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1 Introduction

Hydrogen is currently regarded in the mid-term as a promising energy vector in both transport and power generation sectors. However, hydrogen is not a primary energy source, since it cannot be found free in our planet and it must be produced from other compounds. Conventional H_2 production is carried out by steam reforming of methane (SMR), which is accompanied by CO_2 generation [1]. Thermocatalytic decomposition of methane has become an attractive alternative for hydrogen production. In this process, methane is transformed into solid carbon and hydrogen, which implies that the latter is free of CO/CO_2 emissions, while moderate energy consumptions are required [2]. Although metal catalysts exhibit high activities, they are rapidly deactivated by carbon depositions [3]. Furthermore, regeneration of metal catalysts by burning those carbon deposits is not a valid option since it would lead to undesirable CO_2 emissions. Alternatively, the use of carbonaceous materials as catalysts for methane decomposition is being extensively explored. The most remarkable advantages of carbon catalysts are: a) high thermal stability; b) regeneration step is not needed; c) the reaction could be catalytically self-provided and d) the carbon produced may have different commercial applications [4]. Numerous types of carbonaceous catalysts have been tested for decomposition of methane [4, 5]. In recent works, we have reported the use of ordered mesoporous carbons (CMK type) in this reaction. The best results were obtained over CMK-5 carbon, characterized by having amorphous pore walls, high surface area and a double mesopore system [6, 7].

In this work, long term catalytic activity and stability of CMK-type carbons, two commercial carbon blacks and one activated carbon were compared when they were used as catalysts under different isothermal conditions in the methane decomposition for hydrogen production.

2 Experimental

2.1 Carbon catalyst preparation

CMK-3 and CMK-5 carbons were synthesized using a nanocasting pathway with pure silica SBA-15 as hard template. The preparation procedure has been earlier reported [7], being based on the method described by Ryoo and col [8].

For the SBA-15 preparation, tetraethylorthosilicate (TEOS, Aldrich) and non-inonic triblock copolymer (Pluronic P-123, Aldrich) were used as silica source and as structure directing agent, respectively.

For the synthesis of CMK carbons, furfuryl alcohol (FA, Acros Organics) was used as carbon precursor, oxalic acid (OA, Acros Organics) as polymerization catalyst and trimethylbenzene (TMB, Aldrich) as solvent. The synthesis steps were as follows: a) infiltration of a solution containing 0.012 g OA / 3 mL FA in TMB into the SBA-15 pores by the wetness impregnation technique; b) polimerization at 90 ºC, and c) calcination under inert atmosphere at 850 ºC; d) silica termplate removal by dissolution with an ethanol-water mixture containing 1M NaOH; e) filtration and washing of the black powders, and f) drying at 90 ºC overnight. Two CMK type samples were so obtained by using volumetric FA/TMB proportions of 100 % (CMK-3) and 60 % (CMK-5), respectively.

For comparison purposes, three commercial carbons were used as reference materials: mesoporous activated carbon (AC-mes, Darko) and two carbon blacks from Cabot Corp (black pearls 2000, CB-bp, and vulcan XC72, CB-v).

2.2 Carbon catalyst characterization

Textural properties of the catalysts were measured by N_2 physisorption analyses (77 K) using a Micrometrics Tristar 3000 instrument. Samples were previously degassed at 200 ºC under nitrogen flow. The surface area was calculated by applying the Brunauer–Emmet–Teller (BET) equation. Pore size distribution of mesoporous carbons was calculated using the Barret–Joyner–Halenda (BJH) model and with the application of the t-plot methods the micro and mesopores contribution in carbon catalysts were determined.

2.3 Methane decomposition reactions

Methane decomposition reactions were performed on a simultaneous DSC-TGA thermobalance (TGA-DCS1, Mettler Toledo). A flow of 200 $ml \cdot min^{-1}$ of 10 % CH_4 in Ar was employed as reactive gas. Reactions were operated under isothermal conditions using different temperatures in the range 890-990 ºC. Previous to the reaction, carbon catalysts were dried at 250 ºC with nitrogen. Hydrogen production was indirectly measured through the weight increase of the catalysts during the reaction due to solid carbon deposition, according to the following reaction scheme:

$$CH_4\,(g) \rightarrow 2\,H_2\,(g) + C\,(s) \qquad (1)$$

3 Results and Discussion

Figure 1.A. shows the N_2 (77 K) adsorption-desorption isotherms of all samples and Figure 1.B the BJH pore size distribution of mesoporous carbons. The samples AC-mes and CB-bp present a type II isotherm, according to IUPAC classification; they show an important adsorption at low values of relative pressures, indicating the presence of micropores together with a significant adsorption at intermediate relative pressures due to the mesoporous feature of the catalyst. On the other hand, CB-v sample exhibits the lowest porosity, which is consistent with being formed mainly by non-porous nanoparticles. In the case of CMK carbons, both samples exhibit type IV isotherms, clearly denoting the presence of mesoporosity. CMK-3 shows a single adsorption step, which indicates that this material is formed by just one type of mesopores (3 nm). In contrast, two steps can be observed for the CMK-5 sample (3 and 5.8 nm). Consequently both CMK samples have in common a pore system of 3 nm diameter size. These mesopores are generated by the removal of the silica walls in SBA-15, while the second type of mesoporosity is due to the partial filling of the SBA-15 pores with the carbon precursor during the CMK-5 preparation.

