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# New Synthesis and Uses of High-Specific-Surface SiC as a Catalytic Support that Is Chemically Inert and Has High Thermal Resistance

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A new method for preparation of high-specific-surface (60–400 $m^2/g$) SiC is described. This method consists of the attack of high-specific-surface activated carbon by SiO vapor generated by the high-temperature reaction of Si and $SiO_2$. The high specific surface is probably due both to the low temperature of the reaction between SiO and C and to the presence of a stable carbon skeleton. Before reaction, the carbon can be doped with different additives to improve the surface interaction between SiC and the impregnated active phase. The action of uranium doping is also shown. SEM, XRD, thermogravimetry, TPR, XPS, BET, and porosimetry have been used to characterize the supports and the catalysts. Test reactions (hydrodesulfurization by CoMo) are also reported.

## INTRODUCTION

Most of the heterogeneous catalysts, except those of the zeolite family and the molybdates, are composed of a support and an active phase. Although the support is generally considered inert for the chemical reaction itself, its role is considerable: dispersing and stabilizing the active phase, modifying the geometric shape or the electronic properties of the active phase, resisting high temperatures, improving mechanical strength and the shaping of the pellets or extrudates, helping in the recovery and the reprocessing of the components of the active phase, and, finally, acting chemically by its acidic or basic centers in acid–basic reactions or for storing coke. It must be chemically resistant, cheap, abundant, and not strategically limited.

Until now, the industry has focused its attention on two families of supports: (1) amphoteric or acidic oxides, mainly alumina, silica, aluminosilicates, and to a lesser extent titanium oxide; (2) carbon or carbon-like supports. To improve these different supports, attempts have been made to control their solidification, their purity, their crystallinity, their porosity, and their specific surface or to dope or modify them by addition covering most of the other elements of the periodic table. These additives sometimes also modify the active phase itself.

Among all these characteristics and properties, two caught our attention for this study: recovery of the active phase and thermal stability as applied to hydrotreatment, molybdenum-based catalysts. Some preliminary studies on other high-temperature reactions (automotive exhaust gas catalysis and oxidation of the methane in higher hydrocarbons) are in progress. To reach this goal we have developed a new preparation (*1*), the characterization and the use of silicon carbide and uranium-doped silicon carbide. This highly thermal- and chemical-resistant material, a very efficient conductor of heat and electricity (the best among the ceramics used), is also one of the toughest abrasives after diamond. The industrial preparation of SiC (carbo-

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rundum), the Acheson process, involves carbon (generally carbon black, coke, or even coal) and silica (Fontainebleau sand), both very cheap materials, which are heated together to give a very low specific surface (0.1–1 $m^2/g$). To form SiC fibers, new processes start with carbon fibers on which organochloric Si compounds (chlorosilanes) are decomposed in the gas phase at high temperature (1200–1800°C).

By this method one can expect to cover any resistant support with a thin layer and keep the shape memory of a high specific surface. For this reason, in our first attempt we tried to prepare SiC on a high-specific-surface carbon, hoping to obtain the memory of the carbon skeleton. We had no success with this method (maximum 25 $m^2/g$), even after changing the starting carbon, the precursor, and the different reaction conditions. We believe that a thermodynamic barrier is reached because of the high temperature required (1400°C), which leads to the formation of a low-specific-surface SiC. In addition, the reaction is too fast and probably the low-specific-surface SiC plugs the pores of the support.

During this same period, Vannice *et al.* (*2*) published the results obtained by using another method [decomposition of silanes (*3*) in the gas phase] and, as we did, they reached a maximum specific surface of 46 $m^2/g$ with an average value of 35 $m^2/g$ under the best conditions. They probably reached the same thermodynamic barrier that we reached in the decomposition of chlorosilanes. The solution then was to find a new reaction working at lower temperatures (*1*).

## PREPARATION OF THE SiC

### *Chemistry and Thermodynamics*

The Acheson process can be described by the equation

$$3C + SiO_2 \rightleftarrows SiC + 2CO. \qquad (1)$$

This reaction is very endothermic; the variation of free enthalpy is positive until 1600°C. For these reasons, the temperature for industrial preparation is above 1800°C, leading to very low specific surface α-SiC.

The decomposition of silane or chlorosilane probably proceeds through a radical mechanism in which Si radicals react with C radicals formed by the decomposition (with release of hydrogen):

$$(CH_3)_4Si \xrightarrow{\Delta} (Si^{\cdot} + C^{\cdot} + H^{\cdot}) \rightarrow SiC + H_2 + \text{other hydrocarbons and silanes.} \qquad (2)$$

These reactions also require high temperatures (1400°C), although not as high as that used in the Acheson process, which is why β-SiC is formed. Nonetheless, the specific surface is still affected by these high temperatures. The advantage of these radical processes is to supply SiC powder, which is very useful for ceramic sintering processes.

