Deactivation study of CuCo catalyst for higher alcohol synthesis via syngas

Yanzhang Yang^{a, b}, Xingzhen Qi^a, Xinxing Wang^a, Dong Lv^a, Fei Yu^a, Liangshu Zhong^{a,*}, Hui Wang^a, Yuhan Sun^{a,c,*}

^a CAS Key Laboratory of Low-carbon Conversion Science & Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, PR China

^b University of the Chinese Academy of Sciences, Beijing 100049, PR China

^c State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China

*Corresponding author. Tel.: +86-021-20325009; Fax: +86-021-20325039. E-mail address: zhongls@sari.ac.cn (L. S. Zhong); sunyh@sari.ac.cn (Y. H. Sun).

Abstract

Change in catalytic performance and catalyst structural evolution during the deactivation of the CuCo/TiO₂ model catalyst for higher alcohol synthesis via syngas were investigated. The catalytic activity decreases continuously with time-on-stream, although there is no obvious change in total alcohol selectivity. However, the products shift gradually to low carbon number, and the chain growth probabilities of both alcohols and hydrocarbons decrease with reaction time. Using ethane hydrogenolysis as the probe reaction, the catalytic activity also declines with time-on-stream, indicating the decline in the number of surface metallic cobalt assemblies. To elucidate the structural evolution of the catalyst, the calcined, reduced, and used catalysts were analyzed by various techniques. The bulk crystalline phase of the calcined catalyst is CuCo composite oxide, with small CuO nanoparticles spreading on the catalyst surface. After reduction, the oxides are transformed into CuCo alloy and Cu nanoparticles. For the used sample, severe sintering occurs and Co_xC forms on the catalyst surface, both of which reduce the number of surface Co atoms and leads to catalytic deactivation.

Keywords:

Higher alcohol synthesis; Syngas; Copper-cobalt catalyst; Deactivation; Sintering;

1. Introduction

Higher alcohols can be used as fuel, fuel additives, and intermediates for value-added fine chemicals [1]. With increasing environmental concerns and depletion of nonrenewable petroleum resources, higher alcohol synthesis (HAS) via syngas derived from coal, natural gas, and biomass has attracted much attention in academic and industrial fields [2]. The main objective is to increase $C_{2+}OH$ selectivity by controlling CO activation, carbon chain growth and termination via catalyst **innovation**. Various types of catalysts have been reported for higher alcohol synthesis, and typical catalyst systems include modified methanol **catalysts**, Rh-based **catalysts**, Mo-based **catalysts**, and modified Fischer-Tropsch (**FT**) **catalysts**. Due to the low cost and high **catalytic** activity, modified FT catalysts **are** a promising catalyst system for higher alcohol synthesis with industrial prospects [3, 4].

The modified FT catalysts are **usually** a combination of a FT catalyst component (Fe, Co) and another active metal or metal oxide **component**, which function as CO dissociation and insertion sites, respectively. Since the first report in the 1980s [5], CuCo-based higher alcohol synthesis catalysts have attracted much attention due to its high total alcohol selectivity, high C_{2+} alcohol selectivity and low **cost** of active metals. It is generally accepted that [6, 7] copper-cobalt alloy is the true active site for higher **alcohol** formation, **where** copper and cobalt species play different **roles** with copper species as a CO insertion site [3, 8] and cobalt species as a CO **dissociation** site [9-11], although Co_2C/Co [12] and $Co/Co^{\delta+}$ [13] pairs have been also proposed **as** active sites for alcohol formation. However, the low stability **of the CuCo catalyst hinders** its industrial applications. **Thus, it is highly desirable to elucidate the deactivation mechanism in order to further improve the performance of this promising catalyst.**

Although there have been many reports **on** the catalyst preparation [14-16] and optimization [17] to improve the alcohol selectivity, the deactivation process of CuCo-based HAS catalysts is rarely studied [18], **especially under high pressures favorable for HAS**. In our previous **studies on the CuFe-based catalysts**, we found the **synergy** of dual active sites **to play** an important role in HAS and the phase separation of Fe and Cu components **to significantly lower** the catalytic performance for HAS

