

Electronic Supplementary Information (ESI)

Novel Cu-Fe Bimetal Catalyst for the Formation of Dimethyl Carbonate from Carbon

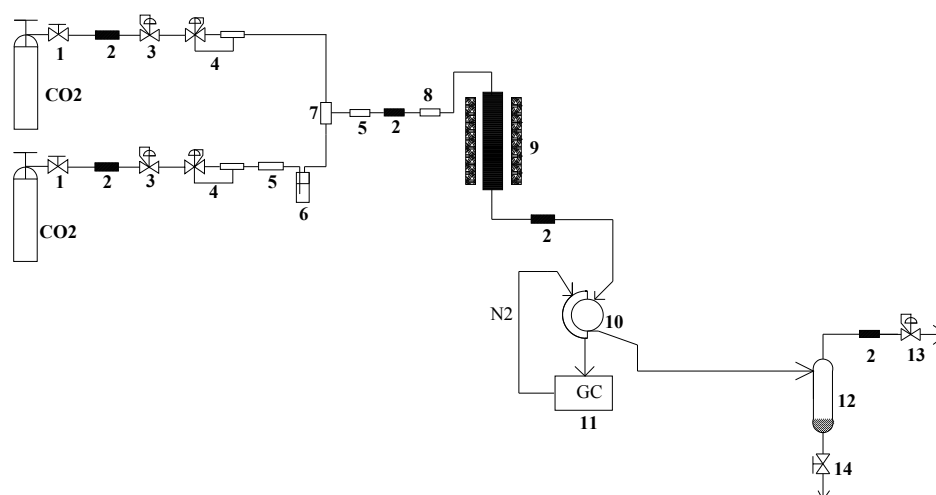
Dioxide and Methanol

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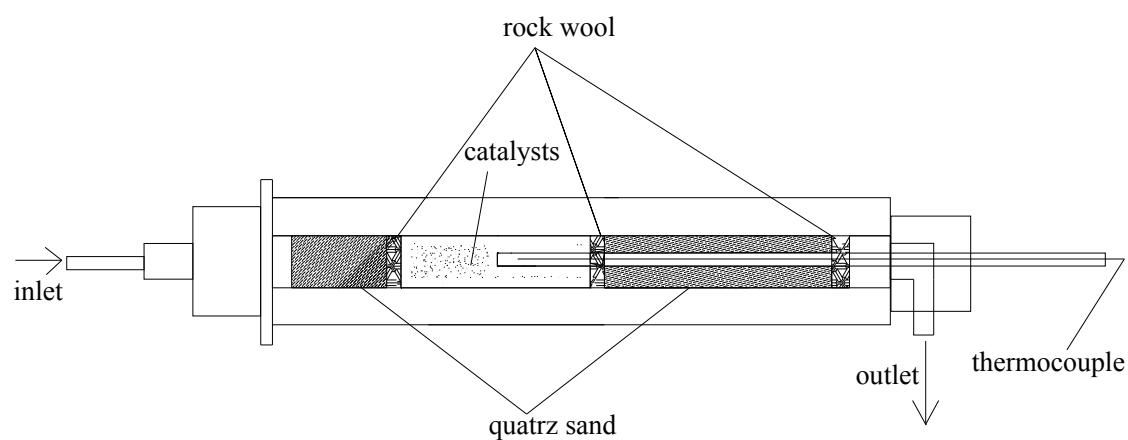
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Experimental Apparatus



Scheme 1 Diagram of apparatus for synthesis of DMC: 1.Pressure reducer valve; 2.Filter; 3.Pressure regulator; 4.Mass flow controller; 5.One-way valve; 6.Bubbler (methanol); 7.Blender; 8.Preheater; 9.Reactor; 10.Six-way valve; 11.Gas chromatography; 12.Cooling separator; 13.Back-pressure regulator; 14.Cut-off valve



Scheme 2 Diagram of the reactor

Experimental Data

1. Effects of molar ratio, weight load of metals and catalyst support on the catalytic activity.

Table S1 Dependence of methanol conversion and DMC selectivity on the loading and molar ratio of metals in the catalysts

