GRAPHITISED CARBON AS SUPPORT FOR Ru/C AMMONIA SYNTHESIS CATALYST

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ABSTRACT

In the present work we compared the catalytic activity and mainly the stability under the usual ammonia synthesis conditions, of some carbon supports, differing as for their nature, purity and temperature of pre-treatment. The effect of catalyst composition (metal and promoters loading) on stability was also investigated. XRD and N_2 adsorption/desorption analysis helped in elucidating the effect of carbon treatment. It was found that only after the support has been heated at least at 1900°C the stability of the tri-promoted catalyst becomes fully satisfactory and virtually independent of Ru loading. For practical purposes such high-temperature treatment must be compatible with the preservation of a sufficiently high surface area.

Keywords: Carbon supported Ru catalyst; Graphitisation; Ammonia synthesis.

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INTRODUCTION

Since the beginning of the 20th century, ammonia is being produced by catalytic reduction of N_2 with H_2, known as the Haber–Bosch process. The catalyst most widely used is Fe, promoted with K_2O, Al_2O_3 and other unreducible oxides and the best compromise between thermodynamic and kinetic effects is presently achieved by carrying out the reaction at 380–520°C and 120–220 bar [1,2]. In order to reduce the synthesis pressure, several alternative catalytic materials were investigated and Ru was recognised to be more active than Fe since a long time [3]. However, its high price requires the development of a supported catalyst. Hence, various supports were tested such as SiO_2 [4], Al_2O_3 [5,6], zeolites [7,8], MgO [9], carbon-covered alumina (CCA) [10,11], more or less graphitised carbon [12,13], graphitic nanofilaments [14] or carbon nanotubes [15], $MgAlO_4$ spinel [16] and lanthanide oxides [17]. It appeared very soon that the usual oxidic carriers do not give good results and recently it was found that some active carbons, when subjected to special thermal treatments, can give active and stable Ru catalysts [3,18,19]. Such supports, together with proper Ru promotion, allowed to develop the first commercial non-Fe ammonia process [20,21]. However, the stability of the catalyst under high pressure hydrogen remains a key point. Indeed, Ru itself can catalyse the methanation of carbon in the reaction environment. So, in order to improve support resistance, some pretreatments at high temperature were studied. The higher the temperature of heat treatment, the higher is the stability of the support, but surface area strongly decreases [19]. A further treatment in air at 425°C has been proposed, aiming at recovering the original surface area and porosity at least in part [19,20]. An additional heating at 900°C in flowing H_2 was also reported, to eliminate the impurities contained in the carbon or added during the preparation of the catalyst [22].

Due to the electron withdrawing effect of active carbon, unpromoted Ru/C shows poorly active for ammonia synthesis [23,24]. The most widely used promoters belong to groups 1A and 2A of the periodic table or to lanthanides. These elements show a promoting activity which is inversely proportional to the electronegativity of the metal, so that the best results were obtained with Cs > K > Na [25] and this hypothesis found evidence through XPS analysis [24]. The same correlation between promoting effect and electronegativity was found also with alkali-earth elements, with activity scale Ba > Sr > Ca [26]. The effectiveness as promoter seems then to arise from the electron-donor effect, which has been explained by the formation of a complex with Ru [3]. This seems to be essential in order to increase the rate of the slowest step of the reaction, i.e. the dissociative adsorption of nitrogen. Moreover, alkali promoters seem to interact with the support. Indeed, there are XPS and UPS evidences that Cs and K form intercalation compounds with graphite when heated in H_2 [27], so that carbon can stabilise high alkali loading. Furthermore, these promoters showed a positive effect also on thermal stability of the support [24,28].

The aim of the present work was then to compare the activity and mainly the stability under the usual ammonia synthesis conditions, of some catalysts prepared from carbon supports, differing for their nature, purity and temperature of thermal pre-treatment. The effect of metal and promoters loading on support stability was also investigated. XRD and N_2 adsorption/desorption analysis helped in elucidating the effect of carbon thermal treatment.

EXPERIMENTAL

Support

Two commercial carbons were employed as support: a granular (1–4 mm) charcoal (G) and an extruded (4mm in diameter) active carbon (E). G was a very pure coconut carbon, prepared by directly grinding and sieving the carbonised and activated raw material, while E was an extruded material, produced from pine wood sawdust. Ash content was determined by heating in air at 950°C till constant weight of the residuum.

