



Design of efficient Fischer Tropsch cobalt catalysts via plasma enhancement: Reducibility and performance (Review)



Wei Chu^{a,b,*}, Junqiang Xu^{c,*}, Jingping Hong^a, Tao Lin^{a,b}, A. Khodakov^d

^a Department of Chemical Engineering & Key Laboratory of Green Chemical Technology of Ministry of Education, Sichuan University, Chengdu 610065, China

^b Sichuan Provincial Engineering Technology Center for Environmental Protection Catalytic Materials, Chengdu 610064, China

^c School of Chemistry & Chemical Engineering, Chongqing University of Technology, Chongqing 400054, China

^d Unité de Catalyse et de Chimie du Solide, UMR 8181 CNRS, USTL, Cite Scientifique, 59655 Villeneuve d'Ascq, France

ARTICLE INFO

Article history:

Received 3 January 2015

Received in revised form 20 May 2015

Accepted 21 May 2015

Available online 25 June 2015

Keywords:

Plasma

Cobalt catalyst

Fischer Tropsch synthesis

Performance

Reducibility

Promoter

Clean fuel

Characterization

ABSTRACT

In this paper, several types of plasma enhanced catalysts for Fischer Tropsch (FT) synthesis were investigated and discussed, in comparison of conventional catalysts, with different carriers [alumina, silica, carbon nanotubes (CNTs)], and/or different promoters (Pt, Ru), etc. For the silica-supported cobalt FT catalysts, the cobalt dispersion was significantly enhanced by plasma treatment. Nano cobalt particle size was smaller when the glow discharge plasma intensity was higher. There were similar cases for the Ru promoted FT catalysts or alumina supported FT catalysts. For the alumina supported cobalt FT catalysts, Pt addition enhanced significantly the catalysts reduction. Due to the combination of higher cobalt dispersion and optimized cobalt reducibility, plasma-assisted promoted catalysts exhibited an enhanced activity in FT synthesis.

© 2015 Published by Elsevier B.V.

1. Introduction

Fischer Tropsch (FT) synthesis converts natural gas-, coal-, and biomass-based syngas into clean liquid fuels, which are totally free of S or N containing compounds and have very low aromatic contents [1–4]. Cobalt-based catalysts could have high activity, high selectivity to linear C₅₊ hydrocarbons (C₅₊ HC), low activities for water–gas shift reaction, and lower price compared to that of noble metal [5–7].

Conventional cobalt FT catalysts were prepared by impregnation of common support (silica, alumina, or Titania, etc.) with aqueous solution of cobalt salt. After decomposition of the supported cobalt salt by calcination in an oxidizing atmosphere, the catalysts were reduced in hydrogen to generate cobalt metal sites [8].

The catalytic support could play an important role in FT synthesis, determining the catalyst structure and catalytic

performance [9–11]. Johnson et al. [12] reported strong carrier effects in carbon monoxide hydrogenation on supported cobalt catalysts. The catalytic performance was a function of the carriers; the order of decreasing CO hydrogenation activity was TiO₂ > SiO₂ > Al₂O₃ > MgO. Bechara et al. [13] found that the textural properties of alumina could result in different chain lengths of hydrocarbons, which was assigned to different residence time and mass transport of hydrocarbons in alumina pores. Iglesia et al. [14] suggested that the carriers could slightly influence the selectivity of C₅₊ HC desired products. Previous reports have also uncovered that use of large pore support improves cobalt reducibility and mass transport in the catalyst. Larger cobalt particle size can be obtained by using large pore materials [15,16].

Plasma technology is a very useful tool for several modern uprising researches and applications [1,2,17–44], such as plasma-mediated synthesis of nano materials in Qiu's group [17,18], environmental plasma-catalysis for the abatement of volatile organic compounds and environmental applications in Mok's group [19], Whitehead's group [20], plasma assisted green house gases conversions in Zhu's group [21,22], methane conversion in plasma reactor in Nozaki's group [23,24], Plasma assisted synthesis of novel enhanced catalysts and nonmaterials in Liu's group [25,26],

* Corresponding authors at: Department of Chemical Engineering, Sichuan University, 24 South Section One, 1st Ring Road (Yihuan Road), Chengdu, Sichuan 610065, China. Tel.: +86 28 85403836; fax: +86 28 85461108.