Entry	(CuO-Fe ₂ O ₃) wt(%)	Mole ratio of Cu:Fe	Methanol Conversion (%)	DMC Selectivity (%)	DMC Yield (%)
1	3	5:2	3.70	89.3	3.31
2	3	2:1	3.73	86.4	3.22
3	3	3:2	4.66	84.7	3.95
4	3	1:1	1.82	83.8	1.53
5	3	2:3	3.67	83.6	3.07
6	3	1:2	4.38	82.3	3.61
7	3	2:5	3.55	81.9	2.91
8	9	3:2	4.63	81.7	3.78
9	15	3:2	4.98	84.5	4.20
10	21	3:2	3.91	83.6	3.27
11	27	3:2	2.73	84.5	2.31
12	3	1:0	1.01	93.3	0.94
13	3	0:1	1.04	90.4	0.89

The SiO₂ supported metal oxides were reduced in H₂ stream under 600°C for 4h. Reaction conditions: Pressure: 1.2MPa; Temperature: 120°C; Space velocity: 360h⁻¹; Catalyst weight: 2g. Time on stream: 7h. The methanol conversions were the average data between 2-4h with time on stream.

The catalytic performance of the direct DMC synthesis from CO₂ and methanol over Cu-Fe oxides loaded on SiO₂ after H₂ reduction at 600°C are shown in **Table S1**. The molar ratios of metals range from 2/5 to 5/2, and the metal oxides contents in the catalysts precursor vary from 3 to 27wt%. As shown in **Table S1**, when only copper (Entry 12) or iron (Entry 13) oxides loaded catalysts are used under reaction conditions, they show a relatively low activity compared to those obtained over the coexistence of copper and iron catalysts. This indicates that the synergetic effect of Cu and Fe clusters in the activation of methanol and CO₂ is a key factor dominating catalytic performance. In addition, we carried out the reaction over Cu-Fe bimetal catalysts with different Cu/Fe atomic molar ratios as listed in Table S1. The

equal amount of Cu and Fe (Entry 4) exhibits the worst catalytic performance, too many Cu (Entry 1) or too many Fe (Entry 7) species in the catalysts results in poor catalytic activities. When the molar ratio of Cu/Fe is 3/2(Entry 3) or 1/2 (Entry 6), they present the better catalytic performances. We further explored the catalytic performance by varying weight loading of the metals for the direct DMC formation. The catalytic activities first increase with increasing metals contents in catalysts (from Entry 8 to 9) and then decrease (from Entry 9 to 11). It appears that there exists an optimum composition for attaining maximum activity, and this composition corresponds to 15% (3CuO-Fe₂O₃)/SiO₂.

2. Effects of reaction conditions on catalytic activities.

Table S2 Effects of reaction conditions on the catalytic performances of the DMC formation from CO₂ and CH₃OH over Cu-Fe bimetal catalysts

Conditions	X_c %	S_{DMC} %	Yield %
Different reaction temperatures (°C): Pressure:1.2 MPa; Space velocity: 360h ⁻¹			
90	2.51	90.3	2.27
100	3.38	89.1	3.01
110	4.24	86.7	3.67
120	4.98	84.5	4.20
130	4.01	83.9	3.36
140	2.52	83.1	2.10
Different reaction pressures (MPa): Temperature:120°C; Space velocity: 360h ⁻¹			
0.3	3.47	79.5	2.76
0.6	4.15	82.7	3.43
0.9	4.70	83.6	3.93
1.2	4.98	84.5	4.20
1.5	5.02	86.2	4.33
Different space velocity (h ⁻¹): Pressure:1.2MPa; Temperature:120°C			
360	4.98	84.5	4.20
540	4.72	86.8	4.10
720	4.58	88.9	4.07
900	4.39	89.5	3.93
1080	4.34	90.2	3.91

The SiO₂ supported metal oxides were reduced in H₂ stream under 600°C for 4h. Catalyst weight: 2g. Time on stream: 7h. The methanol conversions were the average data between 2-4h with time on stream.