[19-22]. Such phase separation weakens the synergy between Cu and Fe species leading to the decrease of alcohol selectivity with time-on-stream. In addition, Carenco et al. [23] studied the change of core-shell CuCo nanoparticles as a result of cleaning pretreatments and when exposed to syngas at atmospheric pressure. It was found that a significant fraction of the particles was strongly depleted in cobalt giving copper-rich nanoparticles after exposure to syngas. Since high pressure benefits HAS [4], it was necessary to explore the structure-performance correlation of the catalysts for HAS at relatively high pressure. As an alternative solution, *in-situ* probe reaction might be used as it can be carried out at relatively high pressure and the information of structural evolution can be obtained based on the result of the probe reaction [24, 25]. Goodwin Jr. et al. [26] used ethane hydrogenolysis as probe reaction to study the effect of component interaction on the activity of Co/CuZnO for CO hydrogenation. It was found that different components of these catalysts were in close contact and few or no large ensembles ($n \geq 12$) of Co atoms existed, suggesting that ZnO and/or Cu covered/blocked a substantial number of Co active sites for CO hydrogenation.

In this paper, a CuCo/TiO₂ model catalyst was prepared by deposition-precipitation method and tested for higher alcohol synthesis in a fixed bed reactor. In addition, the structural evolution at different stages was investigated by various characterization methods. The changes of catalytic performance for syngas conversion and ethane hydrogenolysis as probe reaction were monitored with time-on-stream. The deactivation mechanism was discussed based on the correlation between structural evolution and the change of catalytic performance.

2. Experimental

2.1. Preparation of CuCo/TiO₂ catalyst

The CuCo/TiO₂ catalyst with 30 wt% TiO₂ and Cu/Co atomic ratio of 1/2 was prepared by deposition-precipitation method. Commercial TiO₂ (Aeroxide TiO₂ P 25 from Evonik, Germany) with BET specific surface area of 50 m²/g was used as structural promoter. Other chemicals (Cu(NO₃)₂·3H₂O, Co(NO₃)₂·6H₂O, and Na₂CO₃) are of analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. The solution containing 2 M total metal ions and that of 2 M Na₂CO₃ were added simultaneously into the mother solution containing TiO₂ under strong stirring. The pH of the solution was fixed at about 8, while the temperature was kept at 60-70 °C. The as-prepared solution was aged at 65 °C for 2 h,

and centrifuged with deionized water for 6 times. After drying at 80 °C for 2 h and 120 °C for 20 h, the sample was calcined in air by ramping at 2 °C/min to 120 °C and then maintaining that temperature for 2 h, followed by ramping at 1 °C/min to 330 °C and then maintaining that temperature for 3 h.

The calcined catalyst was reduced in a tube furnace under flowing atmosphere with 10 vol% of H₂/N₂ (200 scc/min), followed by passivation in 1 vol% O₂/Ar for 70 min for characterization. The activation procedure was as follows: room temperature → 120 °C at a ramp of 1 °C/min and kept at 120 °C for 120 min; 120 °C → 180 °C in 60 min and kept at 180 °C for 120 min; 180 °C → 250 °C in 70 min and kept at 250 °C for 300 min. The used catalyst was extracted **by** a Soxhlet equipment several times with octane at 180 °C for characterization.

2.2. Characterization

The actual compositions of the calcined and used catalysts were determined by ICP with a Varian 710-ES Inductively Coupled Plasma Atomic Emission Spectrometer.

Nitrogen adsorption measurements were performed on a Micromeritics TriStar 3020 instrument at -196 °C. About 50 mg sample was degassed at 200 °C in vacuum for 6 h. The specific area was calculated by the Brunauer-Emmett-Teller (BET) equation. The total pore volume and the average pore size were determined through the Barrett-Joyner-Halenda (BJH) method.

XRD patterns for CuCo/TiO₂ were recorded on a Rigaku diffractometer using Cu Ka radiation with scanning angle from 10° to 80°. **The scan speed was 2°/min for calcined and reduced samples, and 0.2 °/min for used sample.** All the measurements were performed at ambient temperature. The samples was loaded into a shallow glass holder and leveled on the surface before measurements.

TPR experiments were carried out on a Micromeritics AutoChem 2920 instrument. About 30 mg sample was purged with 30 mL (STP) min⁻¹ He at 120 °C for 100 min. After cooling to 50 °C, the catalyst was exposed to 30 mL (STP) min⁻¹ of 5% H₂/Ar flow as the temperature ramped to 900 °C. The exhaust was analyzed by a thermal conductivity detector (TCD) and the compositions were identified by **a Mass Spectrometer.**

Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM 2011 electron microscope with 200 kV accelerating voltage. Samples for TEM were prepared by dispersing the nanoparticles in ethanol followed by

ultrasonication. One droplet of dispersion was placed on carbon-coated molybdenum or nickel grids for measurement.