Van Konijnenburg (*4*) has shown that formation of SiC from its elements is thermodynamically possible below the melting point of silicon, 1410°C.

Equation (1) can be broken down into two partial reactions:

$$C + SiO_2 \rightleftarrows SiO + CO \qquad (3)$$

$$2C + SiO \rightleftarrows SiC + CO. \qquad (4)$$

The yield of the reaction depends on the SiO concentration and is strongly diminished by the formation of CO, which has to be actively pumped off.

Considering these equations, (3) and (4), Kennedy and North (*5*) have prepared SiC powder and fibers by mixing $Si/SiO_2$ (equimolar ratio) and carbon under vacuum. These conditions increase the pressure of SiO ($Si + SiO_2 \rightleftarrows 2SiO$). The low pressure favors the formation of SiO at a temperature lower than 1800°C which is the temperature of formation under 1 atm, and diminishes the partial pressure of CO.

### *Conditions of Reaction and Reactor Design*

Our preparation is based on the work of Kennedy and North, but differs on two points: the generation of "SiO," which is separated from its reaction on carbon, and the nature of the carbon used. Reaction (4) is slightly exothermic and its $\Delta G$ is negative and almost independent of the temperature. We thus designed a reactor (Fig. 1) in which the mixture Si–$SiO_2$ is treated just above 1200°C (generally around 1230°C), and the generated SiO vapor is then pumped toward the upper stage of the reactor where the reactant carbon is stored; the reaction between SiO and C occurs at a lower temperature (between 1000 and 1200°C) and gives high-specific-surface $\beta$-SiC. The exact reaction temperature cannot be measured because of the design of our reactor, but can be varied by changing *h*.

Such a design allows both the pumping off of generated CO and the separation of SiO formation from the reactive chamber. It is then easy to act separately on the kinetics of the two equations:

$$\mathrm{Si} + \mathrm{SiO_2} \rightleftarrows 2\mathrm{SiO} \tag{5}$$

$$\mathrm{SiO} + 2\mathrm{C} \rightleftarrows \mathrm{SiC} + \mathrm{CO}. \tag{6}$$

Approximately, for a pressure of 1 Torr of SiO, the inversion temperature of the equilibrium equals 1285°C; for a pressure of 0.1 Torr, 1150°C. The best yield was obtained for an SiO pressure around 0.6 Torr.

