



Oxygen removal from syngas by catalytic oxidation of copper catalyst



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ABSTRACT

The syngas from biomass gasification may contain trace oxygen besides of gaseous hydrocarbons, which will result in the temporarily or even permanently deactivation of Fischer–Tropsch (F–T) catalysts. In this paper, CuO–CeO₂/Al₂O₃ catalyst was developed to efficiently remove the trace oxygen from biomass syngas. The experimental results demonstrated that CuO–CeO₂/Al₂O₃ catalyst was considerably effective in removing oxygen to the level of below 1 ppm, its lifetime and deoxygenation capacity were 160 h and 3000 ml/g, respectively. Moreover, the optimum conditions of CuO–CeO₂/Al₂O₃ catalyst were 200 °C, 3.45 × 10⁵ Pa, and 3000 h⁻¹ gas hourly space velocity.

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1. Introduction

The synthesis of transportation fuel has been the hot topic of biomass utilization due to the depletion of oil, national energy security and environmental issues. At present, the most potential routes for producing transportation fuels from biomass is gasification, followed by Fischer–Tropsch (FT) synthesis [1]. However, the syngas from biomass gasification may contain some trace pollutants such as 10,000–15,000 ppm tars, 2000–4000 ppm ammonia, 100–500 ppm H₂S [2,3] and 0.1–1% oxygen [4,5] besides gaseous hydrocarbons. Unfortunately, it has been discovered that trace oxygen can temporarily or even permanently deactivate the commercial FT catalysts. Yan et al. reported that the lifetime of F–T synthesis catalyst was only 40 h without the cleaning process. However, the lifetime of catalyst would be over 1000 h after the oxygen in the syngas was removed to the level below 1 ppm, as shown in Fig. 1 [6].

It was reported that the catalyst oxidization by precious metals could remove oxygen to a level of below 0.02 ppm due to the reaction between oxygen and hydrogen or carbon monoxide. The mechanism of the H₂ oxidation reaction over Pt surface was studied by using mass spectrometry and laser-induced fluorescence [7]. Lei et al. pointed out that oxygen content in hydrogen could be reduced from 0.4% to 2 × 10⁻⁶–3 × 10⁻⁶ (v/v) in the reaction temperature range of 150–170 °C with a space velocity of 5000 h⁻¹. Meanwhile, the increase reaction temperature had little influence on the removal efficiency of oxygen [8]. However, the widely application of removing oxygen from the syngas was suppressed because of the high cost of noble metals and sulfur poisoning.

CuO is a cheap catalyst with high activity, which has been also widely used in a variety of catalytic reactions including the oxidation of carbon monoxide and hydrocarbons [9]. Avgourpoulos et al. reported that CuO–CeO₂ catalyst had the same activity as Pt/Al₂O₃ catalyst [10]. Wan et al. pointed out that Cu⁺ species were active phase after the pretreatment by CO [11]. In the presence of rich hydrogen, hydrogen molecules were firstly absorbed on the catalyst surface, followed by disassociating from the catalyst surface and forming hydrogen atoms. At the same time, oxygen also reacted with catalyst and formed the oxides of O²⁻. Lastly, hydrogen atoms easily reacted with O²⁻ and formed water [11].

In the system of rich CO, the reaction complies with the Langmuir–Hinshelwood mechanism [12]. During catalytic processes, the adsorbed oxygen reacts with carbon monoxide, which results in forming a CO₃ complex as an intermediate stage. The reaction releases much heat and leads to the sharply increase of temperature. The high temperature may change the crystal and pore structure of the deoxidant catalyst, which may lead lower the dispersion caused by the sintering. Zhu [13] and Zeng [14] stated that Au/CeO₂ and CuO/CeO₂ catalyst had a strongly active for CO oxidation due to their oxygen storage capacity. BASF also proved that CuO catalyst tablets could remove oxygen or CO/H₂ from gas stream [15].

