

# Effect of air-exposure on reduction behavior of a Fe–Mn–Cu–K/SiO<sub>2</sub> Fischer-Tropsch synthesis catalyst

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## Abstract

It was found that air-exposure suppressed the sequent reduction behavior before a Fe–Mn–Cu–K/SiO<sub>2</sub> Fischer-Tropsch synthesis (FTS) catalyst was loaded in reactor. Thermogravimetry and mass spectrometry analysis (TG–MS), in situ diffuse reflectance infrared Fourier transform (DRIFT) analysis, CO<sub>2</sub> temperature-programmed desorption (TPD), in situ syngas reduction and Mössbauer spectroscopy were used to reveal the intrinsic relationship between air-exposure and reduction behavior of catalysts. The result of in situ reduction indicates that the air-exposure restrains the reduction of Cu-promoted catalyst and suppresses the formation of active sites. Results of TG–MS indicate that water and CO<sub>2</sub> are adsorbed on surface of catalysts when catalysts were exposed to air. Copper promotion enhances the selective adsorption of CO<sub>2</sub> in air. The species formed upon CO<sub>2</sub> adsorption are irreversible surface carbonates, which cannot be removed under the typical or higher temperature used in FTS reaction. The surface carbonates formed in air-exposure restrain the role of Cu in reduction and lead to the low extent of reduction or carburization.

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**Keywords:** Fischer-Tropsch; Fe–Mn catalyst; Copper promotion; CO<sub>2</sub> adsorption; Air-exposure

## 1. Introduction

The Fischer-Tropsch synthesis (FTS) process is of considerable significance for its conversion of coal and natural gas into clean liquid fuels and chemicals. In the industrial FTS process, the slurry column reactor is very attractive compared with the fixed-bed reactor, and has been used in Sasol [1] due to its excellent performance, such as no diffusion limitations, high heat transfer capabilities and low costs. However, the high attrition resistance of the catalyst is required for the separation of liquid product from the catalyst in the slurry bubble column reactor. Therefore, silica is usually used as a support for FTS catalyst to obtain the desired physical strength and make it to be attrition-resistant. However, the addition of SiO<sub>2</sub>

as a structural promoter also leads to the corresponding poor reducibility due to the strong metal-support interaction [2]. Hence, copper is usually added to improve the reducibility for the iron-based catalysts supported on silica, i.e. to decrease the required reduction temperature of the silica supported iron-based catalysts [3–7].

Although the effects of copper were reported by many researchers and the similar results were verified again on the Fe–Mn–Cu–K/SiO<sub>2</sub> catalysts developed in our group, improper pretreatment could lead to the invalidation of copper in reduction. For instance, an interesting phenomenon was observed during in situ reduction in syngas, that is, the calcinated catalyst precursor became difficult to be reduced again when exposed to air for certain time. It is well known that the calcinated catalyst is inevitable to be exposed to air in the industrial applications except that it is protected using inert gas during the whole preservation and loading process.

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Therefore, to investigate the possible causes for the interesting phenomenon becomes very important for the industrial FTS process.

In this paper, thermogravimetric and differential thermogravimetry (TG-DTG) with mass spectrometry (MS) analysis, in situ diffuse reflectance infrared Fourier transform (DRIFT) analysis, CO<sub>2</sub>-TPD, in situ reduction and Mössbauer spectroscopy were used to investigate the inherent cause of the experimental phenomenon. Using these methods, it is revealed that the invalidation of copper results from the formation of irreversible carbonate when catalyst is exposed to air.

## 2. Experimental

### 2.1. Preparation of catalysts

The catalysts used in this work were prepared using the combination of co-precipitation and spray drying. In brief, a solution containing Fe(NO<sub>3</sub>)<sub>3</sub>, Mn(NO<sub>3</sub>)<sub>2</sub> and silica sol with Fe/Mn/SiO<sub>2</sub> ratio of 100/12/12 was used in precipitation with NH<sub>4</sub>OH solution as precipitator at pH 8.5–9.5 and  $T = 70\text{--}80\text{ }^{\circ}\text{C}$ . After precipitation, washing and filtration, a precipitate containing Fe, Mn and Si elements was obtained. Cu(NO<sub>3</sub>)<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> solutions were respectively added into the precipitate and spray drying was followed to obtain desired catalyst precursors with particle size of 20–70  $\mu\text{m}$ . Then, catalyst precursors were calcinated at 500  $^{\circ}\text{C}$  for 5 h. The final obtained catalysts were composed of 100Fe/12Mn/3K/12SiO<sub>2</sub> (Cu00) and 100Fe/12Mn/3K/3Cu/12SiO<sub>2</sub> (Cu03) in mass ratio, respectively.

After calcination, catalysts were divided into two groups. One was protected in a silica gel desiccator and immediately transferred into reactor; the other was exposed to air before loaded into reactor. The two groups were named as the protected samples and the exposed samples, respectively.