It was also important to study the amount

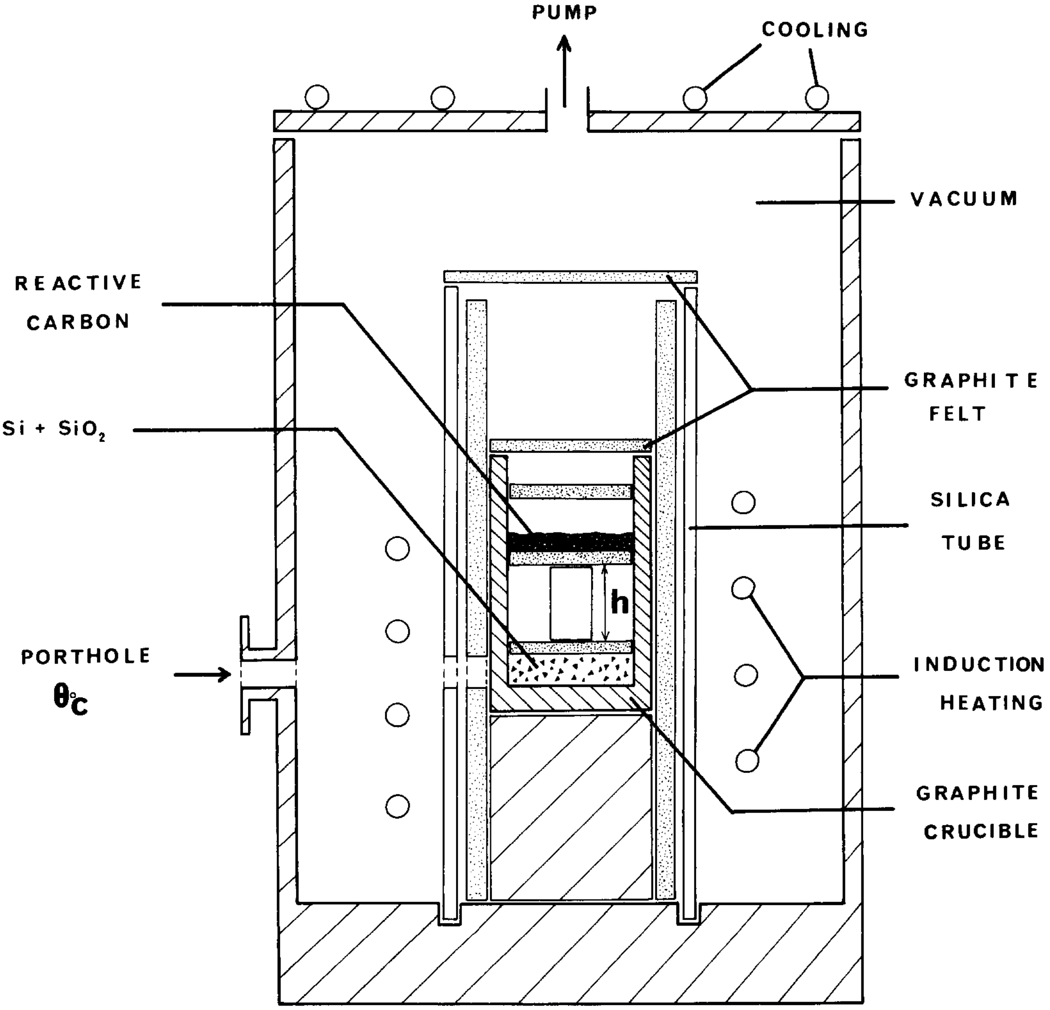

FIG. 1. Reactor design.

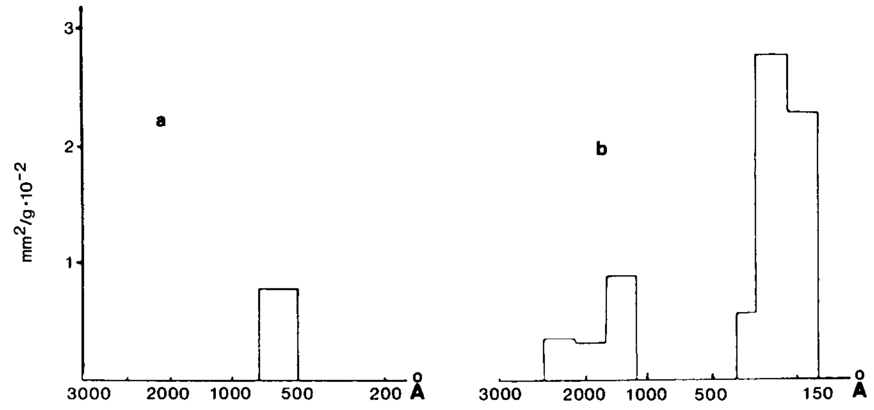

FIG. 2. Porosity distributions of activated carbon (a) and SiC 125 $m^2/g$ (b).

of $Si/SiO_2$ relative to carbon to reach the highest yield; a ratio of 2 to 1 in mass gives an excess of "SiO" with a very high yield.

### *Nature of Carbon*

Different carbons have been used (graphite, black, activated, etc.) but we shall report only the results on activated carbon because at this stage it gave the highest specific surface. One of these carbons was obtained from Fluka, (Puriss) Activated Charcoal; its elemental analysis is C = 89.4%, H = 1.1% and O = 9.5%. Such a high concentration of oxygen, probably as lactone functions on the surface, increases the pressure of CO and is probably at the origin of the formation of whiskers of SiC (see later) through the reaction

$$3CO + SiO \rightleftarrows SiC + 2CO_2 \quad (7)$$

as these whiskers form mainly on the top graphite lid.

The surface area of this activated carbon is between 1150 and 1200 $m^2/g$. The macroporosity above 150 Å is reported in Fig. 2; but it is well known that most of the pores have a diameter well below 30 Å in these activated carbons.

### *Characterization*

Different techniques were used to analyze the SiC formed: SEM to examine the shape of the particles, XRD and XPS to analyze the composition of the surface, thermogravimetry to analyze the amount of unreacted carbon, BET with nitrogen to measure the specific surface, and mercury porosimetry to evaluate the pore volume and pore distribution.

*SEM.* In Figs. 3a–c are shown the main features. The morphology of the carbon (Fig. 3a) is strongly affected by the formation of SiC (Fig. 3b); the pores seem much bigger. SiC is either in microgranule form or whiskers (Fig. 3c).

*XRD.* When the experiment is conducted correctly, the sample contains only β-SiC before and after calcination at 1100°C in air for 2 h (Fig. 4). No diffraction lines corresponding to crystallized $SiO_2$ have ever been observed in these diagrams.

*XPS.* The surface, even before calcination, is covered by a skin of silica (*6*) which, as is shown later, strongly influences the catalytic application of the product. No quantitative analysis has yet been successful in measuring the amount of $SiO_2$, because it is very small (below 1%). This same feature has been observed by Rahaman and De Jonghe (*7*).