XPS spectra were obtained using Al K α ($h = 1486.6$ eV) radiation on a Thermo Scientific K-Alpha spectrometer. Charging effects were corrected by using the C 1s peak due to adventitious carbon with E_B fixed at 284.6 eV. The surface composition of the calcined samples was obtained on the basis of the peak area intensities of the Co 2p $_{3/2}$ and Cu 2p $_{3/2}$ transitions using the sensitivity factor approach [27].

2.3. Catalytic evaluation

CO hydrogenation test was carried out in a stainless steel continuous flow fixed-bed reactor. The calcined catalyst powder was granulated into 40-60 mesh, and then 1.5 g of the catalyst pellets were mixed with 3.0 g silica sand of the same size before being loaded into the reactor. The catalyst was **reduced *in situ*** in 10 vol% H $_2$ /N $_2$ at atmosphere pressure with gas flow rate of 8000 mL (g $_{cat.}^{-1}$ h $^{-1}$). The activation procedure was the same as the reduction of catalyst for characterization. After the reactor was cooled to 200 °C, 10 vol% H $_2$ /N $_2$ gas was replaced by 10 vol% syngas/N $_2$ with H $_2$ /CO = 2/1 molar ratio and the system was pressurized to 6 MPa controlled by a back-pressure valve, **while** the reactor was heated slowly to 250 °C. The reaction was carried out with syngas with gas flow rate of 6000 mL (g $_{cat.}^{-1}$ h $^{-1}$) controlled by a calibrated Brooks mass flow controller, and with the composition of H $_2$ /CO/N $_2$ = 65/32/3 molar ratio, of which N $_2$ was added as internal standard.

The outlet gas was analyzed on-line by GC after passing through a hot trap (100 °C external) and a cold trap (ice-water bath). H $_2$ and CO were examined through a TDX-1 carbon molecular sieves column by a thermal conductivity detector (TCD) using Ar as the carrier gas. **N $_2$, CO, CH $_4$ and CO $_2$ were analyzed through a TDX-1 carbon molecular sieves column by a TCD using He as the carrier gas.** C $_1$ to C $_{10}$ hydrocarbons were separated through a modified alumina packed column with Ar carrier, then were analyzed by hydrogen flame ionization detector (FID). The aqueous products and liquid oil products, gathered from cold trap and hot trap, were analyzed off-line by GC. The aqueous products were analyzed through two Porapak Q columns furnished with a FID (for C $_1$ -C $_5$ oxygenates recognition) and TCD (for H $_2$ O and MeOH recognition), respectively. The liquid oil products were analyzed through a HP-1 column with N $_2$ carrier by FID. All the data were collected after 24 h on-stream when the steady state was achieved. The mass balance, carbon balance and oxygen

balance were estimated at each liquid product gathering time, and were between 95% and 105%. The CO conversion was calculated according to the internal standard method assuming that the N₂ amount remained constant after reaction and the carbon selectivities of different products were obtained by calculating the percentage of the carbon number of the specific product to that of all products.

Ethane hydrogenolysis test was carried out in the same reactor as for CO hydrogenation. Prior to the reaction, the catalyst (1.5 g 40-60 mesh sample, diluted with 3.0 g inert quartz sand of the same size) was reduced/activated *in situ* in accordance with the conditions used for CO hydrogenation. After the reactor was cooled to 200 °C, the feed gas was replaced by 10 vol% syngas/N₂ with H₂/CO = 2/1 molar ratio and the system was pressurized to 2 MPa controlled by a back-pressure valve, while the reactor was heated slowly to 250 °C. The reaction was conducted in flowing mixed gas with the composition of H₂/C₂H₆/N₂ = 30/1.5/40 molar ratio with gas flow rate of 3000 mL (g_{cat.}⁻¹ h⁻¹). The tail gas was detected on-line GC after passing through a hot trap (100 °C external) and a cold trap (ice-water bath). CH₄ and C₂H₆ were examined through a modified alumina packed column with Ar carrier and by FID. The ethane conversion was calculated according to the normalization method.

The equation of ethane conversion is $\text{Conv. (C}_2\text{H}_6) = \frac{C_{\text{CH}_4}}{C_{\text{CH}_4} + 0.53 * 2 * C_{\text{C}_2\text{H}_6}}$, where

C_{CH_4} and $C_{\text{C}_2\text{H}_6}$ represented area concentrations of CH₄ and C₂H₆ peaks in the chromatogram, respectively, and 0.53 was the specific molar sensitivity factor of C₂H₆ compared to CH₄.

