Applied Catalysis A: General 480 (2014) 86–92

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Effects of the reduction temperature over ex-chloride Ru Fischer–Tropsch catalysts supported on high surface area graphite and promoted by potassium

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ARTICLE INFO

Article history:
Received 25 February 2014
Received in revised form 25 April 2014
Accepted 26 April 2014
Available online 4 May 2014

Keywords:
Fischer–Tropsch reaction
Ex-chloride Ru catalyst
High surface area graphite
Potassium promoter
CO adsorption microcalorimetry

ABSTRACT

For ex-choride Ru catalysts supported on high surface area graphite and promoted by potassium oxide, the influence of the reduction temperature on the surface properties and on the catalytic performance in the Fischer–Tropsch reaction (1 bar, $H_2/CO = 2/1$) is investigated. The Ru metallic particle size generated on these catalysts was studied by CO chemisorption and checked by TEM. Characterization of the catalysts by XPS analysis and microcalorimetry of CO adsorption reveals the presence of residual chloride anions after reduction (hydrogen flow) at 573 and even 673 K. The chloride traces neutralize the effects of the potassium promoter in the Fischer–Tropsch reaction. When catalysts are reduced at 773 K, lower methane selectivity and higher olefin/paraffin ratio are observed for those with potassium added. Our results show the significance of the reduction treatment and the presence of residual chloride anions to achieve a ruthenium based Fischer–Tropsch catalyst with improved selectivity to light olefins.

1. Introduction

Nowadays Fischer–Tropsch (FT) synthesis enjoys great attention as an option for the transformation of various non-petroleum carbon resources, such as, natural gas, coal and biomass, into clean transportation fuels or valuable chemicals from syngas (H_2 and CO) [1]. Although many catalysts have been developed [2–9], some challenges still remain in the research area of FT. Selectivity control is one of the most difficult and interesting challenges. The reaction mechanism for FT synthesis is quite complicated. It is now widely accepted that the hydrocarbon products in FT synthesis generally follow the Anderson–Schulz–Flory (ASF) distribution, which is determined by a polymerization mechanism [10,11]. Such a distribution is unselective, and the development of novel FT catalysts which can selectively produce hydrocarbons in a certain range has attracted extensive attention. The nature of the catalysts, this is, the chemical state of active components and the nature of supports and promoters, is a crucial factor affecting the product selectivity and the CO conversion for FT synthesis. Although iron and cobalt are the more common metals for FT, ruthenium catalysts, despite higher price, possess some unique features in FT synthesis (highest activity and outstanding chain-growth probability), and are suitable for fundamental research to gain insights into the catalyst functioning and reaction mechanisms [4]. It is known that FT catalysts generally require promoters such as alkali metals, noble metals or transition metal oxides to attain optimum catalytic performance [12]. Modification with alkali metal ions can enhance the chain-growth probability and the olefin selectivity and accelerate the activity for both FT synthesis and water gas shift (WGS) reaction [13,14]. On the contrary, the presence of electronegative elements such as Cl, S and P decrease the catalytic activity for CO hydrogenation and enhance methane formation on group VIII transition metals [15,16].

Most FT catalysts use a support which has been found to have significant influence on the reducibility, activity and selectivity properties of the active phase [17,18]. The choice of support with a proper interaction with the active metal (or metal precursor) is important because the balance between the reducibility and the dispersion determines the FT catalytic performances. Various supports such as alumina [19,20], silica [21,22], titania [23] and carbon materials [5,24–26] have been reported by many groups.

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http://dx.doi.org/10.1016/j.apcata.2014.04.046

Among them, carbon materials are considered to be more inert than the conventional oxide materials. The versatility of their surface chemistry provides new possibilities to tune the metal-support interactions and to prepare size-controllable metal nanoparticles [27–29]. Surface functionalities (e.g., carboxylic acid groups or adsorbed hydrogen species) may also participate in hydrogenation reaction altering the FT selectivity [4]. Furthermore, carbon materials such as, high surface area graphite, carbon nanofibers, carbon nanotubes or hierarchically ordered mesoporous carbons possess high external surface areas without micropores which prevent mass transfer problems in the reaction. The porous channels in carbon nanotubes or ordered mesoporous carbons may also exert a confinement effect, resulting in unique catalytic properties [30–32].

Studies on carbon supported Ru catalysts for FT reaction with controllable product distribution have to date been scarce. Wang and coworkers [24,33] recently claimed that the use of CNT as the support for Ru instead of the conventional metal oxides, zeolites or activated carbons provides a significantly higher selectivity toward C_{10}–C_{20} hydrocarbons, which are the diesel fuel fraction products. However, in the former work, where FT catalytic performance of ruthenium catalysts on various supports is compared [24], the authors found that graphite supported Ru exhibits similar selectivity to Ru/CNT, so this does not seem to be a result of the particular CNT structure but to the graphitic support properties.