*Thermogravimetry, BET, and porosimetry.* SiC loses weight by following two rates, one starting at 650°C and a second between 800 and 900°C (Fig. 5a). Careful

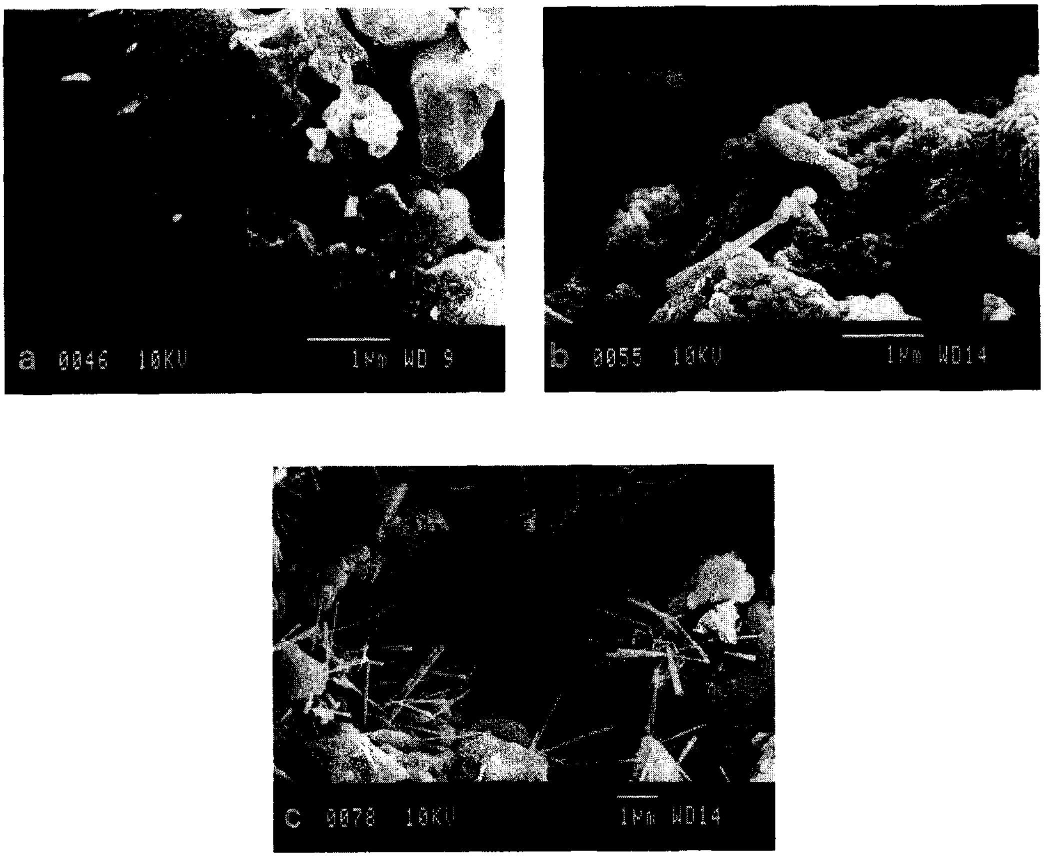

FIG. 3. Scanning electron micrographs of (a) activated carbon, (b) SiC after reaction, and (c) a SiC sample rich in whiskers.

measurement of the mass before reaction and after calcination shows that the loss in mass corresponds exactly to the combustion of unreacted carbon. It is tempting to propose from these thermogravimetric results that two forms of carbon, probably

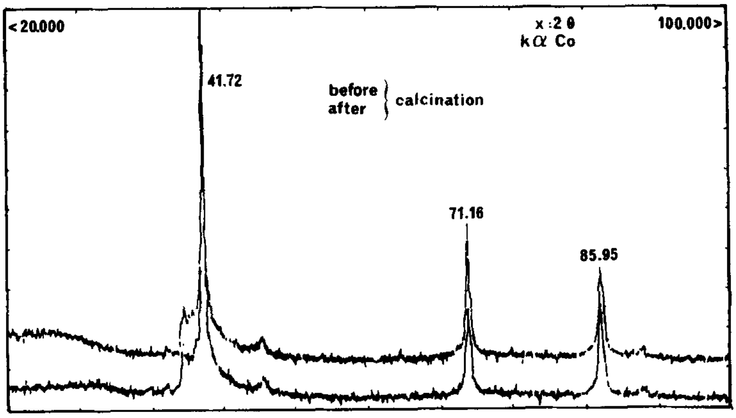

FIG. 4. SiC X-ray patterns before and after treatment in air at 1100°C.