According to the previous investigations¹⁻³, the reaction conditions affect the catalytic performances considerably. In this paper, catalytic reactions were carried out under different temperatures in a range of 90-140°C, pressures of 0.3-1.5MPa and space velocities of 360-1080h⁻¹ with time on stream for 7h, and the effects of reaction conditions on the catalytic performances over the 3Cu-2Fe/SiO₂ catalysts are summarized in **Table S2**. Obviously, the reaction temperatures have great effects on the DMC formation. The activities first increase in the range from 90 to 120°C, and subsequently decrease with further increasing reaction temperatures up to 140°C. As indicated in literature⁴, the DMC formation is more favorable at lower reaction temperature, because this synthetic reaction is an exothermic one. In **Table S2**, the catalytic performance at lower reaction temperature than 120°C was mainly governed by the activation rate of CO₂ and CH₃OH, and at reaction temperature higher than 120°C, the reaction is restricted by the reaction equilibrium. The best catalytic performance at 120°C is probably due to the mutual action of the kinetics and thermodynamics.

Pressure also plays a key role in the direct DMC formation. According to **Table S2**, the catalytic performances slightly increase with the increasing pressures. The pressures do not show great effects on the catalytic performances when the reaction pressures reach to above 0.6MPa. This suggests that higher reaction pressure is benefited in the reaction equilibrium yet it is not required for the direct DMC synthesis.

Space velocity influences the catalytic performance by controlling the resident time of the reactants adsorbed on catalysts. As it is seen in **Table S2**, the catalytic performances decline marginally with increasing space velocity, which is accounted for that the increase in space velocity will diminish the resident time of the reactants adsorbed on catalysts.

3. Figure S1: Laser Raman Spectra of the 3Cu-2Fe/SiO₂ before and after being evaluated.

Raman spectroscopy was used to detect the differences of chemical environment before and after the catalyst being evaluated, and the results are presented in **Fig. S1**. Both fresh and used catalyst showed Raman vibrations centered at 516.8, 606.4, 965.5 cm⁻¹. These bands were well identified as the stretching mode of Fe-O, Si-O, the -OH on the surface of SiO₂⁵, respectively. The Raman shift observed at 1366.3 cm⁻¹ was related to the vibration of Si-O-Si in the SiO₂. The new broader band appearing at 1178.7 cm⁻¹ presented in **Fig. S1 (B)** was corresponding to the anti-symmetric stretching vibration of Fe-O⁶, probably because the coordination of Fe species changed after reaction for 7h. Accordingly, the catalysts were gradually deactivated with time on stream during the reaction process. The Raman shift observed at 1596.0 cm⁻¹ was associated with the C-O vibration mode, indicating that the organics were deposited on the catalyst during the evaluation process.