3. Results

3.1. Composition and texture

The bulk composition and textural properties of the calcined, reduced and used catalysts were analyzed by ICP-AES and BET, respectively (Table 1, Fig. S1). According to the ICP results, the ratio of Co to Cu of the calcined catalyst was 1.73, which were close to the theoretical value (2.00), indicating the complete precipitation of precursor salts. In addition, the ratios of Co to Cu of the reduced and used catalysts were 1.81 and 1.75, respectively, which were close to the composition in the calcined sample. The specific surface area (S_{BET}) and the pore volume followed the same order: calcined > reduced > used. The reason for the decrease of specific surface area and

pore volume after reduction was due to particles sintering as shown in the TEM images. For the used catalyst, stacking pores probably disappeared due to the harsh reaction conditions, leading to the further decline of the specific area and pore volume of the catalyst.

Table 1

Bulk composition determined by ICP-AES and textural properties of CuCo/TiO₂ catalysts determined by BET.

CuCo/TiO ₂ catalysts	Atomic ratio specific to Cu ^a			<i>S</i> _{BET} (m ² /g)	Pore volume (cm ³ /g)
	Co	Cu	Ti		
Calcined	1.73	1.00	0.87	93	0.4
Reduced	1.81	1.00	0.84	39	0.3
Used	1.75	1.00	0.83	22	0.2

^a The theoretical specific values of Co, Cu and Ti are 2.00, 1.00 and 0.90, respectively.

3.2. XRD

XRD patterns of CuCo/TiO₂ catalysts are shown in **Fig. 1**. The calcined catalyst showed distinct peaks at around $2\theta = 31.3^\circ$, 36.8° , 59.4° and 65.2° , which could be attributed to Cu_{0.3}Co_{0.7}Co₂O₄ (JCPDS # 25-0270). The comparison made between positions of diffraction lines of CuCo/TiO₂ catalyst and those of cobalt oxide spinel as well as cobalt-copper mixed oxide spinel are shown in **Table S2**. Both reduced (**Fig. 1b**) and used (**Fig. 1c**) catalysts showed diffraction peaks at around $2\theta = 43.9^\circ$, 51.1° and 75.2° , which were located between those of cobalt (JCPDS # 15-0806) and copper (JCPDS # 04-0836), suggesting the co-existence of CuCo alloy and copper considering the limited solubility of Cu in Co [28]. The XRD pattern of used catalyst with high resolution showed peaks at $2\theta = 37.0^\circ$, 38.6° , 41.3° , 42.9° , 45.9° , 56.5° , 64.5° , 76.4° and 82.7° which were ascribed to Co_xC (JCPDS # 05-0704). In addition, there also appeared peaks at $2\theta = 25.3^\circ$, 37.0° , 37.9° , 38.6° , 48.1° , 53.9° , 55.1° , 62.1° , 68.9° and 70.2° , corresponding to TiO₂ anatase (JCPDS # 21-1272) and at $2\theta = 27.5^\circ$, 36.1° , 41.3° , 44.0° , 56.6° , 62.7° , 64.2° , 68.9° and 76.4° corresponding to TiO₂ rutile (JCPDS # 21-1276) for all samples. The crystalline domain sizes at the (311) direction of Cu_xCo_{1-x}Co₂O₄ in the calcined sample or at the (111) direction of CuCo alloy (or Cu) in the reduced and used ones were calculated based on the strongest peak

(excluding that of TiO_2) according to the Scherrer formula and it followed the order: used (10.3 nm) > reduced (10.2 nm) > calcined (6.7 nm).

Fig. 1. XRD patterns of CuCo/TiO₂ catalysts: (a) calcined; (b) reduced and passivated; (c) used.