### 2.2. Catalyst characterization

#### 2.2.1. TG-DTG with MS analysis

The thermogravimetric analysis was performed using TGA92 (Setarm, France). The effluent was monitored using a mass spectrometer (OmniStar 200, Balzers, Switzerland). Typically, 20–30 mg sample was treated at ambient conditions for 30 min and then temperature was increased from room temperature to 500  $^{\circ}\text{C}$  at a ramp of 10  $^{\circ}\text{C}/\text{min}$  and held at 500  $^{\circ}\text{C}$  for 5 min before cooling. In the whole process, argon was used as the carrier gas with the flow rate of 50 ml/min.

#### 2.2.2. DRIFT analysis

IR spectra were collected using an infrared spectrometer (Equinox55, Bruker, Germany), equipped with KBr optics and a MCT D316 detector which works at the liquid nitrogen temperature ( $-196\text{ }^{\circ}\text{C}$ ). The infrared cell with ZnSe windows

was connected to a gas-feed system with a set of stainless steel gas lines, which allowed the in situ measurement for the adsorption of probe molecules. Thermal desorption of the adsorbed probe molecules in argon flow was temperature-programmed and monitored by infrared spectroscopy with a temperature increasing rate of 10  $^{\circ}\text{C}/\text{min}$ . In all cases, the gas flows were maintained at 50 ml/min. All the spectra were recorded with a resolution of 4  $\text{cm}^{-1}$  and accumulation of 64 scans.

#### 2.2.3. CO<sub>2</sub>-TPD

The temperature-programmed desorption experiments were performed in an atmospheric quartz tube flow reactor (5 mm i.d.). A flow of helium (purity: 99.9%) maintained at 50 ml/min, was used as the carrier gas, which passed through a series of desulfurizer, molecular sieve and silica gel traps to remove impurities. CO<sub>2</sub> was measured by a gas chromatography using a thermal conductivity detector (TCD). Catalyst sample (200 mg) was loaded in the quartz tube reactor. Then, the sample was heated in Ar from 50 to 500  $^{\circ}\text{C}$ , held at 500  $^{\circ}\text{C}$  until the base line levels off and then cooled to 50  $^{\circ}\text{C}$ . Following, CO<sub>2</sub> adsorption on catalyst was performed at 50  $^{\circ}\text{C}$  for 30 min. Then, the sample was purge with He at 50  $^{\circ}\text{C}$  for 30 min to remove weakly adsorbed species. After this step, CO<sub>2</sub>-TPD was carried out with temperature increasing to 500  $^{\circ}\text{C}$ . In all the temperature-programmed run, a ramp of 10  $^{\circ}\text{C}/\text{min}$  was used.

#### 2.2.4. Mössbauer spectroscopy

The Mössbauer spectra of catalysts were recorded at room temperature using a CANBERRA Series 40 MCA constant acceleration Mössbauer spectrometer (CANBERRA, USA), and a 25 mCi <sup>57</sup>Co in Pd matrix. The spectrometer was operated in the symmetric constant acceleration mode. The spectra were collected over 512 channels in mirror image format. Data analysis was performed using a nonlinear least squares fitting routine that models the spectra as a combination of singlets, quadruple doublets and magnetic sextuplets based on a Lorentzian line shape profile. The spectral components were identified based on their isomer shift (IS), quadruple splitting (QS) and magnetic hyperfine field (Hhf). All isomer shift values were reported with respect to metallic iron ( $\alpha\text{-Fe}$ ) at room temperature. Magnetic hyperfine fields were calibrated with the 330 kOe field of  $\alpha\text{-Fe}$  at ambient temperature.

### 2.3. In situ syngas reduction

The in situ reduction was conducted in a slurry phase reactor. Catalyst (20 g) was loaded into reactor with liquid paraffin (ca. 380 g) as the initial solvent. The catalyst samples were reduced in syngas (H<sub>2</sub>/CO = 0.67) at 0.5 MPa, 1000 h<sup>-1</sup> and 280  $^{\circ}\text{C}$  for 8 h. After reduction, the catalyst samples (ca. 1 g) were drawn online for Mössbauer spectroscopy analysis. The CO<sub>2</sub> concentration in tail-gas was analyzed online using a gas chromatograph (Model 4890D, Agilent, USA).

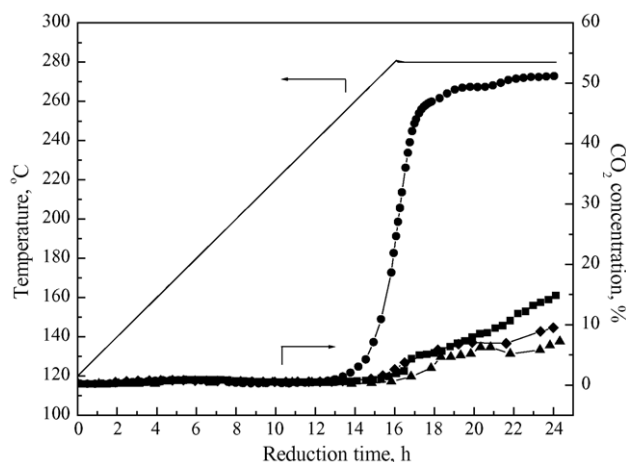


Fig. 1. In situ reduction of catalysts with syngas in slurry phase reactor. Reduction condition:  $\text{H}_2/\text{CO} = 0.67 \text{ mol/mol}$ ,  $0.5 \text{ Mpa}$ ,  $1000 \text{ h}^{-1}$  and  $280 \text{ }^\circ\text{C}$  for 8 h: (●) the protected CuO<sub>3</sub>, (■) the exposed CuO<sub>3</sub>, (◆) the protected CuO<sub>0</sub> and (▲) the exposed CuO<sub>0</sub>