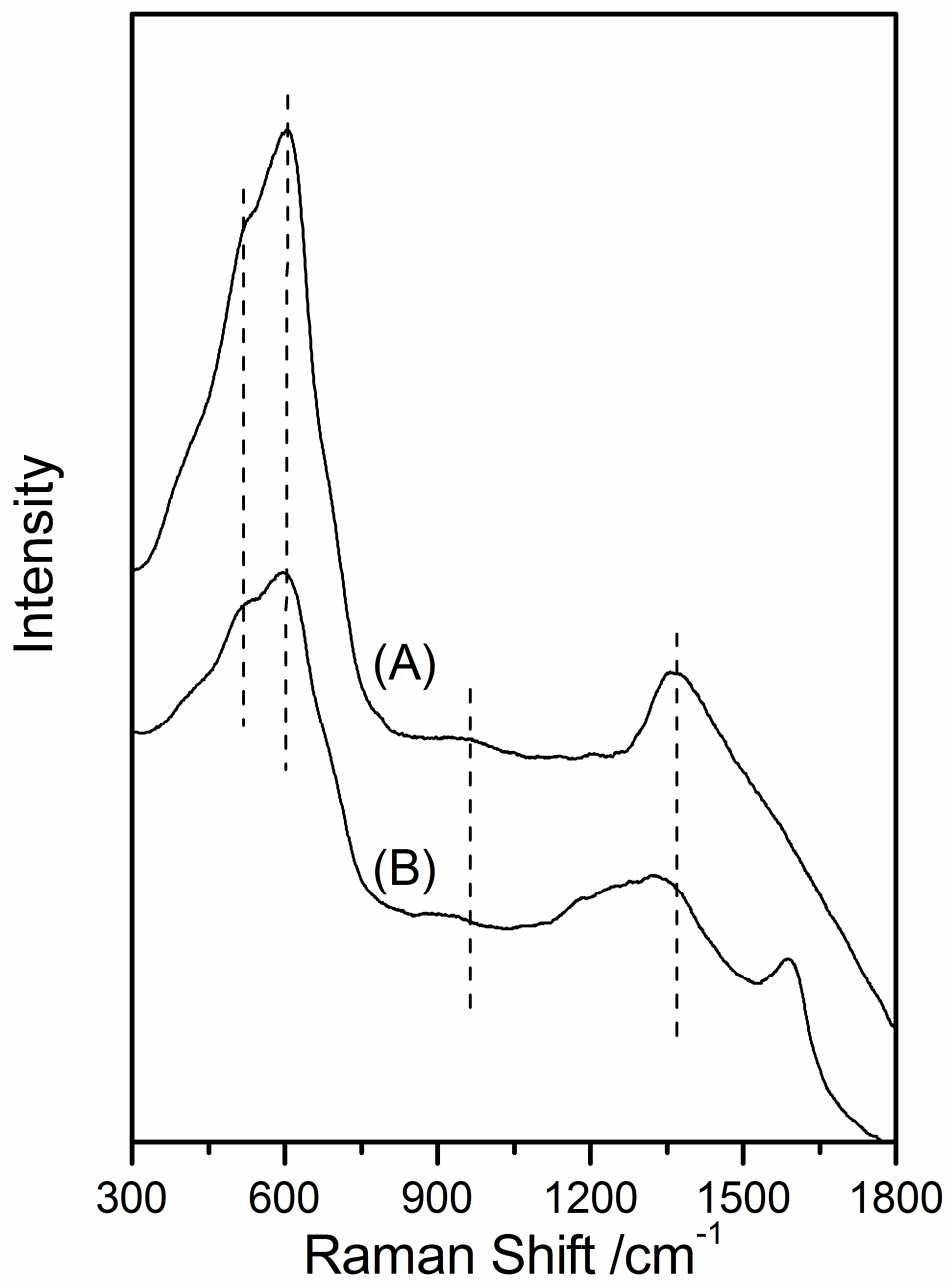
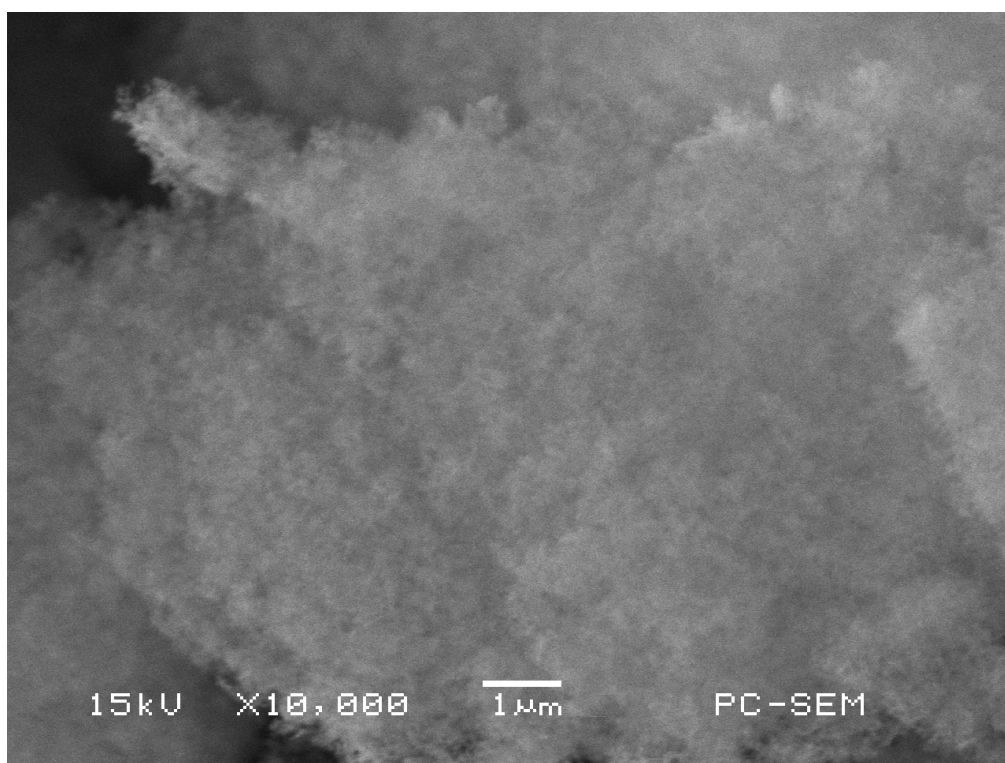