E-mail address: chuwei1965@scu.edu.cn (W. Chu).

& plasma enhanced preparation of more efficient nano catalysts in Chu's group [1,2] etc. In principle, plasma is an ionized gas mixture that can be generated by a number of methods, including electric discharges (radio frequency glow, microwave, plasma jet, etc.). According to the literature reports, various catalysts such as Pd/HZSM-5 [27], Pt/NaZSM-5 [28], and Pd/Al₂O₃ [29] were treated by plasma treatment and tested in different catalytic processes, including methane combustion, NO reduction, partial oxidation of methane, ethylene selective hydrogenation, and other processes [30–34]. The plasma facilitates the decomposition of metal precursors during catalyst preparation, thus by using this special treatment. Some specific properties could be evidenced in the catalytic processes [35–44].

Based on our recent works and those of related plasma enhanced catalysts for FT synthesis, this review paper will address mainly about the effects of the cobalt catalysts reducibility and synergism on the catalysts performance in FT synthesis to clean Fuels. Especially the glow-discharge technique [45–47], which is simple, quick, audio-visual, and easy to control treatment process, is typically applied in catalysts treatments to develop the active FT catalysts. Several types of catalysts were illustrated, while the reducibility and performances were analyzed and mainly discussed.

2. Preparation of plasma assisted Co-alumina-based FT catalysts

2.1. Pristine Co-alumina catalysts or with promoters

Alumina was one of the more utilized carriers for FT catalysts. The cobalt oxide interacted strongly with the alumina support, forming relatively small cobalt nanoparticles and more difficultly reducible cobalt species [48]. Cobalt reducibility was one of the most important issues of alumina-supported cobalt FT catalysts. Promoter addition could improve the cobalt reducibility and then the catalytic performance.

In our previous experiments [8], the conventional alumina supported cobalt catalyst (Co-alumina-200 sample) had a mild activity for the FT synthesis. The CO conversion was 3.3% at 1 bar and 463 K, 1800 ml/g/h; while the selectivity of desired products C₅₊ HC was 75.7% and the by-product methane selectivity was only 8.3%. When the reaction temperature increased from 453 K to 473 K, there was a slight decrease of C₅₊ HC while the methane selectivity was augmented gradually. The trends were more rapidly shifting when the reaction temperature reached 483 K and further. Cook et al. [49,50] reported that the noble metal (NM) – promoted 25%Co/La/Al₂O₃ catalysts were prepared by a three-step (co-dep) or four-step (seq-dep) wet impregnation. The co-dep method to add noble metal promoters to Co FT catalysts was significantly better than the seq-dep method; it produced catalysts that had higher activity and lower methane selectivity, and it required less work in their preparation.

Lancelot et al. [51] reported that the CoPt/Al₂O₃ catalyst was synthesized via incipient wetness co-impregnation, and characterized. They provided the direct experimental evidence of surface oxidation of supported cobalt metal nanoparticles in the FT reaction. In addition to other deactivation phenomena, the uncovered surface oxidation of cobalt nanoparticles was likely to be a major reason for catalyst deactivation at higher reaction temperatures.