### 3. Results and discussion

#### 3.1. Effect of air-exposure on in situ reduction

The protected and the exposed samples for CuO<sub>0</sub> and CuO<sub>3</sub> catalysts were reduced in CSTR to study the effect of air-exposure on reduction. Fig. 1 shows the variation of CO<sub>2</sub> concentration in tail-gas during reduction. CO<sub>2</sub> concentration is a convenient measure of catalyst reduction or activation, since it is directly related to the formation of active phase of the catalysts. As shown in Fig. 1, when reduction temperature is increased to  $280 \text{ }^\circ\text{C}$ , CO<sub>2</sub> concentration in tail-gas on the protected CuO<sub>3</sub> catalyst immediately reaches the maximum and then levels off, while that on the exposed CuO<sub>3</sub> catalyst does not. For CuO<sub>0</sub> catalyst, there is almost no difference in CO<sub>2</sub> concentration of tail-gas for the exposed and the protected samples. These results indicate that air-exposure has no influence on the reduction behavior of the CuO<sub>0</sub> catalyst, whereas, it apparently suppresses the reduction behavior of the CuO<sub>3</sub> catalyst. After reduction, samples of the exposed and the protected CuO<sub>3</sub> catalyst are, respectively, drawn out to determine the iron phase composition with Mössbauer spectroscopy. The Mössbauer spectra of reduced catalysts are presented in Fig. 2 and the corresponding iron phase

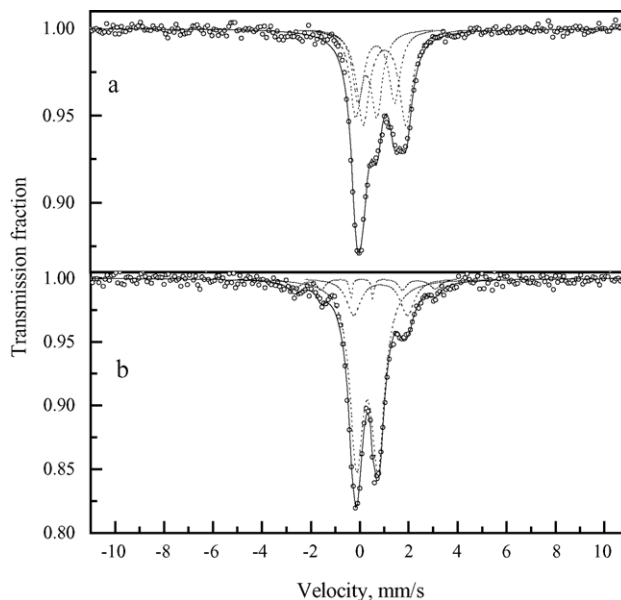


Fig. 2. Mössbauer spectroscopy of CuO<sub>3</sub> catalyst after in situ reduction. Open symbol: experimental data, solid line: fitted overall spectrum, dot line: fitted sub-spectrum: (a) the exposed sample and (b) the protected sample.

compositions obtained from Mössbauer spectra are listed in Table 1. Fig. 2a shows the spectrum of the exposed sample, in which Fe<sup>2+</sup> occupies the large contribution and no iron carbide is detected. However, in the spectrum of the protected sample (Fig. 2b), a small contribution of  $\chi\text{-Fe}_5\text{C}_2$  (8.7%) is recorded. The results indicate that the air-exposure suppresses the reduction or carburization of CuO<sub>3</sub> catalyst in syngas. Iron carbides are known as possibly main active phases for the FTS reaction [8–12]. Therefore, it is clear that air-exposure apparently affects the formation of active phase on Cu-promoted catalyst during in situ syngas reduction. Since the reduction behavior of Cu-free catalyst is not changed, the air-exposure suppresses the role of copper in reduction. It is likely due to the water or CO<sub>2</sub> adsorption on catalysts. Therefore, further investigation is required to reveal the air adsorption behaviors on catalysts.