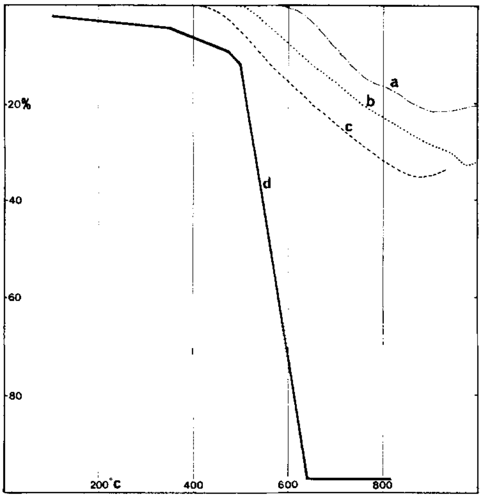

FIG. 5. Thermogravimetry. (a) SiC, 125 $m^2/g$. (b) SiCU, 266 $m^2/g$. (c) SiCCe, 301 $m^2/g$. (d) Activated carbon, 1200 $m^2/g$.

covered by a protective layer of SiC, form a skeleton that confers the high specific surface on the SiC. The starting carbon burns completely in air before reaching 600°C (Fig. 5d). A typical experiment shows a surface of 197 $m^2/g$ before calcination and one of 59 $m^2/g$ after calcination, with the loss in mass amounting to 20% of the initial mass.

It is important to point out that the key to success is not to reach 100% yield even at low temperature. Excessively high reaction temperatures result in low specific surfaces (see above), but too long a reaction time, even at low temperature, also results in low specific surfaces. The best length of reaction and the best partial pressure of "SiO" obviously depend on the geometry of the reactor and on the mass of reactant.

The distribution of porosity between 3000 and 150 Å for a typical SiC sample and for the starting activated carbon is shown in Fig. 2. A measurement below 150 Å will be reported later. However, it is already very interesting to note the presence of a bimodal distribution on the SiC with a large maximum around 200 Å, whereas most of the pores on the activated carbon are too small for catalysis. The pore volume counted from 7.2 μm to 150 Å reaches 0.3 $cm^3/g$. The density, 3.44, is very close to the value for pure α-SiC, 3.23.

## CATALYTIC TESTS AND TEMPERATURE-PROGRAMMED REDUCTION

*Catalysis.* To test the relative activity of sulfided CoMo catalysts for hydrodesulfurization (HDS) of thiophene, a series of catalysts containing the same amounts of cobalt and molybdenum in an atomic ratio of about $\frac{1}{2}$ have been prepared on different supports and compared with an industrial $CoMo/Al_2O_3$ catalyst, HR306, Procatalyse. The tests were performed at 227°C under normal pressure under conditions that have already been described (*8*). Table 1 summarizes all the data concerning these tests.

The most active catalyst is supported on active carbon as already observed by different authors (*9*, *10*), but it is not very useful from an industrial point of view because of the presence of very small micropores, which block the access of heavy molecules to the active sites and are also responsible for diffusion phenomena (the reactions reported here are diffusion free).

The second most active catalyst is the alumina-supported HR306 with a specific rate of 15,000 × $10^{-10}$ for only 220 $m^2/g$, which shows that a strong interaction with the support of the oxidic precursor (see TPR below) is responsible for very high dis-

TABLE 1

HDS Catalytic Activity

| Support | % Mo[a] | % Co[a] | Specific surface | $r \times 10^{-10}$[b] |
|---|---|---|---|---|
| γ-$Al_2O_3$ HR306 | 8.0 | 2.8 | 220 | 15,000 |
| $SiO_2$ | 8.3 | 2.3 | 550 | 2,500 |
| Act. C Fluka | 6.2 | 2.3 | 1200 | 20,900 |
| SiC from silane | 8.0 | 3.0 | 30 | 250 |
| SiC from SiO[c] | 7.0 | 2.5 | 171 | 2,630 |
| SiC from SiO[d] | 7.0 | 2.5 | 37 | 1,080 |
| SiCU from SiO | 9.8 | 2.5 | 363 | 7,500 |

[a] From atomic absorption or, for ceramic supports, neutronic activation.

[b] Specific rate in mol/g cat · s × $10^{-10}$ at 227°C.

[c] Before calcination.

[d] After calcination.