Fig.S1 Raman spectra (785nm) of catalysts: (A) fresh 3Cu-2Fe/SiO₂ (B) (A) after being evaluated

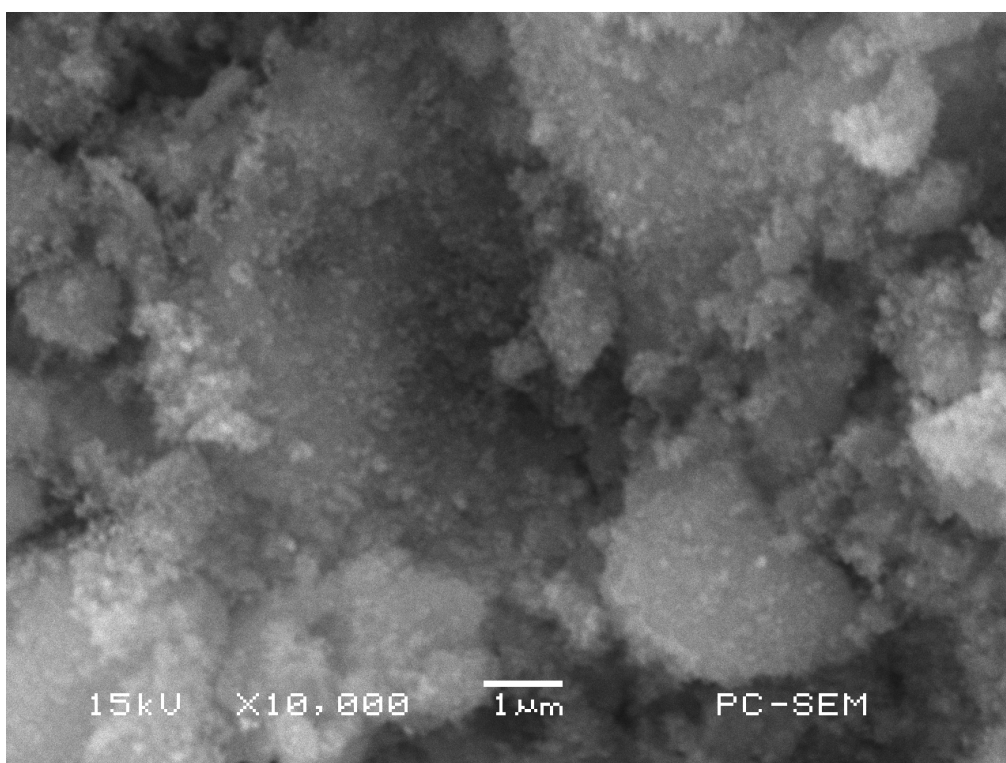
4. Fig.S2: SEM images of SiO₂ and the supported Cu-Fe clusters.

The SEM images of SiO₂ and the fresh catalyst are presented in **Fig. S2**. It is apparent that the SiO₂ maintains the original shape (**Fig.S2(A)**) after the Cu-Fe particles are loaded, and the Cu-Fe clusters (white circular dots in **Fig. S2 (B)**) are well dispersed on SiO₂.

