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Platinum-Like Behavior of Tungsten Carbide in Surface Catalysis

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and infilling of the trough occurred during the past 1 million years (Quaternary). Using the seismic signals detected from the two explosions in Lake Managua, we determined the thickness of the trough infilling to be about 1.4 km beneath Managua. The compressional wave and shear wave velocities in this material are 2.6 and 1.3 km/sec, respectively. The compressional wave velocity in the underlying Tertiary volcanic rock that presumably forms the floor of the trough is about 3.6 km/sec. The difference in elevation between the present trough floor and the top of the western wall reaches nearly 1 km near Managua. Thus, we can say that the relative vertical movement along the western edge of the graben has been about 2.4 km.

The number of aftershocks detected during the 20-day period covered by this report (10 to 29 January 1973) varied between 50 and 200 per day. The magnitudes of these earthquakes ranged between 0.0 and 3.0. Approximately ten aftershocks large enough to be felt in Managua occurred during this period. Using the velocity model derived from the two explosions described above, we have located 300 aftershocks to date. As shown in Fig. 2, two clusters can be distinguished within the distribution of aftershock epicenters. After the Managua earthquake a series of seven to ten parallel fault lines trending northeast-southwest through the city could be mapped (4). There is evidence of left lateral motion at several points along the faults (the northwestern side moved in a southwesterly direction relative to the southeastern side). The southern cluster coincides closely with the principal fault mapped in the area, indicated by a dashed line in Fig. 2. The trend of the fault is N40°E.

The directions of the fault movements responsible for the aftershocks can be deduced from the directions of the first motions of the recorded seismic waves. The solution is not unique, since only compressional waves were used. Of the two possible solutions, one is in good agreement with the surface observations (predominantly left lateral movement along faults trending approximately N40°E). As shown in Fig. 3, the aftershocks are concentrated at depths of between 2 and 8 km, with a few as deep as 14 km and as shallow as 1 km. The planes of the active zones are essentially vertical. Thus, we conclude that the aftershock clusters define two steeply dipping

faults, or systems of faults, each about 10 km in length and 10 to 15 km in vertical extent, along which left lateral movement was taking place at the time of our fieldwork. The northern fault system is approximately in line with a fault that cuts through to the southeast along which movement occurred during the devastating earthquake of 1931. If the two faults are part of the same system, the actual length of that system may be much greater than 10 km, with current activity restricted to the segment defined by the aftershocks.

A system of crustal stresses compatible with the inferred directions of faulting is north-south compression and east-west tension. We obtained the same stress distribution from an analysis of aftershocks following an earthquake that occurred in Costa Rica, 235 km southeast of Managua, on 14 April 1973 (5). This suggests that the same stress system may persist over a region including most of Nicaragua and Costa Rica.

This stress system may be explained as a consequence of differential movements between two plates: the Cocos plate on the western side of Nicaragua and the Caribbean plate on the eastern side. According to the hypothesis of Molnar and Sykes (6), the Caribbean plate is presently moving eastward, "dragging" eastern Nicaragua with it, while the Cocos plate is moving in a northerly direction, plunging beneath the western edge of the Central American Arc.

The agreement between the source mechanism of the Managua earthquake

and inferred plate movements implies that the large-scale tectonic processes that formed the Nicaragua Trough are still active. Thus, we must assume that the probability of future earthquakes in the Managua region is high. If a reconstructed city is to survive where the ruins of Managua now stand, it must be built to withstand earthquakes of at least moderate intensity.

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## Platinum-Like Behavior of Tungsten Carbide in Surface Catalysis

**Abstract.** *Tungsten carbide catalyzes the formation of water from hydrogen and oxygen at room temperature, the reduction of tungsten trioxide by hydrogen in the presence of water, and the isomerization of 2,2-dimethylpropane to 2-methylbutane. This catalytic behavior, which is typical of platinum, is not exhibited at all by tungsten. The surface electronic properties of the latter are therefore modified by carbon in such a way that they resemble those of platinum.*

There are several indications in the literature (1-3) that addition of carbon to nonnoble metals (such as Mo and W) confers to them some of the catalytic properties typical of the noble metals (such as Pt and Pd). For example, a study of the reaction of 1,1,3-trimethylcyclopentane in the presence of metal films (Fe, Co, Ni, W, Rh, Pt, and Pd) showed that only platinum rearranged the reactant to appreciable amounts of xylene (1). However on tungsten, while

no xylene was observed initially among the reactions products, it was found after an induction period at the higher temperature studied (1).