The carbons were heated (from 1500°C to 2700°C for 2 h) under inert atmosphere and then ground and sieved to 0.15–0.25 mm particles. An alternative thermal treatment was carried out by heating *in vacuo* at 1800, 1900 and 2000°C on both the original carbons.

The latter were cleaned from dusty fines and some portions were subjected to an additional treatment in flowing air, by heating up to 425°C (symbol O, Table 1)) or 525°C (symbol OO, Table 1), maintained for 12 h, and then cooling down to room temperature (r.t.) The weight loss during oxidation was *ca.* 20% for oxidation at 425°C and *ca.* 35% when the treatment temperature was 525°C. A final reductive treatment followed, in flowing H_2, by heating up to 900°C, maintained for 3 h, and then cooling down to r.t. in flowing N_2. Specific surface area (BET_{SSA}) and pore volume of as supplied and of variously treated carbon samples are given in Table 1. All the N_2 adsorption isotherms of these supports were of type I, except for the E2700 sample, which possessed an elevated macroporosity, preventing the determination of the specific pore volume by N_2 capillary condensation.

Catalyst preparation

An aqueous solution of potassium ruthenate was employed as Ru precursor, deposed on the support through wet impregnation. Reduction of the precursor to metallic Ru was made in flowing H_2 at 320°C for 5 h. The sample was then carefully washed till pH = 7 of the

washing solution, to eliminate any residual potassium. The addition of promoters was carried out by impregnation from a solution of the hydroxides (K, Cs) or of the nitrate (Ba).

Catalyst characterisation

BET surface area and porosity has been measured by N_2 adsorption-desorption at liquid N_2 temperature, by means of a Micromeritics ASAP 2010 apparatus. The effect of high temperature treatment (graphitisation) of the support has been qualitatively analysed by XRD, on a Philips PW 1820 powder diffractometer, by comparing the collected patterns with literature data files [29].

Catalytic activity and deactivation tests

Testing of catalytic activity has been carried out by means of a bench-scale apparatus, centred on a vertical, downflow, Incoloy 800 tubular reactor, 9 mm ID, fitted with an axial thermowell of 1.6 mm external diameter. Reactor temperature was controlled by an Eurotherm 904 TRC and reactant gases flow rate was regulated by means of MKS 1261C mass flow meters. All the catalysts have been tested under standard reaction conditions at 430°C and 100 bar (1 bar=10^5 Pa) total pressure, by loading 0.17 cm^3 of fresh catalyst, uniformly diluted with quartz powder of the same particle size (0.15–0.25 mm), so to have a quartz/catalyst volume ratio of 22/1 and a bed height of 6 cm. The void space over and below the catalyst bed was filled with quartz beads, 0.25–0.85 mm in size. Catalyst activation was achieved by flowing a H_2/N_2 = 1.5/1 (vol/vol) gas mixture (very carefully purified by passing through a trap filled with a frequently regenerated large mass of Fe-based commercial catalyst) at GHSV= 20,000 h^{-1} and 30 bar total pressure, while increasing catalyst bed temperature (5°C/min) from r.t. up to 450°C, kept for 5 h and then cooling down to the reaction temperature. After leading total pressure to 100 bar, the

activity tests were carried out by feeding the same $H_2/N_2=1.5/1$ purified gas mixture at various GHSV values ranging between 30,000 and 200,000 h^{-1}.

Testing of the support resistance towards methanation was done by monitoring by gas chromatography the formation of methane while progressively increasing the reaction temperature up to 700°C.

RESULTS AND DISCUSSION

1 – Characterisation of the support

Both the as supplied active carbons (G and E) possessed a very high BET_{SSA} (higher than 1100 m^2/g) and porosity. Sample G was completely amorphous, while sample E revealed very small peaks corresponding to a negligible amount of graphite (Fig.1). The as supplied extruded carbon E contained up to 14 wt% ashes, while the granular coconut carbon G was much purer (2.7 wt%), the ash from the latter showing a light blue colour.

The high temperature treatment in inert gas brought about a progressive graphitisation of the support (Fig.1), the graphitisation degree being higher, the higher the temperature. Indeed, the typical reflections of graphite became visible with sample G1900 and E2000 (Table 1), growing in intensity with sample E2700, which was a completely graphitised material. The additional oxidation and/or reduction treatments of these samples did not infer any further structural modification, the XRD pattern remaining practically unchanged (Fig.1).

