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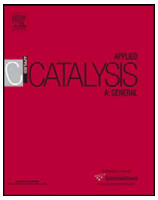

Bimetallic Co-Fe nanocrystals deposited on SBA-15 and HMS mesoporous silicas as catalysts for Fischer–Tropsch synthesis

L.F.F.P.G. Bragança[a,b], M. Ojeda[c], J.L.G. Fierro[c], M.I. Pais da Silva[b,*]

[a] *Departamento de Engenharia Química e Petróleo, Universidade Federal Fluminense, Niterói, RJ, Brazil*
[b] *Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro, R. Marquês de São Vicente 225, Gávea, Rio de Janeiro, 22453-900, RJ, Brazil*
[c] *Group of Energy and Sustainable Chemistry (EQS), Institute of Catalysis and Petrochemistry (CSIC), C/Marie Curie, 28049, Madrid, Spain*

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ABSTRACT

Fischer–Tropsch synthesis (493 K, 0.62 MPa CO, 1.24 MPa H_2) has been performed over monometallic and bimetallic Co and/or Fe clusters deposited on mesoporous silicas (HMS and SBA-15). Catalysts have been prepared by incipient wetness impregnation and characterized by N_2 adsorption–desorption isotherms, X-ray diffraction (XRD), H_2-temperature programmed reduction (H_2-TPR), and transmission electron microscopy (TEM).

HMS supported Co-Fe catalyst showed the highest activity and C_{5+} hydrocarbon selectivity, while Co-Fe/SBA-15 catalyst revealed the highest selectivity to alcohols. Both bimetallic catalysts were more active toward the C_2–C_4 hydrocarbon fraction, with an enhancement in the selectivity to $C_2^{=}$, $C_3^{=}$ and 1-$C_4^{=}$ olefins. Both bimetallic catalysts showed greater chain growth probability values than the monometallic iron based catalysts although their performance in catalytic tests were more close to the iron catalyst.

1. Introduction

Fischer–Tropsch synthesis (FTS) produces ultra-clean, sulfur-free chemicals and fuels from syngas (H_2/CO mixtures), which can be generated from coal, natural gas or biomass using a suitable heterogeneous catalyst [1,2]. Different transition metals are catalytically active in FTS, but most studies have focused on Co- and Fe-based catalysts [3–5]. Co clusters deposited on different supports, such as SiO_2, Al_2O_3 and TiO_2, are usually preferred for the synthesis of long-chain paraffins [6–9] due to its high activity and selectivity toward C_{5+} hydrocarbons and low activity for the water–gas shift reaction (WGS, $CO + H_2O \rightarrow CO_2 + H_2$) [10]. Fe-based catalysts are less expensive, showing high WGS activity, high selectivity to both olefins and oxygenated products, and are more suitable with low H_2/CO ratio syngas [11,12]. Unsupported Fe-based catalysts are usually employed [13,14]; however, attrition resistance is often an issue when using slurry bubble-column reactors (SBCRs). Silica supported Fe-based catalyst have shown improved attrition resistance [15]. Additionally, the use of bimetallic catalysts influences the observed product distribution and selectivity. Indeed, de la Peña O'Shea et al. [16] investigated mono and bimetallic silica-supported Co and Fe catalysts for FTS in fixed bed and slurry reactors showing that light hydrocarbons were the major products found for the Fe-containing catalysts (mono and bimetallic). Moreover, high selectivities to methane and ethanol with bimetallic catalysts (1% Fe and 10% Co) were observed using a fixed-bed reactor.

Recently, mesoporous materials such as MCM-41 [17], SBA-15 [18] and hexagonal mesoporous silica (HMS) [19], have been explored as supports for metal Fischer–Tropsch synthesis catalysts. These materials usually exhibit high surface areas, narrow pore size distributions, and large pore diameters and volumes. Previous studies have shown that these textural properties influence significantly the reducibility of the CoO_x species formed on the surface and the size of the metallic Co clusters size originated afterwards [20]. Panpranot et al. [17] reported an increase in CO hydrogenation rates shown by small Co clusters when MCM-41 was used as support. Khodakov et al. [21] reported that larger Co particles located in the wider-pore silica were more active in FTS than those located in narrower pore supported Co catalysts. These authors attributed this effect to the lower reducibility of the smaller Co clusters. Martínez et al. [22] have investigated the influence of cobalt loading (10–40 wt.% Co) in Co/SBA-15 catalysts for FTS. They have found maximum CO conversion rates for the catalyst with 30 wt.% Co loading. Also, a better dispersion of cobalt species in the mesoporous silica increased the Co/SBA-15 (20 wt.% Co) activity compared to that shown by Co/SiO_2. Recently, Xiong et al. [23] have reported on the influence of the Co particle size on the C_{5+} hydrocarbon selectivity measured with Co/SBA-15

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* Corresponding author. Tel.: +55 21 35271323; fax: +55 21 35271323.
E-mail addresses: mojeda@icp.csic.es (M. Ojeda), isapais@puc-rio.br (M.I.P. da Silva).

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