The possibility that formation of a transition metal carbide is responsible for the observed change of behavior of tungsten is further suggested by a report that an increase with time in the rate of ethane hydrogenolysis over a molybdenum catalyst can be ascribed to the formation of carbide, as detected

Table 1. Chemisorption of hydrogen on tungsten carbide (WC) after different pretreatments of the catalyst. The reaction temperature was 25°C.

Trial	Pretreatment	Uptake ( $\mu\text{mol g}^{-1}$ )
1	Original sample (exposed to air), evacuated at 150°C for 1 hour	15
2	After trial 1, evacuated at 150°C for 1 hour	None
3	After trial 1, exposed to O <sub>2</sub> (400 torr) at 25°C for 1 hour, then evacuated at 150°C	14
4	As in trial 3, but evacuated at 25°C	38

Table 2. Comparison of the rates of hydrogenolysis ( $r_h$ ) and isomerization ( $r_i$ ) of 2,2-dimethylpropane for platinum, tungsten, and tungsten carbide (WC).

Catalyst	Pretreatment	Reaction temperature (°C)	Rate ( $\mu\text{mol m}^{-2} \text{sec}^{-2}$ )	
			$r_h$	$r_i$
Platinum	Flowing H <sub>2</sub> , 300°C, 2 hours	300	5.4*	2*
Tungsten	Flowing H <sub>2</sub> , 300°C, 2 hours	460	0	0
Tungsten	Flowing H <sub>2</sub> , 750°C, 25 hours	460	$\sim 10^{-3}$	0
Tungsten carbide (WC)	Flowing H <sub>2</sub> , 300°C, 2 hours	370	$\sim 2 \times 10^{-2}$	$\sim 2 \times 10^{-4}$

\* Obtained from (10) and corrected to 370°C by using activation energies reported in (11).

by x-ray diffraction (2). It must also be noted that in the series Mo, Ru, Rh, and Pd, the highest activity for ethane hydrogenolysis is exhibited by Ru, so that Mo<sub>2</sub>C behaves more like a noble metal than Mo. Finally, the activity of tungsten carbide (WC) as fuel cell electrode has been reported, and it compares favorably to that of platinum (3). In view of the unique position of platinum among catalytic metals for a large number of reactions, these observations suggest the possibility of preparing catalysts that possess some of the features of platinum by insertion of carbon into other metals.

To test this concept, we have compared the catalytic behavior of tungsten (General Electric; 1.4 m<sup>2</sup> g<sup>-1</sup>) and tungsten carbide (WC, AEG-Telefunken Forschungsinstitut; 5 m<sup>2</sup> g<sup>-1</sup>) in reactions typical of metals of the platinum group (Pt, Ir, Pd, and Rh). Analysis of both powders revealed no detectable impurities of these noble metals.

Using a gas volumetric apparatus and a method described elsewhere (4), we studied the chemisorption of hydrogen and oxygen on the carbide. The removal of adsorbed oxygen by hydrogen with formation of water at room temperature has been reported only for Pt (4), Rh (5), and Pd (6). It does not occur on other transition metals because they bind oxygen too strongly. Thus, in the case of tungsten, reduction of an oxidized surface requires treatment in H<sub>2</sub> at 750°C for 25 hours (7). In sharp contrast, we found that a WC sample exposed to oxygen can still chemisorb hydrogen at 25°C, and a dose of oxy-

gen at this temperature cleans the surface for a new hydrogen chemisorption. These results, which are summarized in Table 1, indicated that as much as 22 percent of the WC surface participates in the formation of water at 25°C, compared to 84 percent in the case of platinum (4).

Another characteristic of platinum group metals is their ability to dissociate H<sub>2</sub> in the presence of H<sub>2</sub>O at 25°C. This ability is demonstrated by the catalytic reduction of WO<sub>3</sub> to H<sub>x</sub>WO<sub>3</sub> by wet H<sub>2</sub>. In the absence of a catalyst no reduction takes place at temperatures below 400°C. When a mechanical mixture of Pt and WO<sub>3</sub> powders is exposed to H<sub>2</sub> in the presence of water vapor, the H<sub>x</sub>WO<sub>3</sub> formation occurs at 25°C (4). For such a low-temperature reduction, the catalyst is a source of hydrogen atoms and must be unaffected by the presence of water, which acts as a cocatalyst in the reduction (8). Following the procedure used in (9) for platinum, we found that WC also catalyzes the formation of H<sub>x</sub>WO<sub>3</sub>. The reduction is slower than in the case of platinum by about two orders of magnitude, and the rate shows a dependence on the surface area, which is not found with platinum. However, there is no question that WC can act as a source of hydrogen atoms in the presence of water.