Together with the progressively deeper graphitisation, the treatment brought about a significant change of BET_{SSA} and porosity (Table 1). Indeed, by treating sample G at 1900°C, a decrease of surface area by *ca.* one order of magnitude was observed. Sample E revealed a bit more resistant from this point of view, maintaining rather high value of

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BET$_{SSA}$ even after heating up to 2000°C (Table 1). However, after heating at 2700°C the completely graphitised material was characterised by a very low BET$_{SSA}$ and by an almost negligible porosity (sample E2700, Table 1). However, in spite of the ineffectiveness of the oxidation-reduction treatment on support structure, its effect on surface area was beneficial, allowing to recover almost completely the porosity lost during the high temperature heating (sample G1900OR, Table 1), or even to overcome the BET$_{SSA}$ of the raw material (sample E1500OR). However, pore size distribution of the oxidised samples changed significantly with respect to the raw materials, due to the collapse of most micropores, which could not be recovered by further treatment.

A different procedure was also tested in order to attain the desired graphitisation, consisting of heating *in vacuo* at temperature ranging from 1800°C to 2000°C (symbol V in Table 1). Unfortunately, this method revealed inefficient to obtain a deep carbon graphitisation, the XRD pattern of every *in vacuo*-treated sample remaining practically unchanged with respect to the raw material. Moreover, this treatment brought about a decrease of BET$_{SSA}$ comparable (samples G1800V) or even higher (samples E1800V and E1900V) than that obtained by the treatment in inert atmosphere. Hence, the treatment *in vacuo* showed to lead only to pore collapse without structural reorganisation of the material.

Progressively deeper graphitisation showed also to affect support wettability. Indeed, active phase deposition by impregnation was more difficult for graphitised carbons than for the raw materials. Caution had to be taken in order to obtain the desired metal loading homogeneously dispersed on the support. The oxidation treatment showed beneficial to some extent from this point of view.

Finally, the change of support surface area showed to affect metal dispersion. Indeed, in a previous investigation [30] we have found that Ru dispersion halved when passing from a sample prepared on as supplied active carbon (BET surface area 1400

m^2/g) to a graphitised support (BET surface area *ca*. 170 m^2/g). On the other hand, Ru loading seems to have much higher influence on metal dispersion than the surface area of the support, as evidenced also on other materials [31]. Hence, for Ru loading of industrial relevance (around 5 wt.%) the effect of carbon surface area on Ru dispersion showed of relatively low importance. In fact, when carbon surface area decreased by a factor 8, Ru dispersion decreased by a factor 2 only. This could be due to the inaccessibility of the micropores of the support for the Ru precursor under the present preparation conditions [30,32]. Such micropores have been found on active carbon only. This explains why carbon graphitisation, which makes the micropores almost disappear and is of utmost importance in order to achieve a good resistance to methanation (*vide infra*), can be adopted in the manufacture of the catalyst without depressing excessively catalytic activity [19,30].

2 – Effect of support on catalytic activity

Catalytic activity seems to be affected by carbon purity. Indeed, the sample supported on the purer support G performed much better than the sample supported on carbon E, which contained more than 10 wt% ashes (samples 1 and 9, Table 2, respectively).

The effect of heat treatment of the carbon in inert gas on the activity of the final catalyst can be seen by comparing the data (Table 2) of samples 1, 2, 4, prepared on carbon G, with those of samples 9, 10, 12, 13, prepared on carbon E. All these samples have a similar composition, differing only for the support nature and pretreatment. An increase of activity was observed on passing from catalyst 1 (untreated support) to catalyst 2 (support treated at 1900°C in flowing Ar). However, the treatment at 2000°C (catalyst 4) led to a dramatic decrease of activity. A similar, but higher increase of activity may be

noticed for catalysts prepared on carbon E, on passing from catalyst 9 (untreated support) to catalyst 10 (support treated at 1500°C), while carbon treated at 2000°C and 2700°C (samples 12 and 13) again led to very low activity. Very likely the significant activity increase observed by treating carbon E at 1500°C can be connected with removal of impurities, as a drastic change in the porous texture, observed by passing from carbon G to G1900, gives a much lower activity increase (Tables 1 and 2). Indeed, thermal treatment at high temperature can remove impurities such as H, N, O and S and acidic functional groups, which can negatively affect the electron donating ability from Ru to N_2 [19,33]. The increase of catalytic activity when increasing the graphitisation degree can then be connected at least in part also with an increased support conductivity, favouring the electron transfer between promoters and Ru [13].

