

Biomass derived activated carbon catalysts for the one-step dimethyl ether synthesis from syngas

José Palomo, Miguel Ángel Rodríguez-Cano, José Rodríguez-Mirasol*, Tomás Cordero

Universidad de Málaga, Departamento de Ingeniería Química, Andalucía Tech, Escuela de Ingenierías Industriales, Campus de Teatinos s/n, 29010 Málaga – Spain

*mirasol@uma.es

Introduction

Fossil fuels depletion together with an increasingly stringent in the environmental regulations are the driving force in seeking for alternative clean energy resources. In this scenario, DME is receiving a great deal of attention as a potential renewable substitute for petroleum derivative, since it can be produced from syngas coming from biomass gasification. The development of a DME based economy is related to the implementation of the one-step synthesis process from syngas, in which a bifunctional catalyst is used. In this work we study the behaviour of a carbon-based catalyst for this one-step synthesis process.

Materials and Methods

Two kinds of activated carbons, prepared by chemical (with H_3PO_4) and physical (by CO_2 partial gasification) activation of olive stones, were used as catalysts support. To prepare the methanol synthesis catalytic phases, the activated carbons were loaded with a 20 % (w/w) $\text{CuO}+\text{ZnO}$ (ACGCuZn). As for methanol dehydration catalytic phase, a 5 % (w/w) Zr loaded-chemically activated carbon (ACPZr) was used. The bifunctional catalytic beds were prepared by physical mixing of the individual catalytic phases. Different acid/metal catalysts mass ratios ($W_{\text{ACPZr}}/W_{\text{ACGCuZn}}$) were studied. The syngas to DME experiments were carried out in a fixed-bed reactor ($T=250\text{--}300\text{ }^\circ\text{C}$, $\text{GHSV}=36.4\text{ L}\cdot\text{g}_{\text{Cu}}^{-1}\cdot\text{s}^{-1}$, $P=45\text{ bar}$, $\text{H}_2/\text{CO}=3$).

Results and Discussion

The main difference between the activated carbons was the presence of chemically stable phosphorus surface groups, mainly in form of C-O- PO_3 groups¹, on the activated carbon prepared via chemical activation. The addition of Zr to the chemically activated carbon (ACPZr) resulted in the formation of zirconium phosphate species on the carbon surface, which were capable of promoting the selective methanol dehydration to DME. Cu-Zn loading on the chemically activated carbon resulted in strong interactions between the metallic phase and the phosphate surface groups due to the formation Cu phosphate species (as revealed by XPS). The catalytic results showed very low CO conversion values for ACPCuZn. On the contrary, ACGCuZn exhibited a fairly good catalytic behavior for methanol synthesis (See Figure 1.) and, thus, it was chosen to be used as the methanol synthesis catalyst for the preparation of bifunctional catalytic beds. The physical mixture of both activated carbons (with ratio=1), ACGCuZn+ACPZr, increased the CO conversion and DME selectivity compared to that of ACGCuZn. The bifunctional catalyst, ACPZrCuZn showed less conversion than the physical mixture. This fact is related with the presence of phosphorus

species that avoids the reduction of the metal (copper).

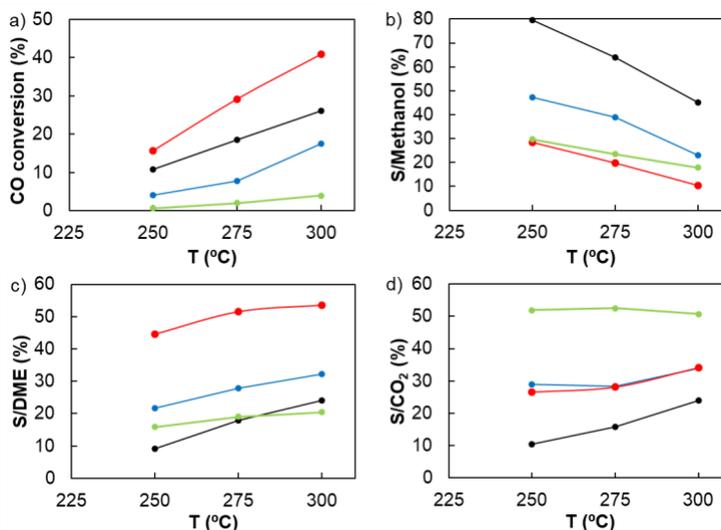


Figure 1. a) CO conversion, and b) methanol, c) DME, and d) CO₂ selectivities for the different prepared catalysts. ● ACGCuZn+ACPZr, ● ACGCuZn ● ACPZrCuZn ● ACPCuZn

The study of the different acid/metal catalyst mass ratios ($W_{ACPZr}/W_{ACGCuZn}$) showed that a value of 2 provided the catalytic bed with enough acid sites to transform all the methanol produced from syngas to DME (Table 1).

Table 1. Conversion (%) and product selectivity (%) for the one-step DME production from syngas with different catalyst mass ratio

T (°C)	Catalyst	CO Conversion	S/DME	S/CO ₂	S/MeOH
250	ACGCuZn + ACPZr	15.7	44.6	26.6	28.4
	ACGCuZn + 2 ACPZr	21.0	56.2	35.1	8.5
275	ACGCuZn + ACPZr	29.2	51.5	28.1	19.7
	ACGCuZn + 2 ACPZr	32.4	58.3	34.5	6.6
300	ACGCuZn + ACPZr	40.8	53.5	34.1	10.3
	ACGCuZn + 2 ACPZr	41.9	56.9	35.8	5.5

Conclusions

The direct DME synthesis from syngas can be efficiently carried out by using carbon-based Cu-Zn and zirconium phosphate catalysts. In this sense, the metallic function showed a good catalytic behavior for CO hydrogenation and, on the other hand, the acid function exhibited suitable catalytic activity for the selective methanol dehydration to DME under the syngas to DME reaction conditions.

Acknowledgment

We gratefully thank MINECO and FEDER (Project CTQ2015-68654-R) for financial support. J.P.J. thanks MECD for a FPU fellowship (FPU13/02413).

References

1. Valero-Romero M.J., García-Mateos F.J., Rodríguez-Mirasol J., Cordero T. (2017). Role of Surface phosphorus complexes on the oxidation of phosphorus carbons. *Fuel Processing Technology* 157, 116-126