#### 3.2. Air-exposure

TG–MS and DRIFT were used to characterize the adsorption behaviors of catalysts in air. Figs. 3 and 4 show the

Table 1  
Mössbauer parameters of the exposed and the protected CuO<sub>3</sub> catalyst samples after in situ reduction

Catalysts	Mössbauer parameter			Assignment	Contribution (%)
	IS (mm/s)	QS (mm/s)	Hhf (kOe)		
Exposed sample	0.29	0.86	179	Fe <sup>3+</sup> (s)	31.1
	0.70	1.49		Fe <sup>2+</sup> (s)	27.8
	1.03	1.75		Fe <sup>2+</sup> (s)	41.1
Protected sample	0.15	0.13	179	$\chi\text{-Fe}_5\text{C}_2$	8.7
	0.31	0.88		Fe <sup>3+</sup> (s)	74.5
	0.85	2.20		Fe <sup>2+</sup> (s)	16.8

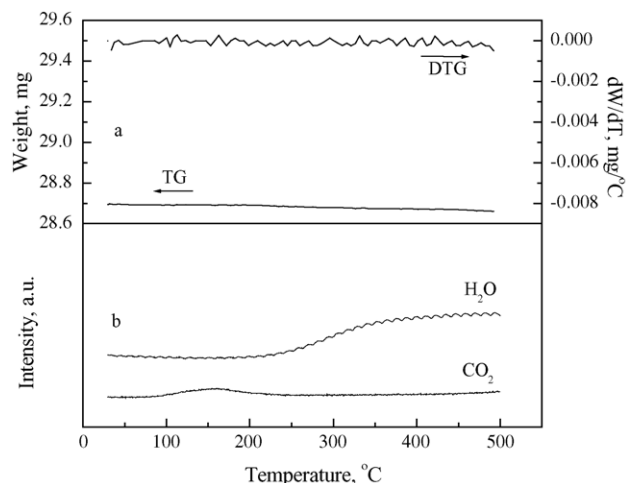


Fig. 3. TG and DTG with MS analysis for the protected Cu00 catalyst: (a) TG-DTG profiles and (b) MS profiles of H<sub>2</sub>O and CO<sub>2</sub>.

TG–MS profiles of the protected Cu00 and Cu03 catalyst samples. As shown in the figures, the weights of the two catalysts do not change at all and nearly no species is desorbed with increasing temperature. Figs. 5 and 6 show the TG–MS profiles of the exposed Cu00 and Cu03 catalyst samples. As shown in TG-DTG profiles of both figures, there is an apparent peak of weight loss at about 100 °C on the exposed samples. From the MS profiles, it is clearly shown that the desorbed species are water and CO<sub>2</sub>. The MS profiles also show that CO<sub>2</sub> evolution peak is mainly at 100 °C, which corresponds to desorption of weakly adsorbed CO<sub>2</sub>. In the range of 250–350 °C, there is a broad and weak peak, which can be assigned to the desorption of strongly adsorbed CO<sub>2</sub>.

Figs. 7 and 8 show IR spectra of the exposed Cu00 and Cu03 catalysts, respectively. These IR spectra were collected during the process of thermal treatment with temperature from 30 to 500 °C in step of 30 °C. In the initial stage of desorption, two strong bands at 3410 and 1630 cm<sup>-1</sup>

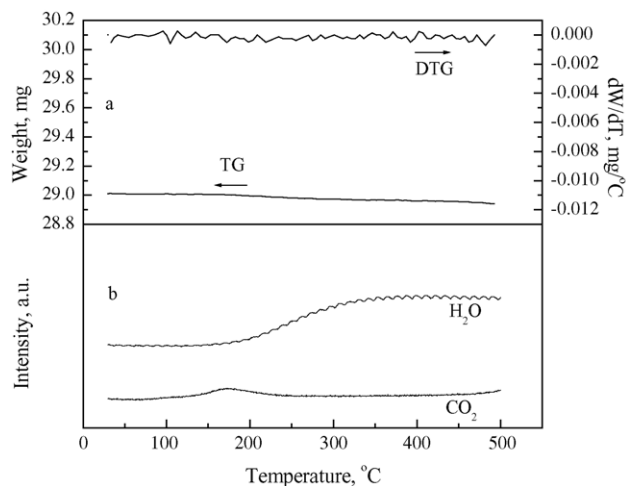


Fig. 4. TG and DTG with MS analysis for the protected Cu03 catalyst: (a) TG-DTG profiles and (b) MS profiles of H<sub>2</sub>O and CO<sub>2</sub>.

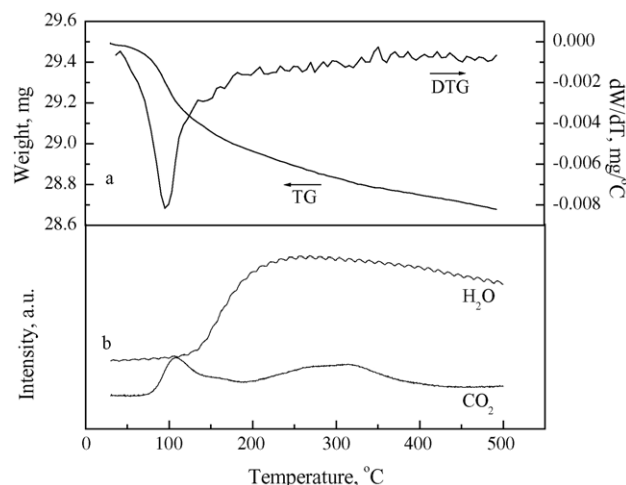


Fig. 5. TG and DTG with MS analysis for the exposed Cu00 catalyst: (a) TG-DTG profiles and (b) MS profiles of H<sub>2</sub>O and CO<sub>2</sub>.

