

POSTER

STUDY BY THERMAL ANALYSIS (TG-MS, DTA) OF CARBOTHERMAL REDUCTION OF SiC FROM RICE HUSKS CATALYZED BY Fe, Co OR Ni

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1. INTRODUCTION

Silicon carbide, SiC, is considered an excellent structural material because its superior thermal, chemical, and mechanical properties at high temperatures, and excellent thermal and chemical stabilities [1].

The industrial manufacture of SiC is by the Acheson process, carbothermal reduction of silica sand with green petroleum coke; however, this process uses a very high temperature (around 2400°C) and the product has a large grain size (> 1 mm), which requires extensive grinding to reduce the powder to sinterable size.

Since the main problem of the carbothermal reduction process is the particle size of reactants and the need for an intimate contact among them, it is not surprising that much attention has been paid to the use of rice husks as a starting material for the production of SiC [2]. Rice husks consist of a cellulosic component that can be easily converted to carbon upon pyrolysis, and silica (up to 28% in some varieties [3]). With the very high surface area and intimate contact available from carbon and silica in carbonized rice husks, it is possible to form silicon carbide at relatively low temperatures. Although the main industrial aim is the preparation of high quality sinterable SiC powder at a reasonable cost, the last reasonable cost.

The aim of the present work is the study of the influence that the catalysts (Fe, Co, Ni) have in the synthesis of SiC.

2. EXPERIMENTAL

The raw material used for the synthesis of SiC was rice husks from Valencia (Spain), with 11.5% humidity and 14.6% ash content. The ash was mainly constituted by silica (98%), the rest of inorganic components being Ca, K and Mg, with traces of Fe. The catalyst were introduced by incipient wet impregnation (minimum volume of solution) with nitrates of iron, cobalt and nickel dissolved in ethanol. Metal loading was determined by atomic absorption spectroscopy after 24h digestion of the dry sample with a 1:1 HCl:H₂O solution.

The synthesis was carried out in two steps. The first one was the pyrolysis under a nitrogen flow (90 ml/min, minimum purity, 99.999%) of the raw material in an horizontal furnace, and the second one the thermal treatment (1400-1500°C) of the resulting char in a high temperature horizontal furnace under a 90 ml/min flow of argon (purity, 99.999%).

The determination of the SiC formed was carried out as follows: combustion (12h in an air flow at 800°C) of the unreacted carbon and digestion of the residue for 48h in a 1:1 HCl:H₂O solution to eliminate the remaining catalyst; the resulting residue was treated with a HF/HNO₃ solution in a platinum crucible to eliminate the silica and the final product was SiC.

Identification of products was carried out by X-ray diffraction (JSO Debye-Flex 2002 from Seifert) fitted with a Cu cathode and a Ni filter and using a 2°/min scanning rate. The morphology of the product was carried out by Scanning Electron Microscopy (JSM 840, from Jeol) fitted with a Link QK 200 dispersive X-ray analyzer.

The DTA measurements were performed using a Perkin-Elmer DTA 1500 system, and TG-MS were performed using a SETARAM TG 92 coupled with a mass spectrometer, Leybold-Heraeus Q200. Runs were carried out at a heating rate of 20K.min⁻¹ from 320 to 1873 K, in helium atmosphere (60 ml.min⁻¹).

3. RESULTS AND DISCUSSION

Our previous works have shown that the SiC obtained from rice husks by uncatalyzed and by catalyzed (Fe, Co, Ni) reaction are different [4]. The most significant differences may be summarized as follows :

- In both cases (catalyzed and uncatalyzed reaction) a mixture of crystals powders and whiskers is obtained.
- The whiskers obtained in both reactions are different.
- The catalyzed reactions lead to the formation of two new phases: i) silicides of Fe, Co and Ni, and ii) graphite.

