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Studies on surface impregnation combustion method to prepare supported Co/SiO_2 catalysts and its application for Fischer–Tropsch synthesis

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ABSTRACT

A series of supported Co/SiO_2 catalysts were prepared by surface impregnation combustion method using cobalt nitrates and citric acid, and the precursors were burnt in different atmospheres. The effects of different calcination atmospheres on the properties of the supported Co/SiO_2 catalysts were systemically studied by TG-DTA, XRD, Raman spectrum, TPR, in situ FTIR, TEM, BET and H_2-chemisorption techniques. The burnt catalyst $C_{argon-air-reduction}$ which was first burnt in argon and then oxidized in air had about 10 nm Co_3O_4 crystalline size, much smaller than that which was directly burnt in air (Co_3O_4 size: about 15 nm) and that prepared by conventional impregnation method (Co_3O_4 size: about 32 nm) using cobalt nitrate as impregnating solution. Characterizations and FTS results of two other references using different organic cobalt salt aqueous (cobalt acetate and cobalt citrate) as impregnating solution were also added in the supporting information. Comparing with our previously reported C_{argon} catalyst directly burnt in the argon atmosphere without further reduction, the influence from surface amorphous carbon and carbonic residues was completely eliminated. The activity of the burnt catalyst $C_{argon-air-reduction}$ prepared by surface impregnation method was threefold higher than that of the reference $C_{N-reduction}$ prepared by conventional incipient-wetness impregnation method. The surface impregnation combustion method described herein was promising to prepare highly dispersed supported metallic catalysts with smaller particle sizes.

1. Introduction

Metallic catalysts are widely used in the catalytic reactions, as a function of hydrogenation, dehydrogenation, isomerization [1], reforming, selective hydrocarbon oxidation [2] and so on. To obtain higher concentration and efficient utilization of surface active sites, nano-structured or subnano-structured metallic catalysts [3–7] with smaller particle sizes have received widespread interest in recent years.

For cobalt-based Fischer–Tropsch synthesis (FTS), the catalytic performance is strongly affected by the sizes of cobalt metal particles and the catalyst preparation methods [8–14]. Cobalt-based FT catalysts are conventionally prepared by aqueous impregnation methods [8–16] on different supports, and then the precursors are calcined in an oxidizing atmosphere to receive Co_3O_4. However, Co_3O_4 crystalline sizes prepared from nitrates by these methods become as large as or more than 20 nm. Chu et al. [17] used glow-discharge nitrogen and hydrogen plasma to pretreat cobalt-based catalysts, and about 10 nm crystalline size of Co_3O_4 was yielded.

Here, surface impregnation combustion method is proposed to prepare nano-structured Co/SiO_2 catalysts. This technique is based on a chemical sol–gel process combined with subsequent combustion process. An aqueous solution containing the desired metal salts and organic fuel is impregnated on the support, forming the xerogel through the sol–gel process. Then, the xerogel is ignited to combust in air, giving a voluminous and fluffy product with a large surface area. In this process, citric acid acts as a kind of chelated agent providing complexing ligands, forming a homogeneous precursor. According to our former work [18], nano-structured (Co size: 4–6 nm) Co/SiO_2 catalysts without further reduction are prepared by a novel surface impregnation auto-combustion method which are only burnt in the argon atmosphere. However, by increasing the content of citric acid in the initial precursors, more carbonic residue is left in the as-burnt catalysts and partly covers the surface of cobalt. H_2 diffuses more quickly than CO inside micropores of these carbonic residues, leading to the higher H_2/CO ratio than the original one at the cobalt surface, resulting in enhanced

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