The oxidation–reduction treatment, following heating at high temperature, did not prove to be particularly useful when the pretreatment temperature was sufficiently low to ensure satisfactory activity. Indeed, on going from catalysts 10 to 11 (Table 2) the activity did not change substantially, while on going from catalysts 2 to 3 an appreciable decrease was observed. A post-treatment oxidation revealed crucial to gain sufficient activity for highly graphitised samples. Firstly, the recovery of sufficient porosity allowed to obtain a more wettable support, making easier the preparation of an uniformly dispersed catalyst. Furthermore, an activity increase was evident when passing from sample 4 to sample 5, even though the activity of the last sample was not optimal. Similar conclusions can be drawn for support E. From the present data it can then be concluded that 1900°C is the maximum temperature for support pretreatment, ensuring satisfactory activity without any further oxidation.

Support pretreatment *in vacuo* proved not beneficial to catalytic activity. Indeed, the activity of sample 6 prepared on carbon G pretreated at 1900°C *in vacuo* was almost half the value obtained with catalyst 2, prepared on the same carbon pretreated in inert gas at

the same temperature. An attempt to increase catalytic activity was done by oxidising that support at 425°C in air, the standard oxidation treatment used for supports treated in inert gas. However, we noticed a higher inertness of the supports treated *in vacuo*, which showed ca. 7% weight loss. A 20% weight loss was obtained only after prolonged oxidising treatment (*ca.* 8-10h) and the effect of this treatment on catalytic activity was negligible. A further attempt was done by increasing the oxidation temperature to 525°C (symbol OO in Table 2), obtaining *ca.* 35% weight loss. A slight increase of catalytic activity was noticed from sample 6 to sample 7 (Table 2). However, no appreciable convenience of treating supports *in vacuo* can be drawn from the present data.

Finally, the reduction treatment at 900°C was reported by Aika and coworkers in order to eliminate electron attractive impurities present on the support [21]. However, we did not notice any significant influence of this treatment on catalytic activity (samples 7 and 8, Table 2).

3 – Support stability under the reaction conditions

The risk of support degradation by Ru-catalysed methanation under ammonia synthesis conditions has been recently recalled [28]. This phenomenon could have dramatic consequences in industrial reactors, should the catalyst not be sufficiently resistant to methanation. Therefore, it is of utmost importance to evaluate this property on a quantitative basis through a specially designed standard test. For this purpose we have developed a methanation test, which consists in monitoring the methane formation during ammonia synthesis at 100 bar upon heating up to 700°C. In our opinion this test seems more exhaustive than that developed by others [28], carried out under atmospheric pressure in hydrogen at 520°C.

Our data of methane formation as a function of temperature are shown in Fig. 2. Sample codes refer to the catalysts listed in Table 2. Both the as supplied supports showed poorly stable under ammonia synthesis conditions, starting to form methane at very low temperature, *i.e.* below (sample 9) or slightly over 500°C (sample1). Carbon G revealed a bit more stable than E, although yet unsuitable for practical application (samples 1 and 9, Fig.2). Hence, graphitisation seems unavoidable in order to obtain stable catalysts. However, heat treatment at too low temperature, *e.g.* 1500°C does not allow sufficient inertness of the support in reducing atmosphere, sample 10 performing similarly to catalyst 9 from this point of view. By treating at least at 1900-2000°C a better resistance towards methanation can be achieved (Fig.2). Indeed, samples 2, 4 and 12 started to form methane at higher temperature (*ca.* 600°C) and methane formation was slow even at the highest temperature attained in this test. Further oxidation or oxidation-reduction did not affect catalyst stability. Moreover, no significant difference of this parameter was observed when treating the support in inert gas or *in vacuo* (samples 2,3 and 8, Fig.2b). Hence, the heat treatment *in vacuo* very likely did not bring to long range reordering into a graphitic structure, as revealed by the completely amorphous XRD pattern, but increased anyway support resistance to methanation. The latter can likely occur through elimination of reactive surface groups caused by heating at high temperature, no matter if in inert atmosphere or under vacuum.

