

TUNGSTEN CATALYSTS SUPPORTED ON ACTIVATED CARBONS

C. Moreno-Castilla, M.A. Alvarez-Merino and F. Carrasco-Marín
Departamento de Química Inorgánica. Facultad de Ciencias
Universidad de Granada. 18071 Granada. Spain

Introduction

Tungsten catalysts supported on different inorganic solids such as oxides and metal halides have been prepared and used in different reactions such as hydrogenation of carbon monoxide and transformation of alkenes. However, there are no studies of the use of these catalysts supported on carbons, in spite of the great interest to use these materials as supports [1] due to the versatility of their characteristics such as: surface area, porosity and surface chemistry. The aim of this work was to study the behaviour of different W catalysts supported on an activated carbon obtained from almond shells on the hydrogenation reactions of carbon oxides and ethylene.

Experimental

The activated carbon used in this work as support was obtained from almond shells. The raw material was carbonized at 1123 K in N₂ flow and steam activated at 1023 K for 13 h to obtain an activation degree of 40 %BO. The activated carbon so obtained will be referred to in the text as S.

Tungsten catalysts were prepared by impregnation of carbon S with an aqueous solution of (NH₄)₂WO₄ with pH=6.3. Four catalysts were obtained with a metal loading of 4.8; 9.1; 14.9 and 23.1 %W. All samples so prepared were dried overnight at 383 K. Prior to the characterization of the supported catalysts or the study of their catalytic activity, they were heat treated either in He or H₂ at different temperatures between 748 and 1223 K for four hours.

The support and supported catalysts were characterized by physical adsorption of N₂ at 77 K and CO₂ at 273 K by applying the BET equation and the Dubinin-Astakhov equation, respectively. The supported catalysts were further characterized by X-ray diffraction (XRD) and temperature-programmed desorption (TPD).

The hydrogenation reactions of carbon oxides and ethylene were studied with a plug-flow microreactor. About 0.3 g of catalyst was introduced into the reactor and the reactant gases flowed upwards through it. In all cases the conversions were kept low in order to work under differential conditions. Gases were analyzed by gas chromatography following the method described elsewhere. [2].

Results and Discussion

Table 1 shows the values of nitrogen surface area, SN₂, micropore volume, W₀ and pore volume, V_p, with a width greater than 3.7 nm for the support and the supported catalysts after heating them in H₂ flow at 748 K for 4 h. It is seen that the surface area and porosity of the support decreases with the increase in metal loading.

Table 1. Surface characteristics of the support and supported catalysts treated in H₂ at 748 K for 4 h.

Sample	SN ₂ m ² .g ⁻¹	W ₀ cm ³ .g ⁻¹	V _p
S	929	0.424	0.535
S-4.8%W	853	0.416	0.540
S-9.1%W	821	0.397	0.468
S-14.9%W	760	0.383	0.438
S-23.1%W	671	0.353	0.336

The treatment of the supported catalysts in H₂ flow either at 748 or 973 K for 4 h yielded metallic W as detected by XRD. By contrary, the treatment in He flow at the same temperatures and time yielded WO₃. However, when the He treatment is carried out at 1223 K for 4 h, W, WC and W₆C_{2.54} were detected by XRD. This means that at 1223 K in He the tungsten oxide is reduced to metallic tungsten by the support and once in that state is able to react with it partially yielding different carbides. This reduction was also detected by TPD experiments. Thus, the amount of CO evolved from the supported catalysts when they were heated in He flow up to 1273 K (corrected with the CO evolved from the support S) increases linearly with the amount of W as shown in Figure 1.

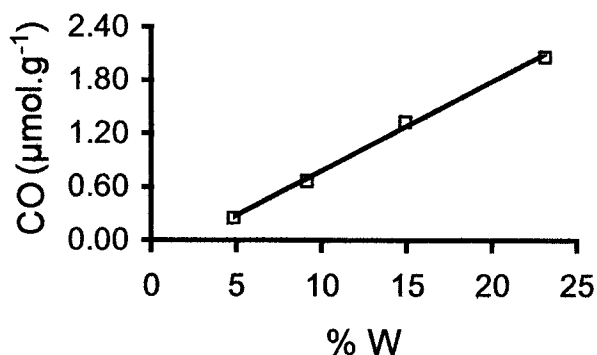


Figure 1. Relationship between CO evolved from the supported catalysts when heated up to 1273 K in He and the amount of W of the supported catalysts.

Table 2 shows the data obtained with some of the catalysts in the H₂/CO₂ reaction. The only products detected were CO and CH₄. The activity for the CO₂

Table 2. Activity and selectivity of some catalysts in the H₂/CO₂ reaction. Reaction temperature 624 K.

Catalyst	Reduction treatment	C	SCH ₄ * (%)	rCO ₂ μmol.gcat ⁻¹ .s ⁻¹	ECO kJ.mol ⁻¹ 574-624 K
S-4.8%W	748K-H ₂	1.57	2.89	0.19	67.2±2.2
S-14.9%W	748K-H ₂	2.95	2.99	0.44	63.2±1.5
S-4.8%W	1223K-He	13.25	0.17	1.11	70.6±1.6
S-14.9%W	1223K-He	10.44	0.53	1.89	70.0±1.9

* Selectivity for CH₄ formation

Table 3. Activity and selectivity of some catalysts in the H₂/CO reaction. Reaction temperature 624 K.

Catalyst	Reduction treatment	C (%)	S*	rCO μmol.gcat ⁻¹ .s ⁻¹	ECO kJ.mol ⁻¹ 574-624 K	Hydrocarbons distribution (%)		
						CH ₄	C ₂ H ₆	C ₂ H ₄
S-4.8%W	748K-H ₂	0.99	44	0.15	64.1±1.6	82.0	14.9	3.1
S-14.9%W	748K-H ₂	3.32	49	0.59	53.8±2.0	80.9	18.5	0.6
S-4.8%W	1223K-He	1.30	41	0.19	70.0±1.9	87.0	11.0	2.0
S-14.9%W	1223K-He	1.50	46	0.33	63.1±2.2	83.6	15.0	1.4

* Selectivity for hydrocarbon formation

conversion, rCO₂, is greater for samples heat-treated in He at 1223 K than for samples heat-treated in H₂ at 748 K. The selectivity to obtain methane was very low and the apparent activation energies were very similar.

Table 3 shows the behaviour of the above catalysts in the H₂/CO reaction. In this case methane, ethane, ethene and CO₂ were obtained. The activity for CO conversion seems to be greater after the reduction in H₂ at 748 K for the catalysts with higher W content than 4%.

The selectivity to produce hydrocarbons is the same after both treatments and slightly increases with the metal content of the catalyst. The apparent activation energy ECO slightly decreases with the metal content and it is of the same order of magnitude after both reduction treatments.

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