 MPa, catalyst weight: 1 g, ethanol solvent: 40 ml, stirring speed: 2000 rpm, reaction time: 8 h, syngas: $Ar/CO/CO_2/H_2$ = 3.13/33/5.23/58.64.

[a] Determined by N_2 physical adsorption-desorption at 77 K.

[b] Determined from N_2O pulse chemisorption.

[c] Calculated by Scherrer formula.

[d] TOF is the total carbon turnover frequency.

[e] HCOOR is ethyl formate.