The highest stability within this set of samples, *i.e.* no methane formation even at the highest temperature, was obtained by treatment at 2700°C (sample 13, Tab.2 and Fig.2a), which brought to a completely graphitised support (Fig.1). On the other hand, these results have to be compared with activity data, which clearly show that a too high pre-treatment temperature depresses activity unacceptably. So it is necessary to find a compromise between activity and stability and it can be concluded that an acceptable balance between activity and stability can be achieved by heating at 1900°C without any

further treatment. However, if higher stability towards methanation is desirable, as for industrial application, it is necessary to pretreat the support at higher temperature, although textural properties have to be recovered through a more or less deep oxidation treatment.

Of course, other variables in catalyst composition and preparation are of fundamental importance as for catalyst stability. For example, we have observed some dependence of resistance towards methanation upon promoters addition [24]. Indeed, by optimising their concentration on the catalyst it was possible to depress the amount of methane formed. However, no shift of the temperature at which methane started forming was observed upon promoters addition. Hence, also from the point of view of support stability, the simultaneous addition of all of the three promoters seems important, although their effect can be beneficial only if the support was correctly pretreated as discussed above [24]. In addition, a deep investigation on catalysts promoted with Ba, Ba+Cs, Ba+K and Ba+Cs+K allowed to draw interesting conclusions on their influence on catalytic activity. Summarising, the unpromoted catalyst confirmed inactive, Ba showed to be very active as promoter for the present reaction, but only when the three promoters were added at once the highest activity was obtained [24].

The last, but not least, parameter influencing support resistance to methanation is Ru loading. Indeed, Ru itself catalyses methane formation. Hence, in principle, its concentration and dispersion could affect this undesired reaction. Study is still in progress on this point in our laboratory. However, from our preliminary data we can observe that Ru loading has only a limited influence on support resistance towards methanation, once proper heat treatment of the raw carbon and promoters deposition in optimal concentration have been done.

CONCLUSIONS

From the present data the following conclusions can be drawn:

i) Ru supporting on carbon can lead to very active and stable catalysts;

ii) Thermal treatments of carbon at high temperature in inert gas bring about a partial graphitisation, together with strong decrease of surface area;

iii) Thermal treatments on carbon at high temperature *in vacuo* lead to the same decrease of surface area, without extensive reorganisation of the solid into a graphitic structure;

iv) Further oxidation or oxidation-reduction treatments do not affect support structure, but allow a considerable recovery of surface area and influence support wettability;

v) Catalytic activity increases after thermal treatment of less pure carbon, while it remains almost unaltered when carbon purity is high. However, when the temperature is too high (>2000°C), a porosity recovery is needed, e.g. through oxidation-reduction of the carbon.

vi) Support stability towards methanation is a fundamental parameter, which can be improved by proper thermal treatment of carbon, by finding a compromise between catalyst resistance and catalytic activity.

vii) Other parameters, such as promoters concentration, could affect support resistance towards methanation, while Ru loading does not seem fundamental from this point of view.

REFERENCES

1 - J.R. Jennings (Ed.), Catalytic Ammonia Synthesis, Fundamentals and Practice, Plenum Press, New York, 1991.

2 - A. Nielsen (Ed.), Ammonia Catalysis and Manufacture, Springer, Heidelberg, 1995.

3 - S.R. Tennison, in: J.R. Jennings (Ed.), Catalytic Ammonia Synthesis, Plenum Press, New York, 1991, p. 303.

4 - T. Lopez, P. Bosch, R. Gomez, React. Kinet. Catal. Lett., 41 (1990) 217.

5 - Y. Kadowaki, K. Aika, J. Catal., 161 (1996) 178.

6 - S. Murata, K. Aika, J. Catal., 136 (1992) 118.

7 - C.T. Fishel, R.J. Davis, J.M. Garces, J. Catal., 163 (1996) 148.

8 - J. Wellenbüscher, F. Rosowski, U. Klengler, M. Muhler, G. Ertl, U. Guntow, R. Schlögl, Stud. Surf. Sci. Catal., Vol. 84, part B, Elsevier, Amsterdam, 1994, p. 941.

9 - O. Hinrichsen, F. Rosowski, M. Muhler, G. Ertl, Chem. Eng. Sci., 51 (1996) 1683.