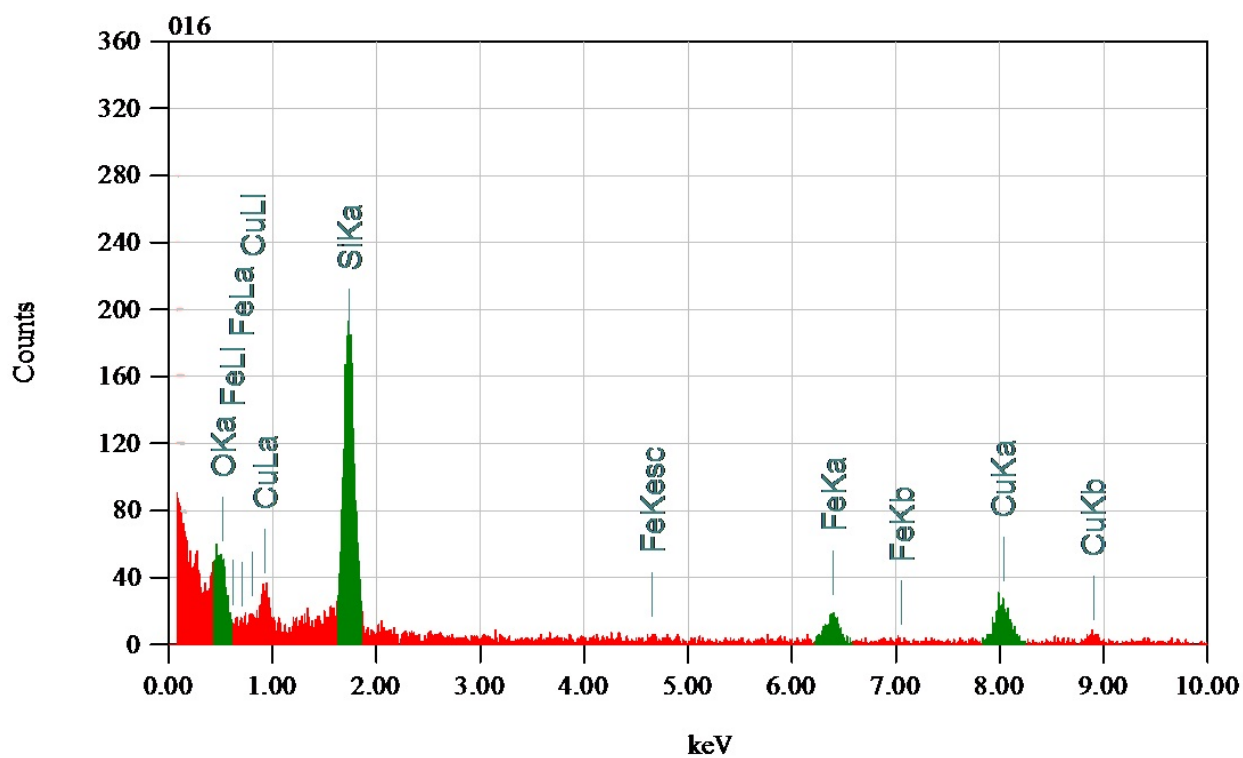
The chemical compositions of these white dots are determined by energy dispersive X-ray detector (EDX) (**Fig. S2(C)**), and they include Cu, Fe, Si and O. The mole ratio of Cu/Fe is near 3/2, which is in agreement with the nominal Cu/Fe mole ratio loaded in the synthetic route.



(A)



(B)



(C)

Fig.S2 SEM micrographs of (A) SiO₂, (B) 15%(3CuO-Fe₂O₃)/SiO₂ reduced at 600°C, (C)
Energy dispersion spectrometer (EDS) of circular particle in (B)