3.3. TPR

TPR profiles of the calcined and used catalysts are shown in **Fig. S2** and **Fig. 2**, respectively. Since the reduction of TiO_2 was negligible below 650 °C as shown in **Fig. S3**, all the reduction peaks observed in the temperature of 100-400 °C could be ascribed to the reduction of CuO and $\text{Cu}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$. The calcined catalyst had two reduction peaks at 142.1 °C and 207.8 °C, respectively. The lower peak was due to reduction of highly dispersed CuO to Cu [29], and the higher one corresponded to the reduction of Cu-Co-O oxide [30]. The hydrogen consumption of the lower peak was roughly three-tenths of the higher one, which further supported that there was $\text{Cu}_{0.3}\text{Co}_{0.7}\text{Co}_2\text{O}_4$ species in bulk. The used catalyst exhibited a main peak at 169.8 °C and another small featured at 223.1 °C, both of which shifted towards higher temperatures than the calcined sample. The agglomeration of catalyst particles and the decrease of the interaction between cobalt and copper could probably explain the shift

of reduction peaks to higher temperatures after reaction. In addition, there were CH₄ formation peaks at 182.7 and 222.4 °C, which could be attributed to the reduction of cobalt carbide with H₂, suggesting the formation of cobalt carbide during the reaction process for higher alcohol synthesis [31].

Fig. 2. TPR-MS profiles of used CuCo/TiO₂ catalyst (red: TCD signal; blue: CH₄ signal).

3.4. TEM

Fig. 3 shows TEM images of CuCo/TiO₂ catalysts at different stages. The calcined catalyst showed roughly spherical nanoparticles with diameters from 6 nm to 10 nm (**Fig. 3a**), which aggregated together separately from or around TiO₂ nanoparticles. After reduction, the sample aggregated to larger particles ranging from 15 nm to 40 nm. In addition, the used catalyst showed more agglomeration of nanoparticles ranging from 25 nm and 55 nm, and there appeared larger dark area than the reduced catalyst, indicating severe sintering of the catalyst during reaction process.

Fig. 3. TEM images of CuCo/TiO₂ catalysts: (a) calcined; (b) reduced and passivated; (c) used.

3.5. XPS

The Cu/Co atomic ratios calculated by XPS were 1.7, 0.9 and 0.5 for calcined, reduced and used samples, respectively. For the calcined sample, the Cu/Co atomic ratio in bulk was 0.58 according to ICP results. The higher Cu concentration on the surface could be attributed to the formation of small CuO particles as observed by TPR. For the reduced sample, another reason for Cu enrichment on surface could be due to the lower surface free energy of Cu compared to that of Co [32]. The Cu/Co atomic ratio on the surface for the reduced catalyst was higher than that for the used sample (0.9 vs. 0.5), indicating cobalt atoms at the surface increased during reaction process. The decrease of Cu/Co ratio after reaction would be due to the formation of surface cobalt carbide, which prevented the transfer of Cu to the surface, and to the agglomeration of Cu as suggested by TPR. The XPS spectra of C1s for the CuCo/TiO₂ catalysts after reduction and reaction are shown in Fig. 4. Both samples showed peaks at 284.6 eV, which was attributed to adventitious carbon and hydrocarbons [33, 34]. The used catalyst had another peak at 283.4 eV, which could be due to Co_xC [35]. In addition, the Co 2p and Cu 2p spectra for the CuCo/TiO₂ catalysts were also analyzed in detail in supporting information. The results were shown in Figs. S4 & S5 and Tables S3. In order to further identify the oxidation states of copper in the catalysts, the Cu L₃M₄₅M₄₅ Auger spectra were also examined and shown in Fig. S6. All Cu 2p_{3/2} spectra of CuCo/TiO₂ catalysts showed characteristics typical of Cu²⁺ species, and Cu L₃M₄₅M₄₅ Auger peaks indicated that the concentration of Cu⁺ in the catalysts followed the order: used > reduced > calcined. After reduction, the Co 2p XPS presented a Co⁰ peak at 778.4 eV, which shifted slightly to 777.9 eV for the used catalyst.

Fig. 4. C 1s spectra for CuCo/TiO₂ catalysts (a: reduced and passivated; b: used).

3.6. CO hydrogenation and ethane hydrogenolysis

As shown in **Table 2**, the activity of CO hydrogenation decreased with time-on-stream ($T = 250\text{ }^{\circ}\text{C}$; $P = 6\text{ MPa}$; $\text{GHSV} = 6000\text{ mL (g}_{\text{cat.}}^{-1}\text{ h}^{-1})$; $\text{H}_2/\text{CO} = 2$). However, the selectivity for both oxygenates and hydrocarbons remained almost unchanged. The selectivity descriptor ($C_{\text{ins}}/C_{\text{dis}}$) described by Martínez et al. [36] at different run times were calculated and there was no obvious change trend with time-on-stream. CO₂ selectivity was rather low, indicating low activity for water-gas-shift reaction. The oxygenate products mainly consisted of alcohols with few aldehydes, which could be explained by the strong hydrogenation ability of Cu