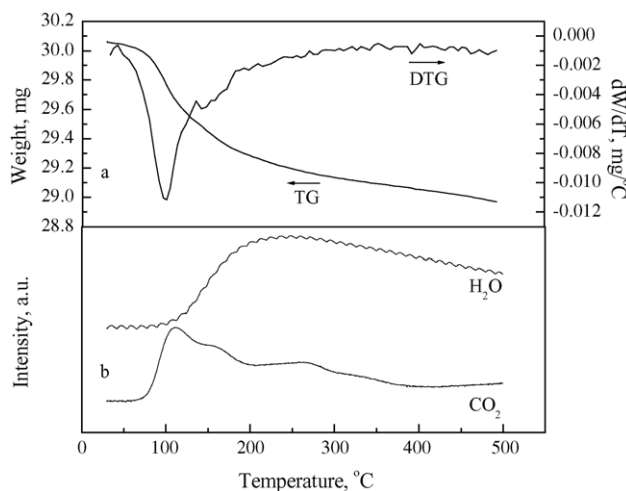


Fig. 6. TG and DTG with MS analysis for the exposed Cu03 catalyst: (a) TG-DTG profiles and (b) MS profiles of H<sub>2</sub>O and CO<sub>2</sub>.

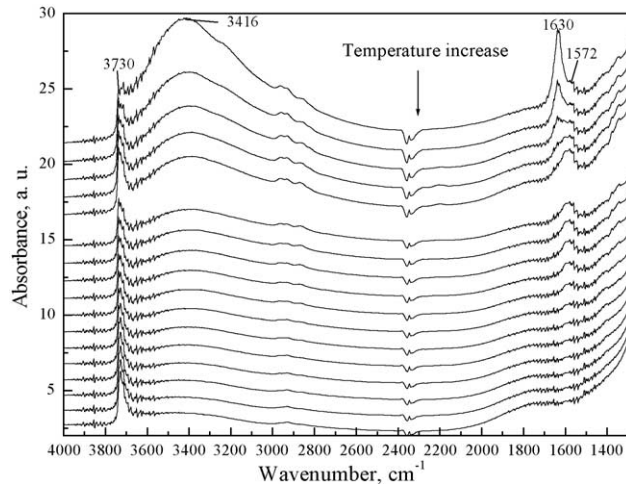


Fig. 7. Infrared spectra of removal of adsorbed species on the exposed Cu00 catalyst sample. The spectra were recorded as a function of temperature (from top to bottom, temperature increasing from 30 to 500 °C with a step of 30 °C).

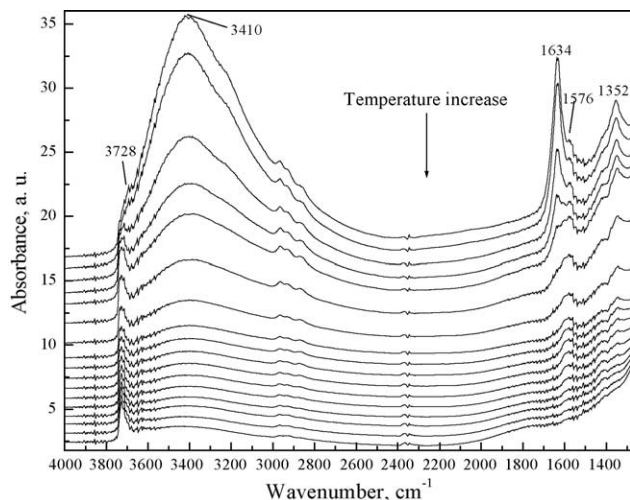


Fig. 8. Infrared spectra of removal of adsorbed species on the exposed CuO<sub>3</sub> catalyst sample. The spectra were recorded as a function of temperature (from top to bottom, temperature increasing from 30 to 500 °C with a step of 30 °C).

are observed. These bands are attributed to the stretching vibration peaks of water adsorbed on catalysts. In the range of 1600–1300 cm<sup>-1</sup>, three weak bands at 1580, 1420 and 1350 cm<sup>-1</sup> are observed, which correspond to the carbonates species formed on the catalysts. The species of water at bands of 3410 and 1630 cm<sup>-1</sup> are easily removed at temperature above 120 °C, whereas, the carbonates species are much resistant to the thermal treatment, which can be removed when the temperature is increased to about 450 °C. The intensity of carbonates peaks on Cu-promoted sample is stronger than that on Cu-free sample, indicating that Cu promotion improves the selective adsorption of CO<sub>2</sub> in air-exposure. Since the water species adsorbed in air can be readily removed at 150 °C in DRIFT analysis, they are also easily removed under the typical temperature for in situ reduction in syngas or FTS reaction. Thus, the effect of water on reduction behavior can be excluded and the adsorbed CO<sub>2</sub> species should be further studied.

