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NOTES

Crystal Face Specificity in Ammonia Synthesis on Tungsten Carbide

Efforts to substitute the rare and expensive platinum metals as catalyst in fuel cells by more abundant substances led to studies on tungsten carbide, which has proved to be resistant in acidic electrolytes and very active for the electrocatalytic oxidation of hydrogen and formaldehyde (*1–3*). Some investigations of hydrogenolysis and dehydrogenation of hydrocarbons on interstitial compounds such as tungsten carbide have been performed (*4–6*), but very little is known about the mechanisms of surface reactions on tungsten carbide. Crystal face specificity is assumed for the decomposition of hydrocarbons (*7*) and found for the carburization of slightly carburized tungsten (*8*).

Since tungsten carbide has hydrogenation properties, some activity for the synthesis of ammonia from nitrogen and hydrogen seemed likely. This has now been tested in a flow reactor at normal pressure and 400–500°C with a stoichiometric synthesis gas. The catalyst bed consisted of grains made from pressed powder. The tungsten carbide powder was obtained by carburizing tungsten trioxide with carbon monoxide, and stoichiometry and phase purity were duly checked. The surface area and pore size distribution were determined by adsorption and condensation of nitrogen. The kinetics were not influenced by pore diffusion because the Thiele modulus (*9, 10*) was much smaller than unity (catalyst particle diameter < 0.5 mm; mean pore diameter > 0.1 μm).

A representation for the contact time dependence of the ammonia yield in Table 1 can be given by the first term of the empirical Temkin–Pyzhev equation (*11*) with the factor $\alpha = 0.5$ (*12*)

$$r_{NH_3} = dp_{NH_3}/dt = k \cdot p_{N_2} \cdot p_{H_2}{}^{1.5}/p_{NH_3}; \quad (1)$$

in the integrated form

$$k' \cdot \tau = p_{NH_3}{}^2. \quad (2)$$

The partial pressures of hydrogen and nitrogen were taken as constant under the experimental conditions used here. An Arrhenius plot is given in Fig. 1. Representations with other rate equations are not excluded.

With respect to ammonia synthesis, tungsten carbide seems to act like tunsten metal, although its physical and chemical bulk properties and the electrochemical behavior differ considerably from those of the metal.

The adsorption behavior of tungsten carbide was therefore tested with hydrogen sulfide, known to be adsorbed very strongly on many metals. H_2S was added at room temperature in a stream of argon and hydrogen ($Ar:H_2 = 9:1$) with 0.65 ppm hydrogen sulfide passing the catalyst bed. The hydrogen sulfide concentration was determined by precipitation as cadmium sulfide and iodometric titration. When 25 μg/m^2 of H_2S had been adsorbed on the catalyst surface, the yield of ammonia produced on this poisoned catalyst was reduced to half the amount (Fig. 1). The synthesis reaction was completely inhibited by the maximum sulfur amount of 50 μg/m^2 which could be adsorbed on tungsten carbide.

The upper limit of the quantity of H_2S which could be taken up indicates that only a fraction of the surface is operative for the sulfur adsorption, because metals generally adsorb maximum amounts which are

TABLE 1

Ammonia Yield versus Contact Time
(2 g WC, 10 m²/g, 773 K)

$p_{NH_3}{}^2[Pa^2]\cdot 10^{-3}$	2.50	1.95	1.52	1.22
$\tau[s]$	0.19	0.14	0.10	0.07

seven to ten times higher (*13–15*). Considerations about the nature of the faces which are exposed at the surface may help to explain the limited adsorption capacity. At a tungsten carbide crystal of hexagonal shape (Fig. 2A) two different types of side planes can be distinguished, because the hexagonal structure of WC is noncentrosymmetric, resulting in a polar character for the crystal faces (*16*). In an ideal crystal the three side planes, $(10\bar{1}0)$, $(\bar{1}100)$, and $(0\bar{1}10)$, expose only tungsten atoms in the uppermost layer. Carbon atoms on these planes would be only twofold coordinated by underlying tungsten atoms and therefore would be in an unstable and improbable position (Fig. 2B). These "metallic" faces will exhibit chemical properties similar to a metal and are especially suited for the adsorption of sulfur or the catalytic synthesis of ammonia. All other planes can expose carbon in the uppermost layer, because here every carbon atom is threefold and fourfold coordinated by underlying tungsten atoms, and they will expose carbon atoms in the uppermost layer, because the repulsive forces can be partially screened by the field of the underlying larger tungsten atoms. All these "carbidic" faces will therefore be inactive for the specific reactions.