species [37]. In addition, both of the alcohols and hydrocarbons shifted to lower carbon with time-on-stream, i.e., the selectivity to methanol and lower hydrocarbons (C_{1-3}) increased while the selectivity to higher alcohols (C_{5+}) and C_{5+} hydrocarbons decreased. The chain-growth probabilities (α) of different products (both alcohols and hydrocarbons) were calculated according to the ASF function (**Fig. 5 and Table S4**) and it was found that the values decreased with time-on-stream. **In addition, the values of alcohols were lower than those of hydrocarbons.** Ethane hydrogenolysis was adopted as probe reaction over the same catalyst ($T = 250\text{ }^{\circ}\text{C}$; $P = 2\text{ MPa}$; $\text{GHSV} = 3000\text{ mL (g}_{\text{cat.}}^{-1}\text{ h}^{-1})$; $\text{H}_2/\text{C}_2\text{H}_6/\text{N}_2 = 30/1.5/40$). It was found that the hydrogenolysis activity also decreased in the studied reaction time (**Fig. 6**), suggesting the concentration of surface Co assembled atoms declined.

Table 2

Catalytic performance of CuCo/TiO₂ in HAS reaction^a.

TOS (h)	CO Conv. (%)	$C_{\text{ins}}/C_{\text{dis}}^{\text{b}}$	Selectivity (C%)			Alcohol distribution (wt%)						Hydrocarbon distribution (O&P, wt%)				
			Oxy.	CH _n	CO ₂	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆ ⁺	C ₁	C ₂	C ₃	C ₄	C ₅ ⁺
24	19.1	0.065	10.9	87.1	2.0	48.0	19.5	10.9	7.5	1.9	12.2	39.7	12.2	19.0	12.1	17.0
48	17.6	0.080	11.3	87.0	1.7	55.1	21.8	12.7	6.1	1.2	3.0	41.2	12.4	18.9	11.5	16.0
72	16.6	0.072	10.1	88.1	1.8	55.7	21.3	14.1	6.1	1.2	1.5	41.5	12.8	18.9	11.4	15.4
96	16.3	0.067	9.1	89.2	1.7	58.5	21.9	12.5	7.1	-	-	43.0	13.3	19.5	11.5	12.7
120	14.6	0.074	10.1	88.3	1.6	58.8	22.1	12.4	6.7	0.1	-	43.1	13.5	19.5	11.4	12.5
144	14.7	0.089	11.9	86.4	1.7	58.2	22.7	12.8	6.3	-	-	43.5	13.7	19.7	11.3	11.8

^a $T = 250\text{ }^{\circ}\text{C}$; $P = 6\text{ MPa}$; $\text{GHSV} = 6000\text{ mL (g}_{\text{cat.}}^{-1}\text{ h}^{-1})$; $\text{H}_2/\text{CO} = 2$.

^b C_{ins} indicates C atoms arising from CO dissociation while C_{dis} indicates C atoms arising from nondissociative CO insertion.

Fig. 5. Changes of chain-growth probability for CuCo/TiO₂ with reaction time.

Fig. 6. CO & ethane conversion vs. time-on-stream for CuCo/TiO₂ catalyst.

4. Discussion

The catalyst evaluation results show that the catalytic reactivity of CuCo/TiO₂ catalyst for higher alcohol synthesis under typical reaction conditions decreases with reaction time. Furthermore, the products shift towards lower carbon number as shown by a lower calculated chain growth ability according to ASF function. It suggests that there are fewer carbon species from CO dissociation on Co atoms or assemblies to form longer C_xH_y alkyl chains. Product analysis further shows that the selectivities of oxygenate and hydrocarbons as well as the selectivity descriptor were independent of reaction time-on-stream. Since the selectivity descriptor represents the balance between the ability to undissociatively insert CO to form oxygenates and to dissociate CO to form C_xH_y alkyl chain [36], the capacity of the catalyst to insert CO decreases to the same extent as that to dissociate CO. When the number of surface Co atoms active for CO dissociation decreases due to agglomeration of particles or transformation into inactive Co_xC, the number of active site for CO insertion also decreases in the same degree.

