Synthesis of spherical shape silicas as support for cobalt based catalysts potential for Fischer Tropsch Synthesis

F. Pardo[*,1,2], Henrik Kusar[1], V. Montes[3], A. Marinas[3], S. Cabrera[2], S. Järås[1], M. Boutonnet[1]

[1] 1KTH - Royal Institute of Technology, School of Chemical Science and Engineering, Chemical Technology, SE-100 44 Stockholm, Sweden

[2]Universidad Mayor de San Andrés, Instituto del Gas Natural, Campus Universitario, Cota-Cota, Calle No. 27, La Paz, Bolivia

[3] Department of Organic Chemistry, Cordoba University, E-14014-Cordoba, Spain

(*)pardo@kth.se

Introduction

Synthetic liquid hydrocarbons are produced from carbon monoxide and hydrogen gases in the Fischer-Tropsch Synthesis (FTS). The great advantage of this process is that clean fuels particularly synthetic diesel can be obtained. There are a vast number of variables in the catalyst preparation procedure that influences the catalyst activity [1, 2].

Cobalt catalysts are preferred for the FTS because greater yields of straight-chain alkanes can be obtained. Many techniques and methods were explored in preparation of cobalt catalysts. The industrially common one is impregnation of the supports like SiO2, TiO2 and Al2O3 by cobalt nitrate aqueous solution on [3].

Silica and alumina are mostly used as the Co catalyst support because of their low affinity to form cobalt-support interactions which decrease the activity of the catalyst. Furthermore, the improvement in its physical properties such as morphology and pore size can lead to better yield of the final product in FTS (long chain hydrocarbons). Mesostructured cellular foam MCF is a mesoporous material with homogeneous spherical structure and pore diameter between 10 to 50 nanometers, these spheres are interconnected by uniform windows that can also be regulated in size diameter. Silica with MCF structure can be used as support for the dispersion of the active phase in catalyst. Silica with homogeneous and open pores morphology like MCF can enhance considerably the diffusion of the reactants and products during the FTS, which can increase the yield of the reaction [5]. The present study is to investigate the effect of (MCM-41, SBA-15 and MCF silicas) supports on cobalt particles and hence on their performance for FTS.

Materials and Methods

The synthesis of the MCM-41, SBA-15 and MCF supports was carried out following the recipes from [3,4,5]. The Co (12wt.%) was incorporated through impregnation from an aqueous solution of Co(NO3)2 followed by calcination at 350ºC for 10h.
The catalysts were characterized by nitrogen adsorption, X-ray diffraction (XRD), SEM-EDAX, TEM, H2-TPR, H2-Chemisorption, TGA and IR. The catalytic test were performed in a fixed bed reactor at 20 atm and 2100C with a feed gas composition H2/CO =2.1.

Results and Discussion

Small pores present in MCM-41 materials (as compared to SBA-15 and MCF) lead to a smaller size of the supported Co particles (Table 1) and to their lower reducibility accompanied by a higher susceptibility to cobalt-silicate formation (Fig. 2). Catalytic and characterization results show the strong impact of support porosity on the structure, reducibility, and FTS catalytic behavior of cobalt species supported by mesoporous silicas. The Co species located in the narrow pore silicas are much less active in FTS though more selective to methane than larger cobalt particles in the supports with large pores.

MESOPOROUS SILICAS	POROSIMETRY			*Co (0) Particle size [nm]
	BET	Av. Pore size Diameter [nm]	Av. Pore size volume [cm3]	
MCM-41	1200	2.6	0.9	-
12%CoMCM-41	990	3.1	0.8	6.7
SBA-15	940	5.7	1.1	-
12%Co SBA-15	720	5.3	0.8	11.2
*MCF	690	Ds=30; Dw=14	2.5	-
*12%Co MCF	550	Ds=30; Dw=12.5	1.8	9.7

Table 1. Porosimetry results *Ds = diameter sphere and Dw = diameter window

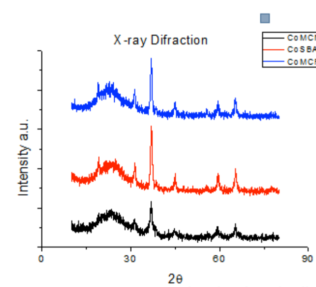

Fig. 1 X-ray espectra showing the cristalinity of the Co_3O_4. Crystals.

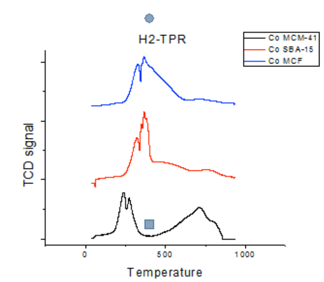

Fig. 2 H2-TPR showing the reducibility of the cobalt and the diferent species formed from the Co_3O_4.

Significance

The advantages of the MCF is its large pore diameters, which overcomes internal mass transfer limitation during the catalytic reactions, which enhance the performance of the activity and selectivity for Fischer Tropsch synthesis, compared with MCM-41 and SBA-15 based catalysts.

References

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