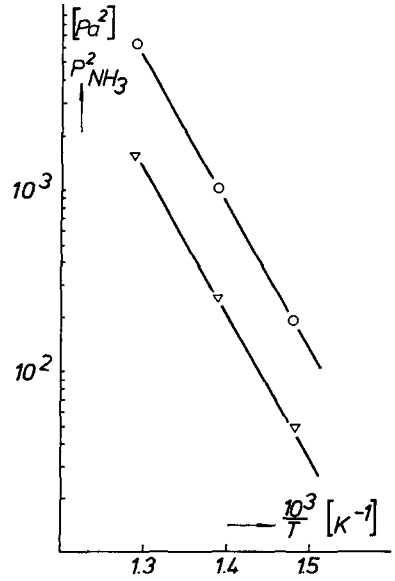

FIG. 1. Arrhenius plot of ammonia synthesis on tungsten carbide (○); semipoisoned with hydrogen sulfide (▽).

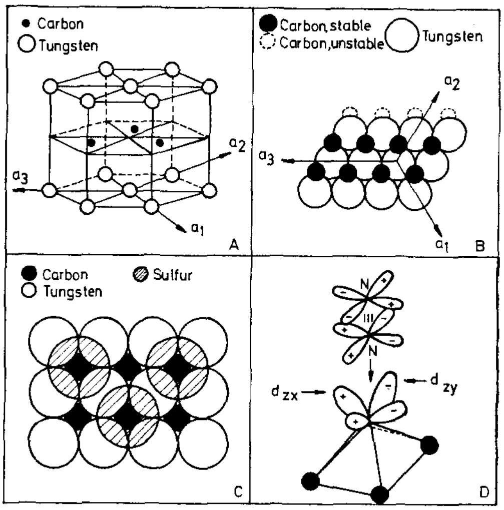

FIG. 2. (A), Model of the hexagonal tungsten carbide lattice. (B), Stable and unstable carbon positions on the boundary planes. (C), Probable adsorption sites for sulfur on the "metallic" side planes. (D), Backbonding of the d_{zx}-, d_{zy}-orbitals of tungsten to the anti-bonding π-orbitals of nitrogen.

The frequency of the metallic faces at a tungsten carbide surface can be estimated with the assumption that the real crystals are mainly multiples of the hexagonal model (Fig. 2A) with dominating basic and prism faces. Higher index faces and preferential directions of growth will be negligible. Support for this assumption can be found in the literature (*17*, *18*). Thus the metallic fraction of surface amounts to about 20% or 2.4×10^{18} metal atoms per square meter (*19*). This has to be compared with the adsorbed 50 $\mu g/m^2$ H_2S giving 10^{18} sulfide ions/m². Since a sulfide ion requires an area of 10–17 Å² (*20*), only every second possible adsorption site can be occupied at best (Fig. 2C). Consequently about 80% of the estimated metallic faces (≈17% of the total WC surface) will be covered with sulfur.

The conclusions are based on the assumption that the chemical compositions of the surface and the bulk are not decisively different. An analysis by high temperature gas extraction gave oxygen contents which were sufficient to cover the total surface. Gases containing hydrogen should be able to remove the oxygen preferentially from the metallic faces. The considerations about the bond structures, which made a distinction between carbidic and metallic faces plausible, should also give reasons for different oxygen bond strength.