### 3.3. CO<sub>2</sub> adsorption on catalysts

As mentioned above, besides the CO<sub>2</sub> selective adsorption occurs on the CuO<sub>0</sub> and CuO<sub>3</sub> catalysts exposed to air, the formed carbonates species are resistant to the thermal treatment. Thus, it is necessary to study the adsorption behavior of catalysts in CO<sub>2</sub>.

The CO<sub>2</sub>-TPD profiles for CuO<sub>0</sub> and CuO<sub>3</sub> catalysts are shown in Fig. 9. As shown in the pattern, there are a minor peak at 100 °C and two stronger peaks in the range of 160–180 and 280–310 °C, which can be attributed to desorption of the weakly and the strongly adsorbed CO<sub>2</sub>. Besides these peaks, a long tail presents at higher temperature, which can be assigned to desorption of stronger chemisorbed CO<sub>2</sub>. Comparing two TPD profiles, it is shown that the addition of Cu improves the intensity of the peak at 290 °C. As described in

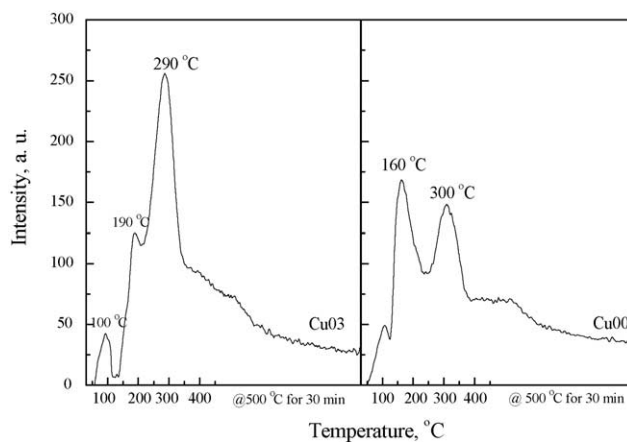


Fig. 9. CO<sub>2</sub>-TPD profiles for CuO<sub>0</sub> and CuO<sub>3</sub> catalysts calcinated at 500 °C.

experimental section, this temperature (290 °C) is higher than that required in syngas reduction. It is possible that the formed CO<sub>2</sub> species at 290 °C are related to the poor reducibility of the protected CuO<sub>3</sub> catalyst. Therefore, the formed species during CO<sub>2</sub> adsorption require to be identified with further investigation.

DRIFT analysis was used to identify the adsorbed species in CO<sub>2</sub> adsorption. CO<sub>2</sub> adsorption was carried out at 200 °C for 10 min after the sample was in situ calcinated at 500 °C in Ar flow. Following the adsorption, the samples were flushed with argon at 200 °C for 10 min and then temperature was increased to 300 °C at the ramp of 10 °C/min. Before CO<sub>2</sub> adsorption and during thermal treatment, IR spectra were collected, respectively. To minimize the interference from the Si–O groups on catalyst sample, the presented IR spectra were subtracted from the IR spectra of the corresponding pre-adsorption samples. The IR spectra of two catalysts are shown in Figs. 10 and 11, respectively. On both CuO<sub>0</sub> and CuO<sub>3</sub> samples, several surface carbonates at bands of 1580, 1450, 1355 and 1257 cm<sup>-1</sup> were formed upon CO<sub>2</sub> admission and resistant to argon flushing and thermal treatment. A band at 2348 cm<sup>-1</sup> exists after adsorption and decreases very fast in intensity with argon flushing.

It is reported in literature that the surface carbonate species are formed on catalysts upon CO<sub>2</sub> adsorption. The main species were (i) chelating or bridging bidentate carbonates [13–21] (1700–1630, 1560–1540, 1360–1340 and 1280–1250 cm<sup>-1</sup>), (ii) unidentate carbonates [13–15,19,22] (1550–1500, 1450–1400 and 1360–1310 cm<sup>-1</sup>), (iii) ionic carbonate CO<sub>3</sub><sup>2-</sup> [13,14,17] (1450–1410 cm<sup>-1</sup>), (iv) hydrogen carbonates [19] (3620, 1640–1590 and 1480–1320 cm<sup>-1</sup>) and (v) CO<sub>2</sub> linearly coordinated on M<sup>n+</sup> sites [14] (2360–2340 cm<sup>-1</sup>).

Except for the difference in intensity, the CuO<sub>0</sub> and CuO<sub>3</sub> catalysts exhibited similar features in carbonates. The bands of 1580, 1355 and 1257 cm<sup>-1</sup> with a shoulder at 1690 cm<sup>-1</sup> can be assigned to the bidentate carbonates. The band of 1490 cm<sup>-1</sup> with a shoulder band at 1440 cm<sup>-1</sup> can be attributed to the monodentate carbonate mode. The band