10 - K.S. Rama Rao, P. Kanta Rao, S.K. Masthan, Appl. Catal., 62 (1990) L19.

11 - S.K. Masthan, P.S. Sai Prasad, K.S. Rama Rao, P. Kanta Rao, J. Mol. Catal., 67 (1991) L1.

12 - Z. Kowalczyk, S. Jodzis, J. Sentek, Appl. Catal. A: General, 138 (1996) 83.

13 - C.Liang, Z.Wei, Q.Xin, C.Li, Appl. Catal. A: General, 208 (2001) 193.

14 - C. Liang, Z. Li, J. Qiu, C. Li, J. Catal., 211 (2002) 278.

15 - H.B. Chen, J.D. Lin, Y. Cai, X.Y. Wang, J. Yi, J. Wang, G. Wei, Y.Z. Lin, D.W. Liao, Appl. Surf. Sci., 180 (2001) 328.

16 - B. Fastrup, Catal. Lett., 48 (1997) 111.

17 - Y. Niwa, K. Aika, Chem. Lett., 1996, p. 3.

18 – Z. Kowalczyk, J. Sentek, S. Jodzis, E. Mizera, J. Gòralski, T. Paryjczak, R. Diduzko, Catal. Lett., 45 (1997) 65.

19 - L. Forni, D. Molinari, I. Rossetti, N. Pernicone, Appl. Catal. A: General, 185 (1999) 269.

20 - US Patent 4,163,775, 7 August 1979, to BP Co.

21 - US Patent No. 4,568,532, 4 February 1986, to Kellogg, M.W. Co.

22 - Z. Zhong, K. Aika, J. Catal., 173 (1998) 535.

23 - K.S. Rama Rao, S.K. Masthan, P.S. Sai Prasad, P. Kanta Rao, Appl. Catal., 73 (1991) L1.

24 - I. Rossetti, N. Pernicone, L. Forni, Appl. Catal. A: General, 208 (2001) 271.

25 - S. Murata, K. Aika, T. Onishi, Chem. Lett., 1990, p. 1067.

26 - K. Aika, T. Takano, S. Murata, J. Catal., 136 (1992) 126.

27 - T. Hikita, Y. Kadowaki, K. Aika, J. Phys. Chem., 95 (1991) 9396.

28 - Z. Kowalczyk, S. Jodzis, W. Rarog, J. Zielinski, J. Pielaszek, Appl. Catal. A: General, 173 (1998) 153.

29 - Selected Powder Diffraction Data, JCPDS, Swarthmore, PA, 1981, File No. 23–64.

30 - I. Rossetti, N. Pernicone, L. Forni, Appl. Catal. A: General, 248 (2003) 97.

31 – F. Rosowski, A. Hornung, O. Hinrichsen, D. Herein, M. Muhler, G. Ertl, Appl. Catal. A: General, 151 (1997) 443.

32 - Z. Kowalczyk, S. Jodzis, W. Rarog, J. Zielinski, J. Pielaszek, A. Presz, Appl. Catal. A: General, 184 (1999) 95.

33 - X. Zheng, S. Zhang, J. Xu, K. Wei, Carbon, 40 (2002) 2597.

Table 1: Main properties of the carbons employed for catalyst preparation. G or E refer to the granular or extruded active carbon, respectively; the following figures refer to the pretreatment temperature (°C) in inert gas. The symbol "O" indicates oxidation treatment, while "R" indicates reduction in flowing H_2. The symbol "V" indicates heat treatment *in vacuo*.

Carbon	BET_{SSA} (m^2/g)	V_{pore} (cm^3/g)[a]	XRD[b]
G	1188	0.49	A
G1900	187	0.11	PG
G1900OR	870	0.44	PG
G2000	105	0.08	PG
G1800V	213	0.14	A
G1900V	119	0.06	A
G1900VOO[c]	966	0.72	A
G1900VOOR[c]	936	0.62	A
E	1253	0.75	A
E1500	964	0.72	A
E1500OR	1472	0.99	A
E2000	575	0.43	PG
E2700	6	n.d.	CG
E1800V	231	0.37	A
E1900V	179	0.33	A

[a] Pore volume measured at $P/P_0=0.99$
[b] recognised XRD phases: A=amorphous, PG=partially graphitised, CG= completely graphitised.
[c] oxidation treatment carried out at 525°C.