The H_2 reduction treatment which precedes catalysis has been classically considered as potentially determinant for the crystalline structure and catalytic activity of the resulting Ru^0 nanoparticles. Previous reports have shown the influence of catalyst pretreatment (gas composition, heating rate, final applied temperature) on the nanoparticle surface structure and catalytic performance [7,33,34]. Moreover, reduction treatment has been considered to determine the degree of interaction between promoters and metallic active phase mainly because this latter may be weakened by strengthening of the metal–support interaction [35–38].

In this work we report a systematic study on the influence of the reduction temperature on the final compositional, structural and catalytic performance of potassium promoted ruthenium catalysts supported on high surface area graphite (HSAG) prepared using ruthenium chloride precursor. We discuss the effects of ruthenium particle size, potassium loading and/or chloride traces in determining the product selectivity to gain insight into the requirements for rational design of active and selective FT catalysts. The catalytic tests were conducted at atmospheric pressure and under differential conditions to avoid secondary reactions. The catalysts were prepared using an inert support to allow a better interaction between promoter and ruthenium phase.

2. Experimental

2.1. Catalyst preparation

The commercial high surface area graphite HSAG-300 provided by TIMCAL (Bodio, Switzerland) with specific surface area of 310 m^2/g was used as support for the preparation of the catalysts. HSAG-300 is a synthetic graphite with ash content below 0.1% (<20 ppm sulphur). The samples were prepared according to the incipient wetness impregnation method, using water/ethanol (1:1, in volume) solutions of the proper ruthenium precursor quantity in order to obtain a 4 wt.% Ru in the final catalysts. The ruthenium precursor used was $RuCl_3 \cdot xH_2O$ obtained from Aldrich. The monometallic ruthenium catalyst was named Ru/HSAG-Cl. After drying at 393 K overnight, aliquots of the parent ruthenium catalyst were impregnated with water/ethanol (1:1 in volume) solutions of potassium nitrate (Aldrich) in an appropriate concentration to obtain Ru/K atomic ratios of 4/1 and 2/1 on the catalysts (samples 4RuK/HSAG-Cl and 2RuK/HSAG-Cl, respectively). Subsequently the catalysts were dried at 393 K overnight.

The metal loading of the ruthenium catalysts was estimated by burning away the carbon in air at 1073 K and weighing the residue (RuO_2, K_2O). Table 1 summarizes the chemical composition of the prepared catalysts.

2.2. Catalyst Characterization

Temperature-programmed reduction (TPR) measurements were carried out in a U-shaped quartz microreactor with 200–300 mg of prepared sample, under a continuous flow of 20 ml/min of a H_2/Ar gas mixture (5% H_2). The temperature was increased from room temperature to 973 K at 8 K/min. H_2 consumption, as well as decomposition products (CO, CO_2 and CH_4), were measured by on-line gas chromatography (Varian 3400) provided with a thermal-conductivity detector (TCD), an automatic sample injection and a Porapak Q column.

The CO uptake on the catalysts and the evolution of the CO adsorption heat were recorded in a Tian Calvet heat-flow microcalorimeter (Setaram C-80 II) isothermally operated at 330 K and connected to a glass vacuum-dosing apparatus. The metal surface was titrated by treating the samples with successive pulses of the probe gas, following the experimental procedure described in detail elsewhere [39]. All the catalysts were first activated by reduction in H_2 flow (20 ml/min) at 573, 673 or 773 K during 2 h. Metal dispersion (D_{CO}) was calculated assuming a molar stoichiometry Ru/CO = 1/1, from the total CO uptake at the monolayer considered to be attained when the evolved heat falls to the physisorption field (40 kJ/mol). The mean metal crystallite size was calculated from the dispersion values assuming the spherical model, $d\,(\text{nm}) = 1.32/D_{CO}$ [40].

Transmission electron microscopy (TEM) measurements were undertaken using a Jeol 2100F field-emission gun electron microscope operated at 200 kV and equipped with an energy-dispersive X-ray spectrometer. For the electron microscopy analysis a small sample amount was dispersed in ethanol and a drop of this suspension was placed on a lacey carbon film coated copper grid (3.0 mm, 200 mesh, Pelco). Average metal particle sizes were determined from TEM analysis. Over 200 individual metal particles were counted for each catalyst and the surface area-weighted metal particle diameter (d_S) was calculated using the following equation [41]:

$$d_S = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}$$

where n_i is the number of particles with diameter d_i.

X-ray photoelectron spectroscopy (XPS) was performed with a ESCAPROBE P spectrometer from OMNICROM equipped with a EA-125 hemispherical multichannel Electronics analyzer. The pressure in the analysis chamber was kept below 10^{-9} Pa. The excitation source was the Mg$K\alpha$ line ($h_\nu = 1253.6$ eV, 300 W). The binding energy of Ru 3p3/2 was referenced to the C 1s line at 284.8 eV. The error in determination of electron binding energies and the line widths did not exceed 0.2 eV.

2.3. Catalytic measurements

The catalytic measurements were carried out in a glass, tubular fixed bed microreactor (5 mm ID) operated under differential conditions (CO conversion below 10%) at atmospheric pressure and temperatures in the range 523–548 K. Typically, samples (0.25 mg) were treated at 573, 673 or 773 K for 2 h under a continuous 20 ml/min H_2 flow. After reduction, the catalyst