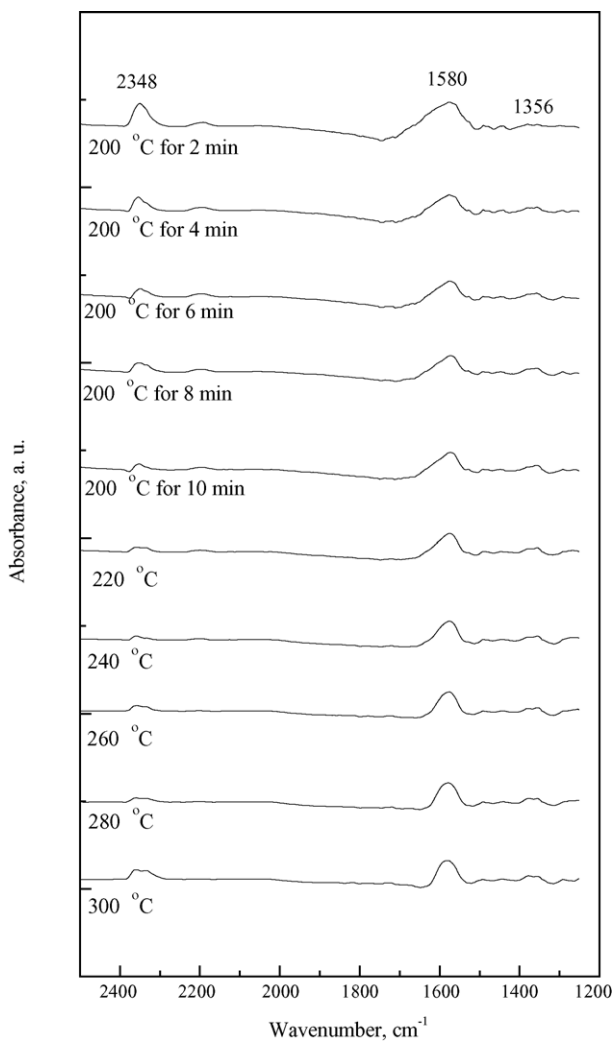


Fig. 10. Infrared spectra recorded from desorption of CO<sub>2</sub> adsorbed at 200 °C on the Cu<sub>00</sub> catalyst in situ calcinated at 500 °C. Each spectrum is reported as the difference from the spectrum before CO<sub>2</sub> admission.

at 1357 cm<sup>-1</sup> may partially be attributed to the monodentate carbonates, due to the bands overlap of monodentate and bidentate carbonates. In addition, linearly coordinated CO<sub>2</sub> was also detected at band of 2348 cm<sup>-1</sup>.

The IR spectra of desorption are indicative of the thermal stability of the different species on catalysts. Linearly coordinated CO<sub>2</sub> was easily removed by the argon flushing, whereas, bidentate and monodentate carbonates are more resistant to the thermal treatment. On the Cu<sub>03</sub> catalyst, the intensities of these carbonates are stronger than that those on the Cu<sub>00</sub> catalyst. Bianchi et al. [23] reported that irreversible surface species are carbonates on copper containing catalysts. Thus, it is concluded that Cu promotion improves the formation of irreversibly adsorbed carbonates.

As discussed above, the air-exposure resulted in the formation of difficultly removed carbonates on both Cu<sub>00</sub> and Cu<sub>03</sub> catalysts. The in situ reduction behavior of Cu-free catalyst was not affected by air-exposure, whereas, that of Cu-promoted catalyst was altered. Thus, it is implied that the

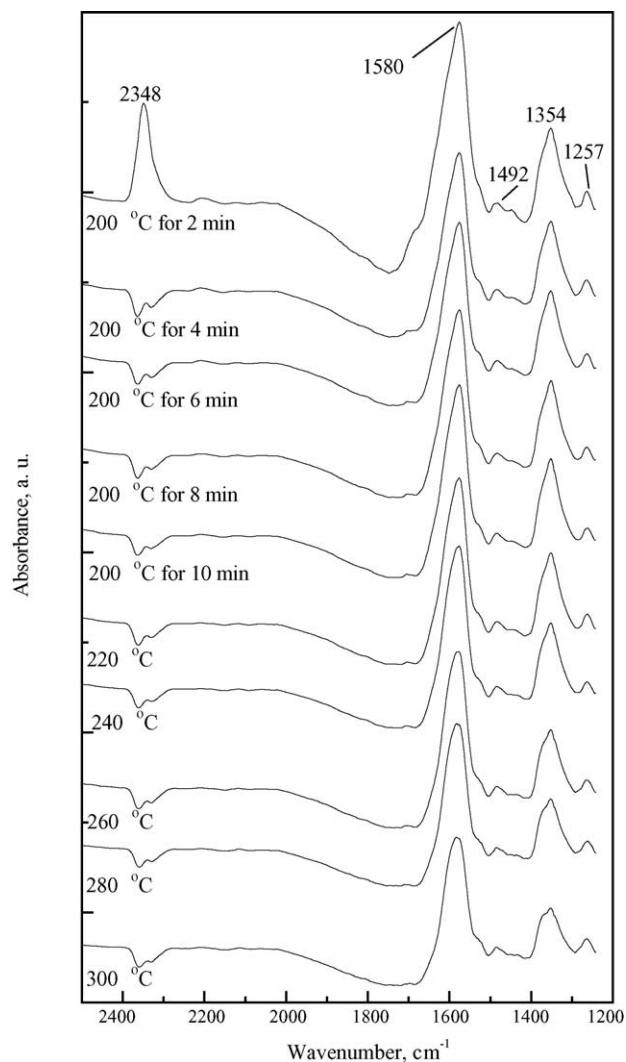


Fig. 11. Infrared spectra recorded from desorption of CO<sub>2</sub> adsorbed at 200 °C on the Cu<sub>03</sub> catalyst in situ calcinated at 500 °C. Each spectrum is reported as the difference from the spectrum before CO<sub>2</sub> admission.