5. Fig.S3, Fig.S4: TPD profiles of the SiO₂ supported Cu-Fe catalysts with various Cu/Fe molar ratios.

The acid-base properties of SiO₂ supported Cu-Fe catalysts with various Cu/Fe molar ratios investigated by TPD techniques are shown in **Fig.S3** (TPD-NH₃) and **Fig.S4** (TPD-CO₂), respectively. There is a major desorption peak in the TPD-NH₃ (**Fig.S3**) at around 200°C over all catalysts, which is ascribed to one kind of weak acid sites. On the other hand, from the profiles of TPD-CO₂ depicted in **Fig.S4**, it is found that there are three peak temperatures, corresponding to three types of base sites on the catalyst surface. The weak base sites at around 120°C are found to be effective in the direct DMC formation. This is in accordance with the relationship between the catalytic performances as functions of reduction (**Fig.1**) and reaction temperatures (**Table S2**), and the base properties (**Fig.8**) of 3Cu-2Fe/SiO₂ reduced at various temperatures. The peak areas of the NH₃ decrease and yet the desorption amount of CO₂ at around 120°C increase with increasing Cu contents in the catalysts apart from Cu/Fe with the equal molar ratio, which owns the minimum desorption amount of NH₃ and CO₂. According to the TPR (**Fig.3**), XRD (**Fig.4**), XPS (**Fig.5, Fig.6**) and TPD (**Fig.7, Fig.8**) analysis, we can conclude that the acid behavior of the catalyst is the function of oxygen deficient Fe₂O_{3-x} (0<x<3), while the base behavior is the results of Cu and Fe metals. These suggest that the larger amount of Cu species definitely give larger number of base sites, and the higher contents of Fe species lead to more acid sites on the catalyst surface as long as the catalysts are reduced under the same conditions. However, the Cu/Fe with the equal molar ratio has the least amount of acid and base sites. This is presumably due to the strong interaction between the Cu and the Fe species when Cu/Fe is 1/1.

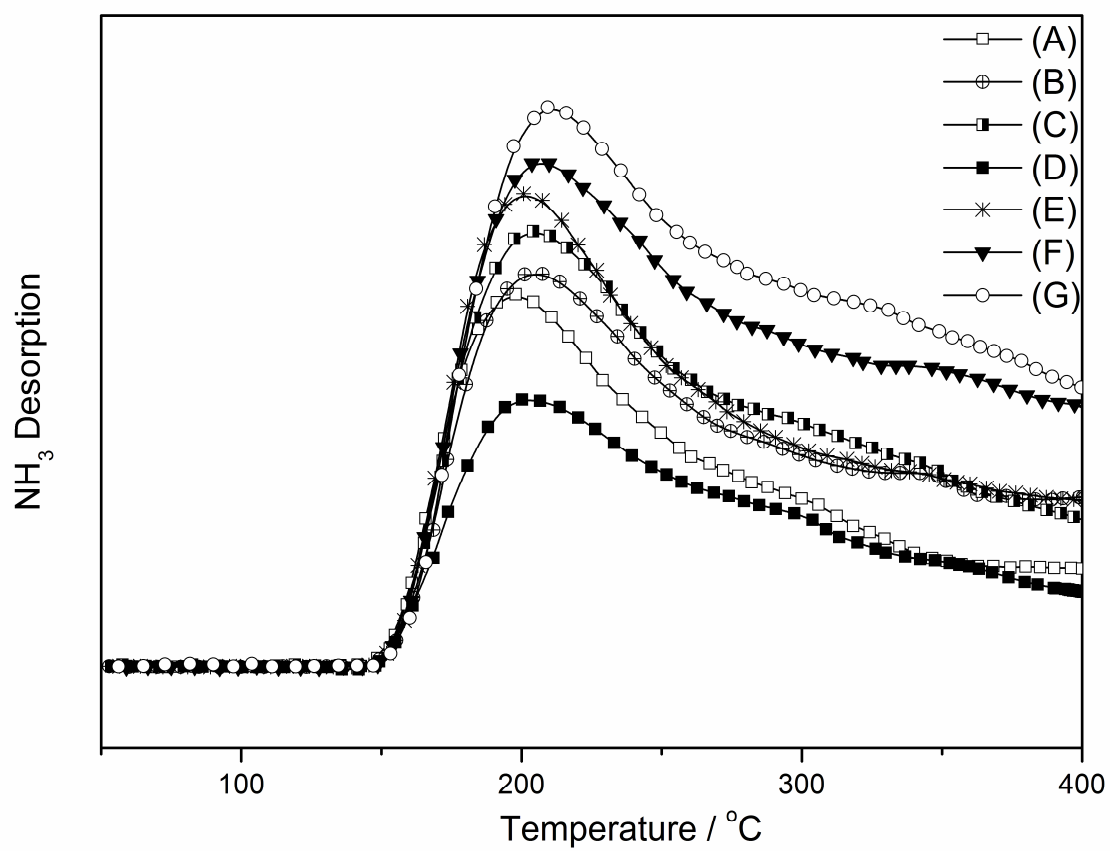


Fig. S3 TPD-NH₃ profiles of 3%(CuO-Fe₂O₃)/SiO₂ with various Cu/Fe molar ratios reduced at 600°C