3.1 Precursor reactions

Before beginning the reaction of the carbon with the silica, the catalyst that is in the oxide form reacts with the carbon to produce the metal (reduced form). This is not a simple process and the results obtained in this work show that there are several stages. As a typical example, Fig. 1 and 2, corresponding to the thermogravimetric analysis and mass spectrometry of produced gases for the sample with nickel nitrate, show the presence of four processes, three of which occur at temperatures below 1000 K, the fourth taking place at around 1500 K. The first three only occur in samples impregnated with the metal precursor, this

indicating that they are related only with transformation of the metal precursor. According to the experimental results, the reactions taking place are:

- a) The first stage is the decomposition of metal nitrate to form the metal oxide, carbon dioxide and nitrogen monoxide.
- b) the metal oxide is partially reduced by the carbon to produce metal monoxide and carbon dioxide
- c) the metal monoxide reacts with carbon to produce the metal, but in this stage carbon dioxide (low temperature) or carbon monoxide (high temperature) are obtained.

On the other hand, the reaction temperature of stage c increases in the order Ni < Co < Fe. These results are confirmed by XRD.

3.2 Silicon Carbide formation

Table 1 shows the initial and end temperature of the reaction for formation of SiC and the energy of activation for this process. When the reaction is catalyzed by the transition metals the results are very similar, in the three cases the beginning of the reaction being about 100 K below the uncatalyzed reaction. The results are compatible with the obtained in previous work [4]. In respect to activation energy, this is lower for the catalyzed reaction and very similar for the three catalysts, this indicating again that the mechanism reaction is the same for the three

metals. The results are in agreement with have reported by Cryshantou [5]. A point to be noted is the presence of CO₂ at high temperature related to the formation of SiC when the reaction is catalyzed, and this has to be taken into account when the possible mechanism for the reaction is established.

4. CONCLUSIONS

The main conclusions of the present work are as follows:

- a) The catalytic effect of Fe, Co and Ni in the synthesis of SiC is proved.
- b) The reactions between the metal precursor and carbon at T < 1000 K have been elucidated.

5. REFERENCES

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Table 1. Initial and end temperature of the reaction for formation of SiC and activation energy for this process

Sample	T _a (K)	T _f (K)	E _a (kJ.mol ⁻¹)
Non catalyzed	1560	1800	139
Fe	1450	1700	115
Co	1445	1705	118
Ni	1452	1706	116

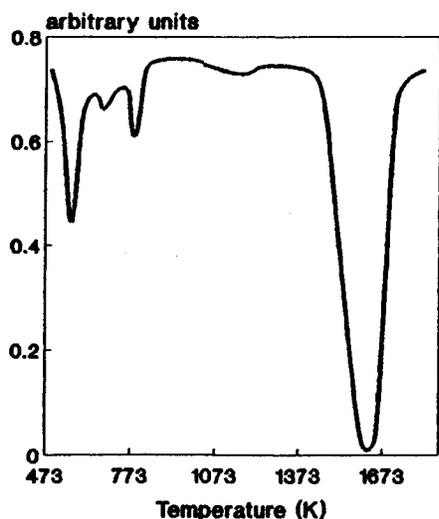


Figure 1. DTG profiles in non isothermal reaction of the sample catalyzed by Ni.

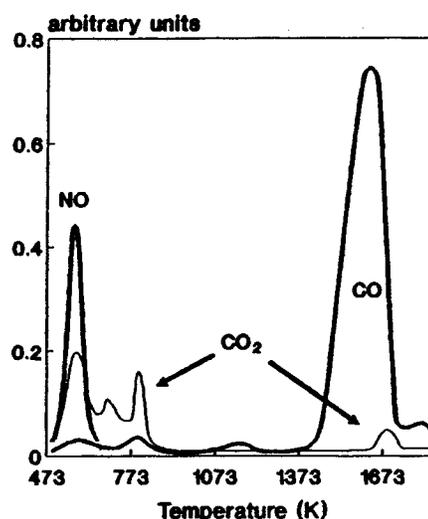


Figure 2. Evolved gases obtained in non isothermal reaction of the sample catalyzed by Ni.