irreversible carbonates do not directly influence the reduction of iron oxide, but suppress the role of copper in reduction. It is well known that Cu can ease the reduction of metal oxides by providing H<sub>2</sub> dissociative sites, whereas, copper oxides does not. Therefore, it may be reasoned that the copper oxide was not be reduced to copper due to the formation of carbonates. Without the role of copper, the reduction behavior of Cu-promoted catalyst is similar to that of Cu-free catalyst during the in situ reduction process. In a word, air-exposure restrains the role of copper, which correspondingly lowers the rate of reduction or carburization and suppresses the formation of active phase during in situ syngas reduction. It should be noted that, due to the low content of Cu in catalyst and the limitation in characterization techniques, it is difficult to identify the state of copper under in situ reduction. The reason for the suppression of Cu promotion during the reduction process needs to be further investigated.

#### 4. Conclusion

Air-exposure restrains the in situ syngas reduction behavior of Cu-promoted Fe–Mn–K/SiO<sub>2</sub> FTS catalyst. It results from the formation of irreversible carbonates species on catalysts in air-exposure. The carbonates do not directly restrain the reduction of metal oxides, whereas, they suppress the role of copper in reduction. Without the role of copper, the exposed CuO<sub>3</sub> catalyst is difficult to reduce or activate.

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#### References

- [1] B. Jager, *Stud. Surf. Sci. Catal.* 119 (1998) 25.
- [2] D.B. Bukur, X. Lang, D. Mukesh, W.H. Zimmerman, M.P. Rosynek, C. Li, *Ind. Eng. Chem. Res.* 29 (1990) 1588.
- [3] T. Grzybek, J. Klinik, H. Papp, M. Baerns, *Chem. Eng. Technol.* 13 (1990) 156.
- [4] D.B. Bukur, D. Mukesh, S.A. Patel, *Ind. Eng. Chem. Res.* 29 (1990) 194.
- [5] R.J. O'Brien, L. Xu, R.L. Spicer, S. Bao, D.R. Milburn, B.H. Davis, *Catal. Today* 36 (1997) 325.
- [6] Y. Jin, A.K. Datye, *J. Catal.* 196 (2000) 8.
- [7] S. Li, A. Li, S. Krishnamoorthy, E. Iglesia, *Catal. Lett.* 177 (2001) 197.
- [8] J.F. Shultz, W.K. Hall, T.A. Dubs, R.B. Anderson, *J. Am. Chem. Soc.* 78 (1956) 282.
- [9] R.A. Dector, A.T. Bell, *J. Catal.* 97 (1986) 121.
- [10] K.R.P.M. Rao, F.E. Huggins, V. Mahajan, G.P. Huffman, V.U.S. Rao, B.L. Bhatt, D.B. Bukur, B.H. Davis, R.J. O'Brien, *Top. Catal.* 2 (1995) 71.
- [11] L.D. Mansker, Y. Jin, D.B. Bukur, A.K. Datye, *Appl. Catal. A* 186 (1999) 227.
- [12] S. Li, G.D. Meitzner, E. Iglesia, *J. Phys. Chem. B* 105 (2001) 5743.
- [13] X. Wang, G. Li, U.S. Ozkan, *J. Mol. Catal. A* 217 (2004) 219.
- [14] F. Prinetto, G. Bhiotti, *J. Phys. Chem. B* 104 (2000) 11117.
- [15] D. Bianchi, T. Chafik, M. Khalfallah, S.J. Teichner, *Appl. Catal. A* 105 (1993) 223.
- [16] C. Schild, A. Wokaun, A. Baiker, *J. Mol. Catal.* 67 (1990) 223.
- [17] N.D. Parkyns, *J. Chem. Soc. A* (1969) 410.
- [18] J.D.C. Yates, *J. Chem.* 65 (1961) 746.
- [19] Y.M. Grigoreev, D.V. Pozdnyakov, V.N. Filimonov, *Russ. J. Phys. Chem.* 46 (1977) 2.
- [20] G. Ghiotti, F. Boccuzzi, R. Scala, *J. Catal.* 92 (1985) 79.
- [21] J.C. Lavalley, *Catal. Today* 27 (1996) 377.
- [22] M.Y. He, J.G. Eckerdt, *J. Catal.* 87 (1984) 381.
- [23] D. Bianchi, T. Chafik, M. Khalfallah, S.J. Teichner, *Appl. Catal. A* 112 (1994) 219.