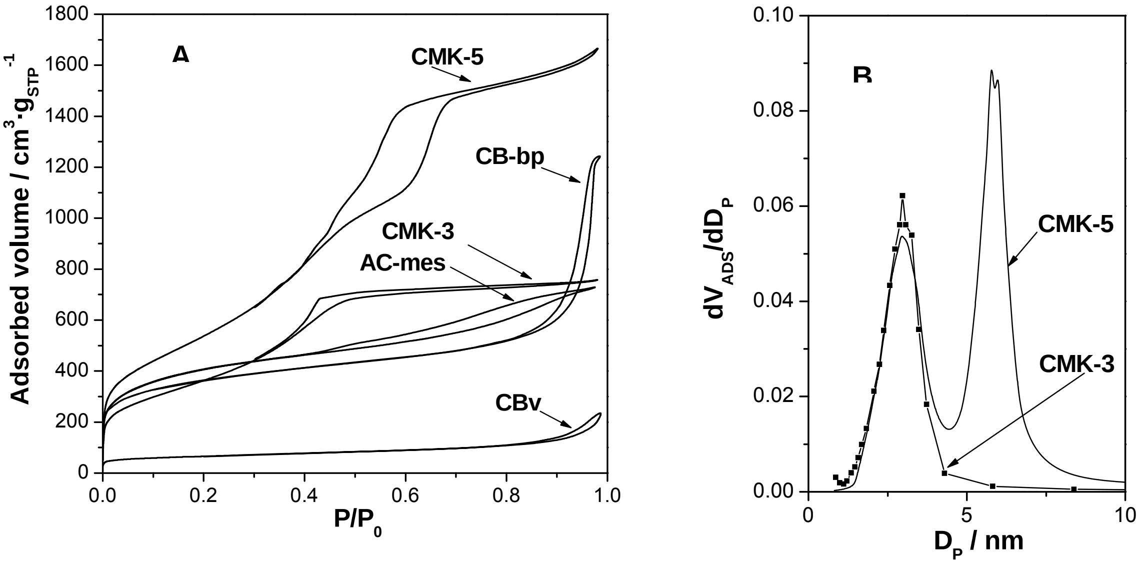

Figure 1: **A. N_2 adsorption-desorption isotherms (77 K) of the catalysts, and B. BJH pore size distributions of mesostructured CMK-3 and CMK-5 carbons.**

Table 1 summarizes the textural properties of the different carbons determined from the nitrogen adsorption isotherms. Except for CB-v carbon, all the samples exhibit large BET surfaces with values higher than 1000 $m^2 \cdot g^{-1}$. In the case of commercial carbons the largest contribution of micropores to the overall surface is observed. In contrast, no microporosity is observed in the case of CMK carbons in agreement with their purely mesoporous nature.

Table 1: Textural properties of carbon catalysts.

	S_{BET} / $m^2\ g^{-1}$	S_{MICRO} / $m^2\ g^{-1}$	V_{PORE} / $cm^3\ g^{-1}$
CMK-5	1940	0	2.37
CMK-3	1323	0	1.08
CB-bp	1285	988	1.93
CB-v	231	134	0.31
AC-mes	1465	542	1.13

The catalytic activity of CMK-5, CMK-3 and commercial carbons towards hydrogen production via methane decomposition was evaluated through thermogravimetric measurements using the installation and conditions described in the experimental section. Figure 2 compares the activity evolution of these carbon catalysts along the reaction time under different isothermal conditions, expressed as catalyst weight increase caused by deposition of the carbonaceous co-products. It can be observed that the AC-mes sample presents the lowest catalytic activity of all samples. In the case of CB-bp carbon, except for 890 ºC, short reaction times are enough to achieve high values of activity, however, the deactivation is faster with increasing temperature at higher reaction times. CB-v carbon presents the highest initial catalytic activity at all temperatures studied, but as reaction times increases hydrogen production rate begins to decrease (acquiring the typical form of a deactivation process). This effect is more pronounced with increasing temperature. For the CMK samples, after a sharp initial change in the slope that takes place at short reaction times, the carbon deposition rate remains almost constant, indicating that these materials exhibit a high resistance to deactivation, being more relevant in the case of CMK-5. This better behaviour of CMK-5 is attributed to their textural properties consisting in a BET surface area close to 2000 m2·g-1 together with a double system of mesopores, which favours a rapid access of the methane molecules to the active sites and prevents the catalyst deactivation by the carbon formed from methane. In these tests, the amount of carbon deposited per gram of catalyst is quite superior to that corresponding to the complete filling of the CMK-5 and CMK-3 pores. Consequently, it must be concluded that the carbon produced from methane decomposition may leave the CMK pores, growing towards the outside part of the catalyst particles.