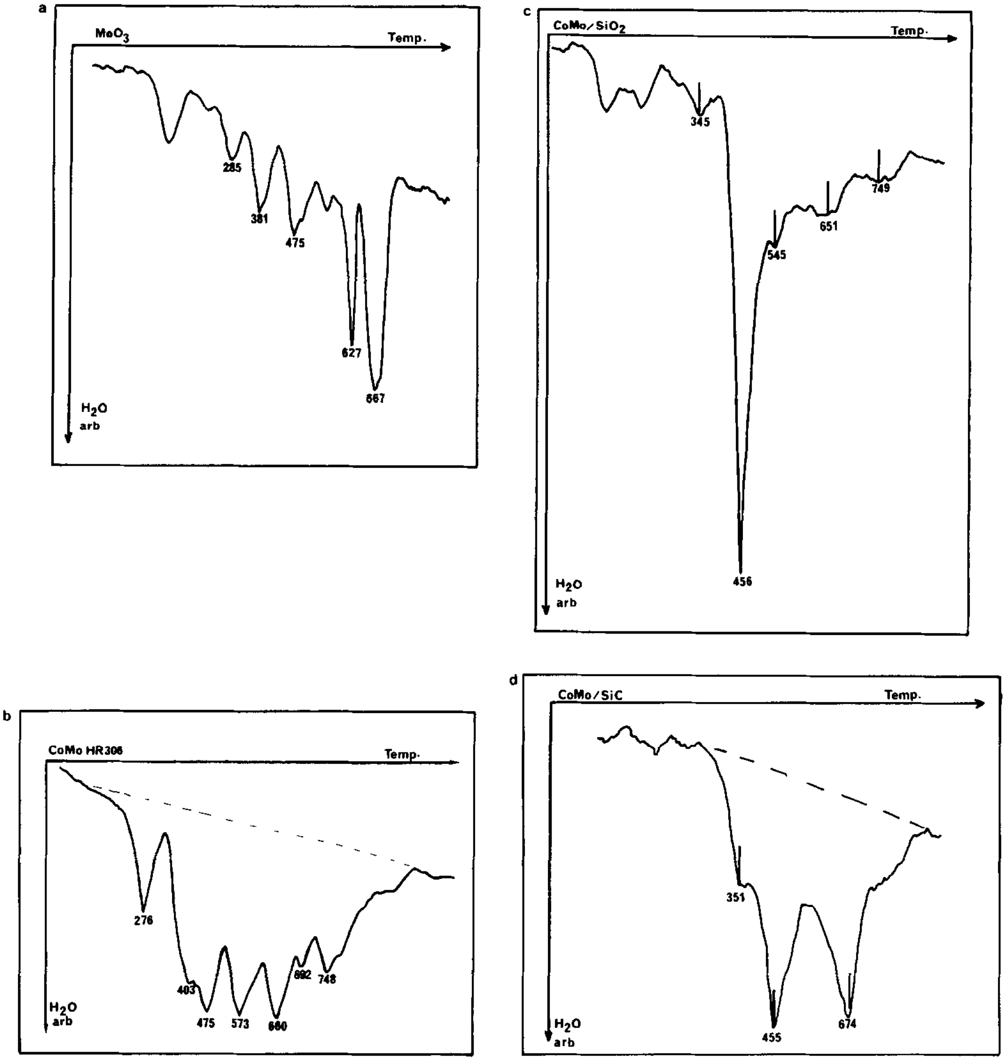

FIG. 6. High-resolution TPR. (a) $MoO_3$ powder. (b) CoMo/$Al_2O_3$ HR306. (c) CoMo/$SiO_2$. (d) CoMo/SiC from SiO after calcination.

persion of the active phase. In comparison, the silica-supported catalyst with a much higher surface (550 $m^2/g$) shows relatively poor activity (2500 × $10^{-10}$) and behaves as CoMoS bulk, see (*10, 11*). The interaction between the oxidic precursor of the active phase and the support is very weak (see TPR).

The SiC prepared from chlorosilane shows a very poor activity (250 × $10^{-10}$) compared to the SiC from "SiO." If the support is not calcined in air at 1100°C its specific surface, 171 $m^2/g$, is much lower than the silica surface (550 $m^2/g$) and yet its activity is slightly higher (2630 versus 2500 × $10^{-10}$). The most surprising result is that even if the support is precalcined at 1100°C, the activity is still very high, 1080 × $10^{-10}$ for a very low surface of 37 $m^2/g$. The range of activity thus lies between silica- and γ-alumina-supported catalysts.

The activity of SiCU catalysts is discussed last.

*TPR.* A high-resolution TPR analysis (*12*) is used to explain the catalytic results. TPR was performed on the oxidic precursor after successive impregnation with molybdenum and cobalt, followed by two calcinations in air at 500°C for 2 h. It has already been reported *(12)* that on alumina (Fig. 6b) the shape of the diagram and the different temperatures of reduction are very close to those of $CoMoO_4$ (a-phase). The interaction of this molybdate with the alumina support is strong because the last reduction occurs above 750°C, above the two strong peaks corresponding to the reduction of $MoO_3$ powder (Fig. 6a), with the two last peaks at 627 and 667°C. The reducibility of the CoMo system on silica is totally different. A single sharp peak is observed at 456°C, accompanied by small structures to 750°C. Quantitative measurement of the water vapor emitted has shown that the oxides are totally reduced to the metallic state for the four samples presented in Fig. 6. Thus, it seems that on silica, the reduction of molybdenum oxide is accelerated and favored by the prereduction of the cobalt oxide, possibly the small peak observed at 345°C. (No sign of molybdate structure is ever observed on this silica sample.) The interaction of these two oxides, Mo and Co, must be very weak with the silica support and probably no chemical bondings occurs between them as it could between Mo oxide and alumina.

