

Effect of air-exposure on reduction behavior of a Fe–Mn–Cu–K/SiO₂ Fischer-Tropsch synthesis catalyst

Chenghua Zhang^{a,b}, Botao Teng^{a,b}, Yong Yang^a, Zhichao Tao^{a,b}, Qinglan Hao^{a,b},
Haijun Wan^{a,b}, Fan Yi^c, Binfu Xu^c, Hongwei Xiang^a, Yongwang Li^{a,*}

^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, CAS, Chinese Academy of Sciences, PO BOX 165, Taiyuan 030001, PR China

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

^c College of Physics and Technology, Wuhan University, Wuhan 430072, PR China

Received 20 April 2005; received in revised form 30 May 2005; accepted 30 May 2005

Available online 5 July 2005

Abstract

It was found that air-exposure suppressed the sequent reduction behavior before a Fe–Mn–Cu–K/SiO₂ 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, CO₂ 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 CO₂ are adsorbed on surface of catalysts when catalysts were exposed to air. Copper promotion enhances the selective adsorption of CO₂ in air. The species formed upon CO₂ 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.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Fischer-Tropsch; Fe–Mn catalyst; Copper promotion; CO₂ 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 SiO₂

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/SiO₂ 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.

* Corresponding author. Tel.: +86 351 4130337; fax: +86 351 4050320.
E-mail address: ywl@sxicc.ac.cn (Y. Li).

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, CO₂-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(NO₃)₃, Mn(NO₃)₂ and silica sol with Fe/Mn/SiO₂ ratio of 100/12/12 was used in precipitation with NH₄OH 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(NO₃)₂ and K₂CO₃ solutions were respectively added into the precipitate and spray drying was followed to obtain desired catalyst precursors with particle size of 20–70 μm . Then, catalyst precursors were calcinated at 500 $^{\circ}\text{C}$ for 5 h. The final obtained catalysts were composed of 100Fe/12Mn/3K/12SiO₂ (Cu00) and 100Fe/12Mn/3K/3Cu/12SiO₂ (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 cm^{-1} and accumulation of 64 scans.

2.2.3. CO₂-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. CO₂ 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, CO₂ 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, CO₂-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 ⁵⁷Co 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 (H₂/CO = 0.67) at 0.5 MPa, 1000 h⁻¹ and 280 $^{\circ}\text{C}$ for 8 h. After reduction, the catalyst samples (ca. 1 g) were drawn online for Mössbauer spectroscopy analysis. The CO₂ concentration in tail-gas was analyzed online using a gas chromatograph (Model 4890D, Agilent, USA).

Download English Version:

<https://daneshyari.com/en/article/9614476>

Download Persian Version:

<https://daneshyari.com/article/9614476>

[Daneshyari.com](https://daneshyari.com)