Furthermore, when the reaction at 990 ºC was extended up to 48 hours CMK-5 is the sample with the greater activity and stability, confirming its potential use as catalyst for hydrogen production by methane decomposition. After 72 hours of reaction time at 990 ºC about 15 and 31 grams of carbon deposits per gram of raw catalysts were formed using CMK-3 and CMK-5 catalysts, respectively.

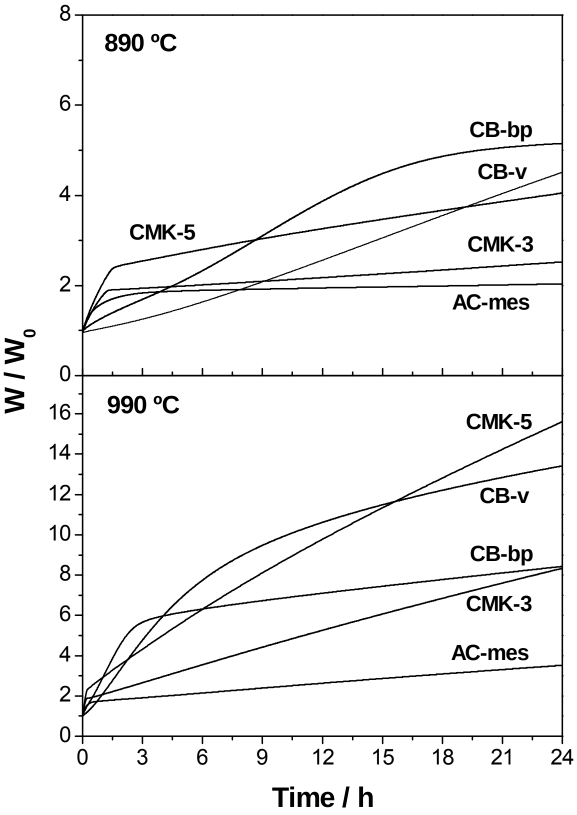

Figure 2: **Catalytic methane decomposition tests. Evolution of weight for different carbon catalysts at different isothermal conditions.**

4 Conclusions

Ordered mesoporous carbons, designated as CMK-3 and CMK-5, have shown to be excellent catalysts for the hydrogen production by methane decomposition. The combination of high textural properties, arising from the structure replication of SBA-15, and the essentially amorphous nature of the pore walls, accounts for their exceptional catalytic activity. Moreover, the presence of uniform mesopores and high surface area in these materials explain their strong resistance to deactivation by the formation of carbon deposits.

Acknowledgements

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References

[1] W.H. Scholz. Processes for industrial production of hydrogen and associated environmental effects. Gas. Sep. Purif. 7 (1993) 131-139.

[2] M. Steinberg. The Hy-C process (thermal decomposition of natural gas) potentially the lowest cost source of hydrogen with least CO2 emissions. Energy Convers. Mgmt. 36 (1995) 791-796.

[3] N.Z. Muradov, T.N. Veziroglu. From hydrocarbon to hydrogen-carbon to hydrogen economy. Int. J. Hydrogen Energy 30 (2005) 225-237.

[4] N. Muradov, F. Smith, A.T. Raissi. Catalytic activity of carbons for methane decomposition reaction. Catal. Today 102-103 (2005) 225-233.

[5] I. Suelves, M.J. Lázaro, R. Moliner, J.L. Pinilla, H. Cubero. Hydrogen production by methane decarbonization: carbonaceous catalysts. Int. J. Hydrogen Energy 32 (2007) 3320-3326.

[6] D.P. Serrano, J.A. Botas, P. Pizarro, R. Guil-López, G. Gómez. Ordered mesoporous carbons as highly active catalysts for hydrogen production by CH4 decomposition. Chem. Commun. (2008) 6585-6587.

[7] J.A. Botas, D.P. Serrano, P. Pizarro, R. Guil-López, G. Gómez. Methane catalytic decomposition over ordered mesoporous carbons: a promising route for hydrogen production. Int. J. Hydrogen Energy (2009), doi: 10.1016/ijhyener.2009.10.031.

[8] R. Ryoo, S.H. Joo, S. Jun, T. Tsubakiyama, O. Terasaki. Ordered mesoporous carbon molecular, sieves by templated synthesis: the structural varieties. Stud. Surf. Sci. Catal. 135 (2001) 150.