It is very interesting to observe on the calcined SiC (Fig. 6d) an intermediate situation. A sharp peak appears at 455°C, probably equivalent to the peak observed on silica (456°C), and a second peak appears at 674°C, which suggests a much stronger interaction between the support and the Co–Mo oxides. A small peak at 351°C corresponds probably, as on silica, to prereduction of a Co oxide. It is tempting to attribute the first peak of reduction (455°C) to the reduction on a part of the surface covered with a $SiO_2$ skin, and the second peak at 674°C to the rest of the surface, bare SiC, or accessible carbon of the skeleton.

We attribute no further significance to this TPR because we have no information on the state of the surface during the reduction process. However, this TPR analysis, with speculation on the interaction between the metallic oxides and the support, explains very well the relative activity of the different CoMo catalysts and confirms that on silica, sulfided CoMo behaves as in the bulk state. The high activity of a CoMo catalyst is thus very much dependent on its dispersion; this observation has been demonstrated elsewhere *(10)*.

## PREPARATION OF URANIUM-DOPED SiC

In a preceding work *(13)*, it was shown that uranium, if correctly impregnated, can strongly improve the dispersive quality of an alumina support. In addition, we could expect that preimpregnation of the carbon support with a well-chosen uranium compound would prevent formation of the silica skin and replace it with an uranium oxide skin.

For the best results, the activated carbon is preimpregnated with an alcoholic solution of uranylacetylacetone (but a solution of any other salt of uranium also gives satisfactory results) and then calcined under argon at 500°C. The product is then placed in the "SiO" reactor and treated like the pure carbon. In Table 2, the specific surface before and after calcination, as a function of the uranium concentration, is reported.

Surprisingly, if the initial specific surfaces are equivalent to the pure SiC surfaces (200–400 $m^2/g$), after calcination in air

TABLE 2

Evolution of the Specific Surface Versus Uranium Concentration

| | Products | | | | | |
|---|---|---|---|---|---|---|
| | SiC | SiCU | SiCU | SiCU | SiCU | SiCCe |
| $m^2/g$ before calcination | 197 | 425 | 265 | 410 | 279 | 320 |
| $m^2/g$ after, at 1000°C in air (2 h) | 59 | 109 | 115 | 131 | 76 | 141 |
| wt% U (or Ce) | 0 | 8.5 | 9.8 | 9.8 | 15 | 5.0 |

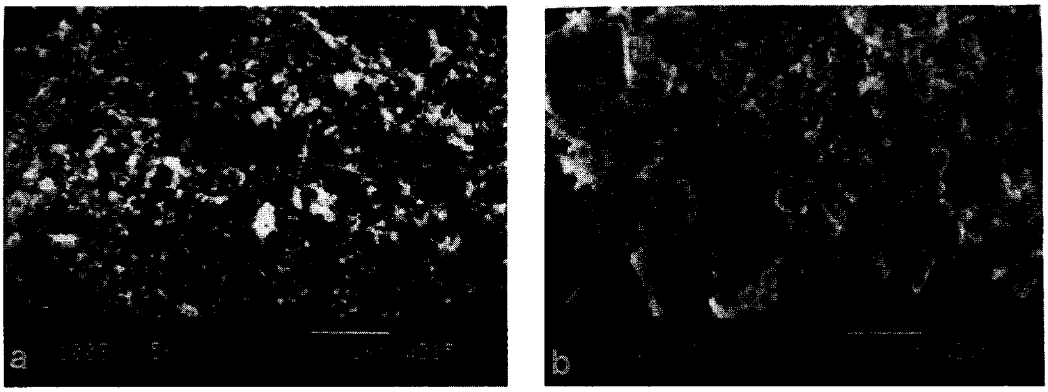

FIG. 7. Scanning electron micrographs of SiCU before (a) and after (b) calcination at 1000°C in air.

at 1000°C, the loss of weight being also equivalent, the final specific surfaces remain much higher (131 $m^2/g$ versus 60 $m^2/g$). The first explanation presumes that uranium atoms are replacing carbon atoms of the skeleton but no evidence allows us to confirm this. In Fig. 7 are shown scanning electron micrographs of a SiCU before and after calcination; they must be compared with the micrographs of activated carbon and pure SiC (Fig. 3). Hardly any whiskers are found and the surface seems to be less homogeneous; after calcination small crystals of $U_3O_8$ would probably be found on the surface.