In order to explore the deactivation process of the CuCo/TiO₂ catalyst, *in-situ* ethane hydrogenolysis was employed to investigate the surface evolution of the catalyst, as it is usually used to detect if there are Co clusters (assemblies) with more than 12 atoms [24, 25]. It should be noted that copper shows hydrogenolysis activity as well at temperature higher than 288 °C [38], although the specific activity of copper is much lower than that of cobalt. In this study, it is reasonable to neglect the activity of copper for ethane hydrogenolysis since the reaction temperature was much lower than 288 °C. According to the rate equation on the specific activity of cobalt for ethane hydrogenolysis proposed by Sinfelt et al. [38], the rate of ethane hydrogenolysis can be estimated to be 6.71×10^{-6} mole/min/m² with the partial pressures of hydrogen and ethane in this study of P_H = 0.84 MPa and P_E = 0.04 MPa. The initial activity for ethane hydrogenolysis over CuCo/TiO₂ catalyst is 0.73×10^{-6} mole/min when the ethane conversion is 0.7%. Therefore, the cobalt surface exposed in the CuCo/TiO₂ catalyst active for ethane hydrogenolysis is 0.11 m² (0.73 divided by 6.71), which is much smaller than that calculated by surface cobalt concentration multiplied by the surface area of the catalyst (about 11.12 m²). Since ethane hydrogenolysis is structure sensitive over cobalt catalyst, the exposed surface area of cobalt of 0.11 m² is actually the area occupied by surface Co assemblies active for

ethane hydrogenolysis. The catalytic activity of CuCo/TiO_2 catalyst for ethane hydrogenolysis continuously decreases with time-on-stream, indicating that the concentration of the exposed Co_{12} clusters on the catalyst surface decreases. Since the surface energy of cobalt is lower than that of copper, it is thermodynamically favorable for the latter to assemble on the catalyst surface [26]. This causes copper atoms to cover surface cobalt atoms, and results in lower amount of cobalt assemblies active for ethane hydrogenolysis. In addition, CO hydrogenation was also performed over the catalyst after ethane hydrogenolysis and the activity of the catalyst was found to be similar to that without hydrogenolysis, suggesting that the catalyst experiences similar structural evolution during ethane hydrogenolysis and CO hydrogenation. However, the XPS results of used catalyst show that the surface Cu concentration is not more abundant after reaction than that after reduction, which can be explained by the sintering of metallic Cu nanoparticles as well as the formation of Co_xC covering the catalyst surface.

The structural evolution of CuCo/TiO_2 was carefully studied at different stages for a deeper insight into the structure-performance relationship. After calcination, the catalyst shows Co_3O_4 -like diffraction pattern without diffraction lines corresponding to CuO. Therefore, copper cobalt mixed oxide can be expected to form. In addition, comparison of diffraction pattern of the sample with those of Co_3O_4 and $\text{Cu}_{0.3}\text{Co}_{0.7}\text{Co}_2\text{O}_4$ indicates that the crystalline phase in bulk is closer to $\text{Cu}_{0.3}\text{Co}_{0.7}\text{Co}_2\text{O}_4$ than Co_3O_4 . For the TPR profile of calcined sample, there are two reduction peaks, with the higher one lower than the reduction temperature of Co_3O_4 due to promotion effect of Cu on the reduction of Co_3O_4 [39]. Assuming that the lower one is due to the reduction of highly dispersed CuO, by calculating the percentage of H_2 consumption of the two peaks the value of x in $\text{Cu}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ was determined to be 0.3, consistent with the XRD results. XPS results of calcined sample indicate that the surface Cu/Co ratio is much higher than that in the bulk, implying Cu gathering on the catalyst surface in the form of CuO. The reduced catalyst shows Cu-Co alloy diffraction pattern. Because the solubility of copper in cobalt is usually less than 10% [6] in a wide range of temperature [40, 41], there should be diffraction patterns of copper crystals overlapping with those of cobalt-copper alloy. It was reported [18, 23] that the deactivation of Cu-Co binary catalyst was due to phase separation of the Cu-Co alloy. However, Cu-Co alloy phase still exists in the used catalyst, indicating that the separation of copper-cobalt alloy may not be the cause of

deactivation of CuCo catalyst investigated in this study. When the catalyst is reduced, most copper from the reduction of either CuO or copper-cobalt composite oxide remains on the surface of the catalyst because of lower surface free energy of copper than that of cobalt and limited solubility of copper in cobalt. Therefore, it can be expected that the interaction between copper and cobalt, especially electronic interaction, is affected by the formation of Co_xC . Since the electronegativity of Cu is higher than that of cobalt, the cobalt is positively charged when interacting with copper, and it prefers to dissociate the CO molecule irreversibly, which is prone to be converted into Co_xC with the help of neighboring Cu atoms. However, the detailed mechanism was still not clear.