The TPR profiles of Pt promoted cobalt catalysts calcined at different temperature were illustrated in Fig. 1. Several peaks can be seen in the TPR curves of cobalt catalysts. In agreement with previous report, low-temperature peaks at 473–573 K were attributed to partial reduction of Co₃O₄ to CoO, whereas high-temperature peaks at 623–1023 K were assigned to the reduction of CoO to the cobalt metallic phase. The peak at 473 K shown in the TPR profile

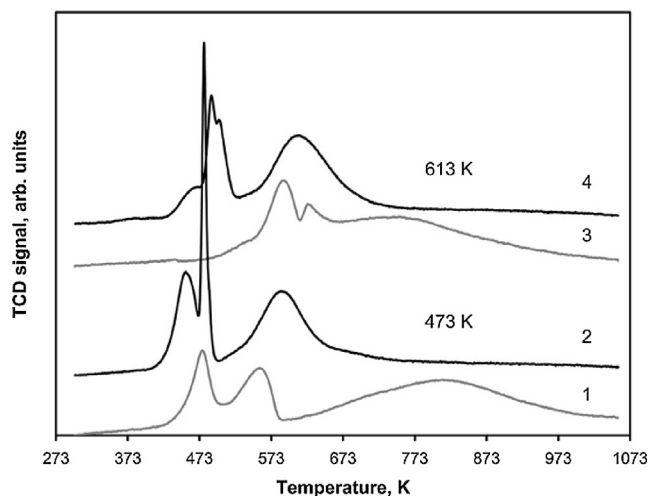


Fig. 1. Effect of Pt promotion on TPR profiles of alumina-supported Co catalysts. (1) Co/Al₂O₃-473, (2) CoPt/Al₂O₃-473, (3) Co/Al₂O₃-613, (4) CoPt/Al₂O₃-613 (5%H₂/Ar, ramping rate 3 K/min).

From Ref. [8].

of Co/Al₂O₃-473 was attributed to the reductive decomposition of residual cobalt nitrate. An intense and narrow TPR peak at 480 K in the profile of the CoPt/Al₂O₃-473 catalyst (Fig. 1) was attributed to the cobalt nitrate decomposition. The position of reduction peaks was found to depend on the temperature of catalyst calcination. Reduction of cobalt oxide species was more difficult in the supported cobalt catalysts, which were calcined at higher temperatures. In agreement with previous papers, promotion with platinum resulted in a lower temperature shift of the peaks of reduction of CoO to metallic cobalt (Fig. 1). Therefore, Pt promotion enhanced the reduction: Co₃O₄ → CoO and CoO → Co steps.

The TPR data suggested that cobalt reducibility was affected significantly by catalysts calcination temperature and also Pt promotion. Cobalt reducibility was relatively low in alumina supported monometallic cobalt catalysts. The higher calcination temperature of the monometallic cobalt catalysts hindered cobalt reduction. Promotion with a small amount platinum resulted in a much enhanced cobalt reduction. The presence of platinum decreased the activation energy of the formation of cobalt metallic phases. Platinum promotion also favored the reduction of smaller Co₃O₄ crystallites and resulted in smaller average size of supported cobalt metal particles in the reduced catalysts. Therefore, the catalytic performance has been improved significantly after the platinum addition.

2.2. Plasma enhanced Co-alumina FT catalysts with Pt promoter

In our previous work, the conventional Co-Al₂O₃ samples and platinum promoted catalysts were prepared by incipient wetness impregnation using precursor solutions of cobalt nitrate and dihydrogen hexachloroplatinate [8]. The cobalt content in catalyst was 15 wt%. The conventional calcined catalysts were denoted as Co(Pt)-Al₂O₃-T, where T indicated the temperature of the calcination treatment and Pt indicated promotion with platinum. The treated supported cobalt catalysts and Pt-promoted samples that were enhanced using glow discharge plasma (shortened to: plasma-assisted catalysts) were marked as Co-Al₂O₃-PNH and CoPt-Al₂O₃-PNH respectively (Table 1).

The original supported cobalt samples and Pt-promoted cobalt catalysts after calcination exhibited XRD patterns characteristic of Co₃O₄ spinel in addition to the patterns of γ-Al₂O₃. The Co₃O₄ crystallite sizes, calculated by using the Scherrer equation, were listed

Download English Version:

<https://daneshyari.com/en/article/53943>

Download Persian Version:

<https://daneshyari.com/article/53943>

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