Fig. 8 gives the X-ray diffraction patterns of SiCU. Before calcination, the ceramic contains both SiC and $U_3O_7$ in crystalline form. After calcination only crystalline $U_3O_8$ is observed. The disappearance of the crystalline SiC structure could be understood if the presence of uranium either favors the oxidation of the SiC or, more probably, by replacing the carbon in the skeleton, leads to an amorphous SiC.

The HDS activity of a CoMo/SiCU cata-

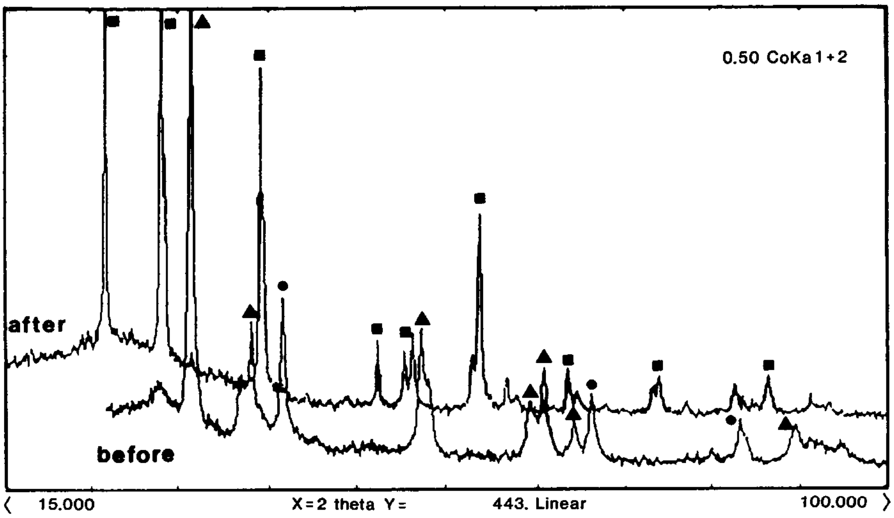

FIG. 8. X-ray diffraction patterns of SiCU before and after calcination. ■, $U_3O_7$ peaks; ●, β-SiC peaks; ▲, $U_3O_8$ peaks.

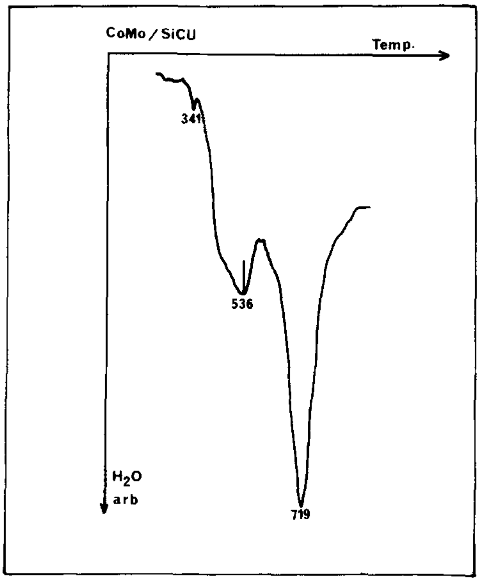

FIG. 9. High-resolution TPR of CoMo/SiCU.

lyst of 363 $m^2/g$ containing 4.1% U, 2.5% Co, and 9.8% Mo is reported in Table 1. This activity of 7500 × $10^{-10}$ mol/g · s is only twice as small as on the best CoMo/$Al_2O_3$ and shows the importance of doping in improving the dispersing property of the support.

The TPR realized on the oxidic precursor of this catalyst (Fig. 9) shows two peaks of reduction at 536 and 714°C, at much higher temperature than on $SiO_2$ or pure SiC. If one attributes this increase in temperature to a stronger interaction of the oxidic phase with the support, and if this stronger interaction leads to a better dispersion, the reason for the increase in activity seems clear. A small peak at 341°C is once more attributed to prereduction of a cobalt oxide. The significance of this TPR diagram is even more difficult to interpret now because of the presence of a new element (U); however, it is also tempting to attribute the first peak (536°C) to a part of the surface covered by uranium oxide and the second peak (719°C) to a part of the surface covered by an unknown composition possibly containing U, C, and Si.

## CONCLUSION

The results obtained when uranium is replaced by Zr, Hf, La, Ce, etc., will be published later, as will results on exhaust automotive oxidation–reduction on a three-way catalyst and methane partial oxidation.

This work has shown that the synthesis of high-specific-surface SiC (from 60 to 450 $m^2/g$) is feasible, that this new material can be used very efficiently for catalyst supports, and, finally, that addition of metal (as U or other metal $IV^+$) specifically improves the activity of the catalysts.

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