(A) 5/2, (B) 2/1, (C) 3/2, (D) 1/1, (E) 2/3, (F) 1/2, (G) 2/5

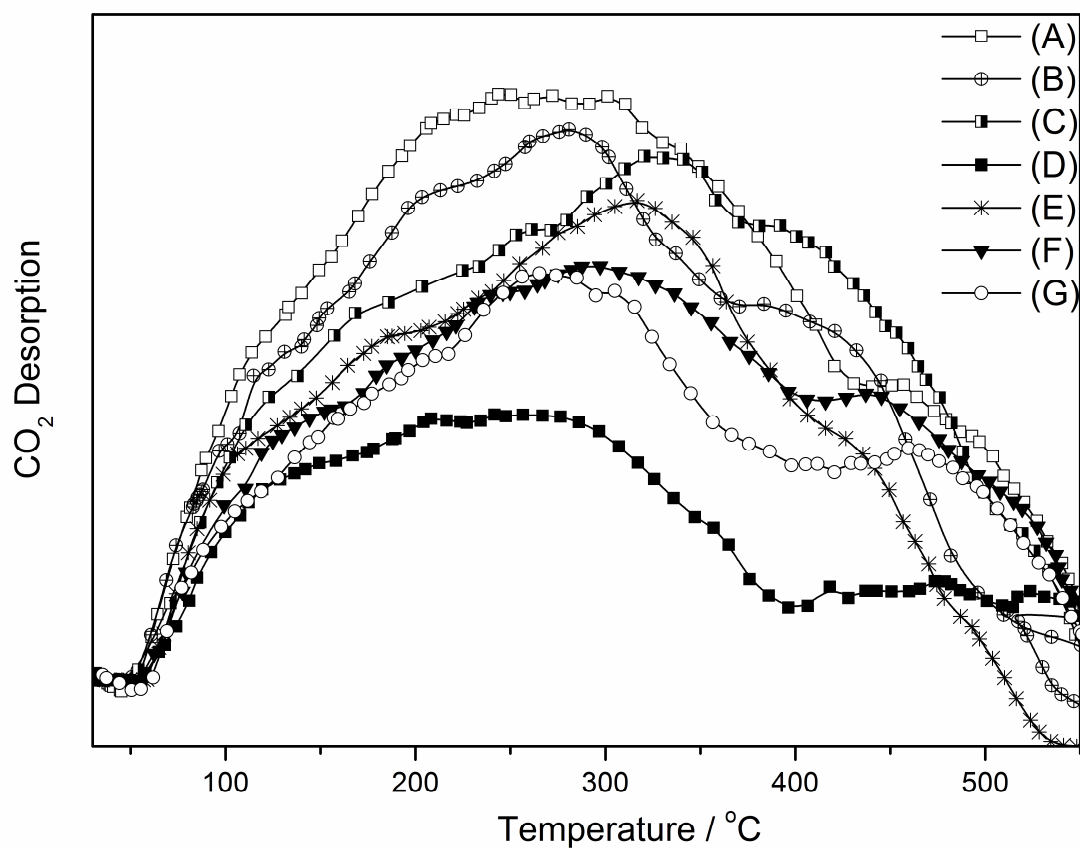


Fig. S4 TPD-CO₂ profiles of 3%(CuO-Fe₂O₃)/SiO₂ with various Cu/Fe molar ratios reduced at 600°C (A) 5/2, (B) 2/1, (C) 3/2, (D) 1/1, (E) 2/3, (F) 1/2, (G) 2/5

References

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