The XRD of used catalyst shows no diffraction peaks of cobalt titanium oxide, indicating that formation of cobalt-support mixed compounds [42] is not the main reason for deactivation. In addition, N_2 -BET and TEM characterization results show that agglomeration of the catalyst [18, 42] leads to the deactivation of the catalyst since the used catalyst shows lower specific surface area and larger nanoparticles than the reduced sample. The existence of Co_xC was verified by XRD, TPR and XPS. As Co_xC was considered to be inactive for CO conversion, the formation of Co_xC during the reaction process should be another reason for deactivation. In order to further confirm the existence of Co_xC , carbon monoxide was removed from the feed gas after carrying out the reaction for a while and it was found that the activity of the CuCo/TiO₂ catalyst for CO hydrogenation recovered to some extent (Fig. S7), which is probably due to the reduction of Co_xC with hydrogen to Co since Co_xC can readily be reduced under hydrogen atmosphere as shown by the H₂-TPR of the used catalyst. However, it is still not clear which process is more significant in the deactivation of CuCo catalyst in this study and what intrinsic effects of the interaction between copper and cobalt on the deactivation are. Since catalysis is a process which happens on the surface of the catalyst, the detailed surface evolution of CuCo catalysts during reaction, especially at the beginning, needs further investigation. Khodakov et al. studied the evolution of alumina-supported cobalt catalysts under realistic conditions of Fischer-Tropsch synthesis using *in-situ* time-resolved XRD. They suggested cobalt sintering during 3–5 h of reaction and cobalt carbidisation at a longer time on stream led to catalyst deactivation [42]. Loosdrecht et al. investigated the deactivation of an industrial Co/Al₂O₃ FT catalyst by pseudo *in-situ* X-ray diffraction, magnetic measurements and X-ray absorption near-edge spectroscopy [43]. The results show

that oxidation is not a deactivation mechanism during realistic Fischer-Tropsch synthesis. As the reaction conditions of higher alcohol synthesis are very similar to that of Fischer-Tropsch synthesis, the above mentioned *in-situ* characterization techniques under realistic Fischer-Tropsch synthesis conditions should be applicable for detailed deactivation study of CuCo HAS catalyst.

In our study, TiO₂ was used as catalyst support. It has been reported that TiO₂ could interact strongly with active metals, i.e. it could be spread over metal's surface and cover the active sites for reaction [44]. However, such metal-support interaction is generally related to high temperature, and the higher temperature is, the stronger the interaction is. In our study, the calcination, reduction and reaction temperatures were 330, 250 and 250 °C, respectively. As the temperatures were not very high, the metal-support interaction may be weak. In addition, TPR results showed that the reduction of the calcined sample was reduced below 250 °C, and there was no reduction peaks higher than 250 °C for the used catalyst, which was much lower than that of the weak reduction of TiO₂ as shown in Fig. S3. As a result, the TiO₂ support in our study seemed to act as “inert” support to spread CuCo nanoparticles. However, although the metal-support interaction was weak in this study, the TiO₂ support may also influence the catalytic performance. Further study about the effect of different support will be investigated in our group.

5. Conclusions

In summary, CuCo/TiO₂ model catalyst prepared by deposition-precipitation method was studied for higher alcohol synthesis and the deactivation mechanism was investigated based on the correlation of catalyst structural evolution and change of catalytic performance. The HAS catalytic activity decreases continually with time-on-stream without pronounced change of total alcohol selectivity. However, the products shift gradually to lower carbon number and the chain growth probabilities of both alcohols and hydrocarbons decrease with reaction time. When ethane hydrogenolysis was adopted as a probe reaction over the same model catalyst, it could be observed that the activity also declined, indicating the number of surface metallic cobalt assemblies decreased. In order to explore the detailed structural evolution, the samples obtained at different stages (calcined, reduced and used samples) were analyzed by various techniques. It was found that the bulk crystalline phase of the calcined catalyst was CuCo composite oxide, with small CuO nanoparticles spread on the catalyst surface. The oxides were transformed into CuCo alloy and Cu after

reduction. For the used sample, severe sintering was found and there was Co_xC formation on the catalyst surface, both of which led to the decline of surface Co atoms and catalytic deactivation.

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