Table 2: Composition (referred to the final catalyst weight) and catalytic activity of differently supported catalysts.

Sample	Support	Ru wt%	Ba wt%	Cs wt%	K wt%	NH$_3$ vol%[a]
1	G	11.9	6.6	7.2	11.9	12.4
2	G1900	11.8	6.6	7.1	6.5	15.0
3	G1900OR	13.0	7.4	7.3	6.1	8.8
4	G2000	12.5	7.2	7.7	6.3	3.8
5	G2000OR	9.8	8.4	10.0	8.2	9.1
6	G1900V	3.5	3.2	5.2	4.9	7.7[c]
7	G1900VOO[b]	3.7	3.1	5.1	5.2	10.0[c]
8	G1900VOOR[b]	4.2	3.5	6.1	5.9	9.5[c]
9	E	13.0	6.7	7.0	6.0	8.9
10	E1500	12.3	6.2	6.9	6.2	14.7
11	E1500OR	13.0	6.5	6.8	5.9	15.2
12	E2000	11.9	11.2	11.5	11.4	1.0
13	E2700	11.0	5.2	6.2	5.6	0.8

[a] measured at P=100 bar, T=430°C, H$_2$/N$_2$=1.5, GHSV=30,000h^{-1}
[b] oxidation treatment of the support was carried out at 525°C, in order to obtain *ca.* 35% weight loss
[c] measured at GHSV=60,000h^{-1}, other conditions remaining unaltered.

FIGURE CAPTIONS

Fig. 1: XRD pattern of some selected carbon supports (Table 1).