The metallic faces which may catalyze the ammonia synthesis should be able to chemisorb a nitrogen molecule in a manner that weakens the bond between the nitrogen atoms, thus enabling the reaction between nitrogen and hydrogen to occur. It can be seen (Fig. 2C) that every tungsten atom at these planes is coordinated by four carbon atoms of the underlying carbon layer. By nitrogen adsorption, stable bond arrangements according to a tetragonal pyramid, with the four carbon atoms in the tetragonal plane and nitrogen at the top, may be formed. The corresponding hybridization may be d^2sp^2. The remaining tungsten orbitals d_{zx} and d_{zy}, which are not required by a σ-bond, are in tungsten carbide presumedly both filled with one electron and therefore suited for π-bonding and π-backbonding with the anti-bonding π-orbitals of the nitrogen molecule, thus weakening the bond between the nitrogen atoms (Fig. 2D).

The observed crystal face specificity in the catalytic activation of nitrogen and the specific chemisorption of sulfur on tungsten carbide supports attempts to regard coordinated surface atoms as active centers for catalysis on solids and thus to postulate parallelisms to homogeneous catalysis on coordination complexes.

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REFERENCES

1. Böhm, H., and Pohl, F. A., *Wiss. Ber. AEG-Telefunken* **41**, 46 (1968).
2. Binder, H., Köhling, A., Kuhn, W., and Sandstede, G., *Angew. Chem.* **81**, 748 (1969).
3. Baresel, D., Gellert, W., Heidemeyer, J., and Scharner, P., *Angew. Chem.* **83**, 213 (1971).
4. Gaziev, G. A., Krylov, O. V., Roginskii, S. Z., Samsonov, G. V., Fokina, E. A., and Yanovskii, M. I., *Proc. Acad. Sci. USSR* (*Dokl. Akad. Nauk SSR*) **140**, 737 (1961) (English).
5. Grosheva, V. M., and Samsonow, G. V., *Kinet. Catal.* (*Kinet. Katal.*) **7**, 782 (1966) (English).
6. Sinfelt, J. H., and Yates, D. J. C., *Nature Phys. Sci.* **229**, 27 (1971).
7. Tardif, A., Michel, J. M., and Wach, J., *Surface Sci.* **26**, 255 (1971).
8. Ollis, D. F., and Boudart, M., *Surface Sci.* **23**, 320 (1970).
9. Thiele, E. W., *Ind. Eng. Chem.* **31**, 916 (1939).
10. Wagner, C., *Z. Phys. Chem.* **193**, 1 (1943).
11. Temkin, M. I., and Pyzhev, V., *Acta Physicochim. USSR* **12**, 327 (1940).
12. Bokhoven, C., van Heerden, D., Westrik, R., and Zwietering, P. *in* "Catalysis" (P. H. Emmett, Ed.), Vol. 3, p. 265. Reinhold, New York, 1955.
13. Bénard, J., *Catal. Rev.* **3**, 93 (1970).
14. Kostelitz, M., and Oudar, J., *Surface Sci.* **27**, 176 (1971).
15. Brill, R., Schaefer, H., and Zimmermann, G., *Ber. Bunsenges. Phys. Chem.* **72**, 1218 (1968).
16. French, D. N., and Thomas, D. A., *in* "Anisotropy in Single-Crystal Refractory Compounds" (F. W. Vahldiek and S. A. Mersol, Eds.), Vol. 1, p. 55. Plenum Press, New York, 1968.
17. Pfau, H., and Rix, W., *Z. Metallk.* **45**, 116 (1954).
18. Barta, J., and Ariel, E., *in* "High Temperature Materials," 6th Plansee Seminar (F. Benesovsky, Ed.), p. 28. Springer, Wien, 1968.
19. Wyckoff, R. W. G., Crystal Structures, Vol. 1, p. 150. Interscience–Wiley, New York, 1963.
20. Landolt-Börnstein, "Zahlenwerte und Tabellen," 6. Aufl., 1. Band, 4. Teil, p. 519 ff. Springer-Verlag, Berlin, 1955.

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