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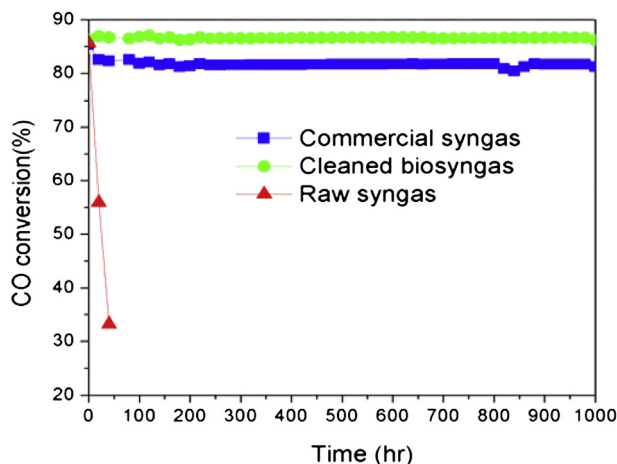


Fig. 1. Comparison of the catalyst lifetime with and without clean process.

Table 1
The compositions of catalyst.

Name	Ce (wt %)	Cu (wt %)	Al ₂ O ₃ (wt %)
Catalyst F	5	10	85
Catalyst P	0	10	90

Ge prepared Mn–Cu–Co/montmorillonite deoxidant by co-precipitation, which could reduce oxygen content from 500×10^{-6} to 0.01×10^{-6} (v/v) at a space velocity of 1000–8000 h⁻¹, and the operation temperature range of 25–200 °C [16]. Ren et al. also developed a Mn–Cu–Co/active carbon deoxidant which had a high selectivity of converting CO to CO₂. After the clean process, the oxygen concentration was below 1 ppm [17].

In this paper, copper catalysts with CeO₂ promoter and alumina support were developed. The optimum operations and their catalyst performances were also investigated.

2. Experimental

2.1. Material and method

It was discovered that the oxides of transition metals combined with other oxides such as cerium had the active radicals – hydroxyl roots, which could store oxygen in its structure. Moreover, Ceria could promote the dispersion of copper on alumina support [18]. Therefore, the activity of catalyst was increased when CeO₂ was incorporated into CuO lattice. In this experiment, CeO₂ and alumina were used as promoter and support, respectively. According to the experimental results of Strohmeier [19], the highly dispersed Cu oxide species were well interacted with support alumina when Cu content in the catalyst was 10%wt. Three catalysts with different components were prepared, and the compositions are listed in Table 1.

The catalysts were prepared by a two-step impregnation method. As for catalyst F, the required amount of cerium nitrate [Ce(N-O₃)₃·6H₂O] (99.5%, Acros Organics) solution was firstly impregnated over the γ-alumina (surface area, 246 m²/g, pore volume, 1.15 mL/g), then the precursor was dried at 120 °C for 6 h, followed by calcinated at 600 °C for 6 h. Thus, CeO₂/Al₂O₃ was prepared.

During the subsequent impregnation, the required amount of copper nitrate [Cu(NO₃)₂·3H₂O] (99.7%, Sigma–Aldrich) solution was impregnated over the prepared CeO₂/Al₂O₃ and dried under 120 °C for 6 h, followed by calcinations under 350 °C for 6 h. The final catalyst was prepared. The properties of the catalysts were listed in Table 2.

2.2. Pretreatment

The reduction can activate surface copper oxide into metal copper, which increases the catalyst activity and its oxygen capacity. Wan et al. [11] demonstrated that the deoxygenation efficiency of the CO-pretreated catalyst was higher than that of fresh catalysts. In these runs, catalyst F was active by CO–N₂ stream (20% CO by volume, N₂ was balanced gas) at 250 °C for 6 h under atmosphere pressure. During the reduced process, the gas flow rate was kept about 20 ml/min. After the reduction, the reactor was purged with N₂ stream until the treated catalyst was cooled to a determined temperature. Lastly, the catalyst was directly exposed to the syngas when the reactor temperature was stabilized.

Table 2
The properties of the catalyst.

Name	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (mm)
Catalyst F	129	0.31	4.7
Catalyst P	187	0.64	7.5

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