Fig. 2: Results of the methanation test of some selected samples: a) support carbon E; b) support carbon G. Figures refer to catalyst code of Table 2.
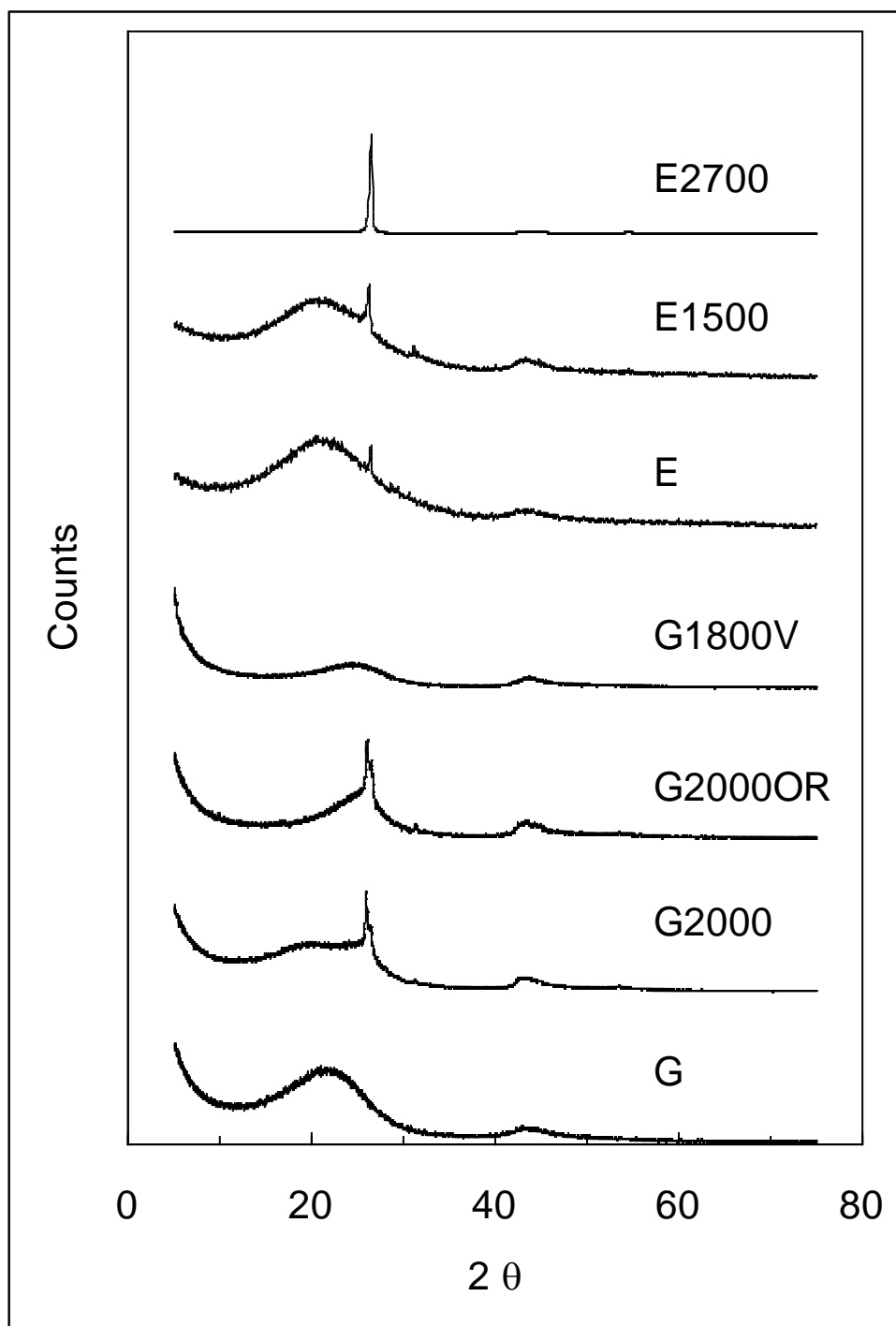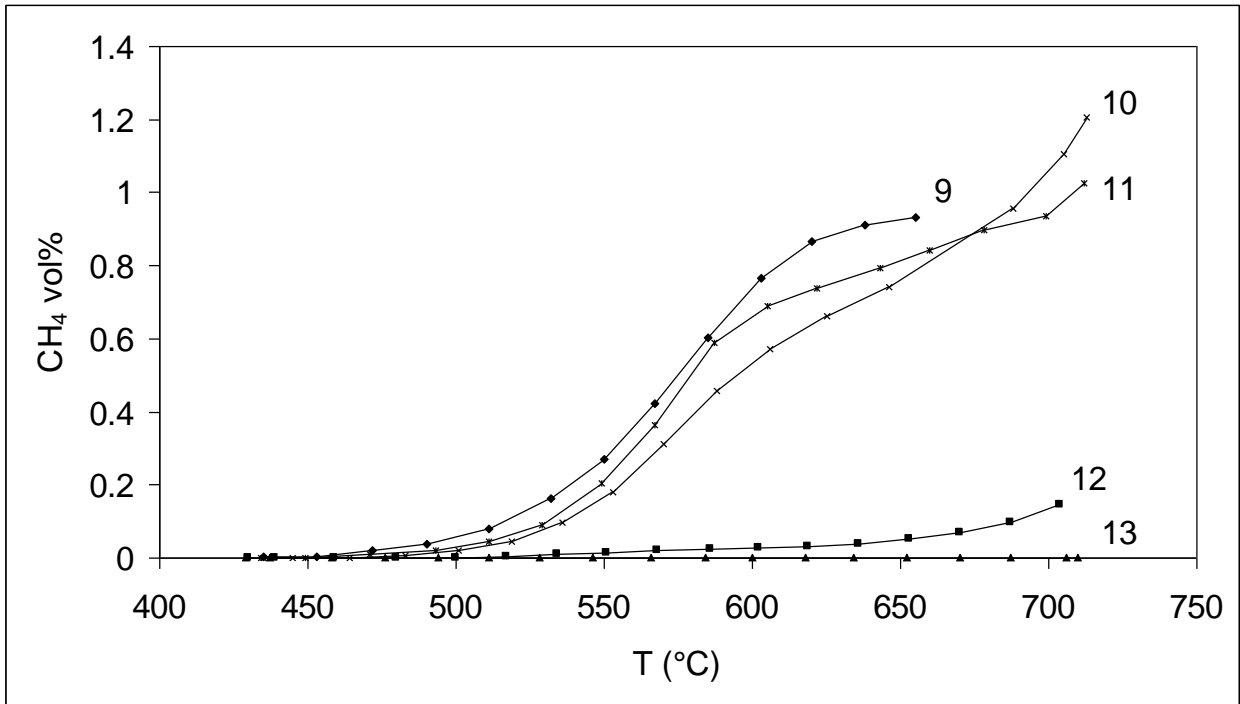
Fig. 1

Fig. 2a

Fig. 2b