A more stringent test of the similarity between Pt and WC is the catalytic isomerization of 2,2-dimethylpropane. Of all the group VIII metals plus Cu and Au, only Ir, Pt, and Au have been found to catalyze the isomerization of 2,2-dimethylpropane to 2-methylbutane

(10), a reaction proceeding through a mechanism similar to that of xylene formation from 1,1,3-trimethylcyclopentane on platinum (1). Our data on W and WC, obtained by the procedure in (10), are shown in Table 2. Drastic reduction was necessary before tungsten showed any catalytic activity toward 2,2-dimethylpropane, and then it only hydrogenolyzed it. This is a trivial catalytic property observed on all the transition metals mentioned above. No isomerization was observed. Tungsten carbide, on the other hand, showed activity after the same mild pretreatment used for platinum, and at 370°C it isomerized 2,2-dimethylpropane. The isomerization activity of WC is lower than that of Pt, but WC can now be added to the very small list of metals that isomerize 2,2-dimethylpropane.

With these preliminary results, we speculate that the success reached in conferring to tungsten some of the catalytic properties of platinum is due to a change in the electron distribution in tungsten by addition of carbon. In particular, carbon seems to tame the much too high reactivity of tungsten toward oxygen by the addition of its valence electrons to those of the metal. If this is so, optimum results should be obtained by careful control of the amount of carbon at the surface. Besides, an important factor in the unique catalytic activity of platinum in the isomerization reactions is its very large electronegativity (11). Again, controlled addition of carbon or other elements to tungsten might affect the electronegativity of the new catalyst in a desirable direction. Finally, the isomerization of 2,2-dimethylpropane and the related rearrangement of 1,1,3-trimethylcyclopentane seem to require an easy change in surface valency (11), a platinum-like property which seems to be acquired to a certain extent by tungsten as a result of carbide formation. Future work along these lines should be rewarding, not only in revealing new active and selective catalysts but also in clarifying the role of electronic distribution in catalysis by metals.

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## Ice Nucleation by Solid Solutions of Silver-Copper Iodide

**Abstract.** *The lattice misfit between ice and silver iodide can be reduced by partial substitution of copper atoms for silver atoms in the silver iodide lattice. The best crystal match is obtained with a composition of CuI-3AgI, which corresponds to the most active silver-copper iodide nucleation catalyst.*

Vonnegut and Chessin (1) showed that a solid solution of 30 mole percent AgBr in AgI causes nucleation in supercooled water at about half the supercooling required for nucleation by pure AgI. According to the nucleation theory of Turnbull and Vonnegut (2), this improved nucleation ability can be attributed to the fact that while the AgI crystal lattice is 1.5 percent larger than that of ice, the lattice of a solid solution with 30 mole percent AgBr in AgI is only 1.0 percent larger. Presumably AgI-AgBr solid solutions with even smaller lattice misfits should be even better nucleation catalysts. However, 30 mole percent is apparently the limit of solubility of AgBr in the AgI lattice, so 1.0 percent is the minimum lattice disregistry that can be obtained with AgI-AgBr solid solutions. The disregistry,  $\delta$ , is defined as  $(a - a_0)/a_0$ , where  $a$  and  $a_0$  are the respective lattice parameters of the catalyst and ice along similar low index planes.

In searching for solid solutions of AgI for which we could control the lattice parameter, our attention turned to CuI-AgI. We have prepared CuI-AgI solid solutions, each having a lattice parameter smaller than that of pure AgI by two techniques. The first was direct fusion at a pressure of  $10^{-2}$  torr and a temperature of  $20^\circ\text{C}$  above the melting point of the solid solution, about  $600^\circ\text{C}$ . The second involved dissolving the proper proportions of reagent grade CuI and AgI in hydriodic acid and then boiling off the solvent. The crystal class of the resulting solid solutions is face centered cubic, but in the (111) plane the crystal structure is similar to that of ice in the (0001) plane. The lattice spacing in the (111) plane is given by  $a\sqrt{2}/2$ , where  $a$  is the edge of a unit cell in the cubic system. The x-ray data in Fig. 1 show that by varying the mole percent of CuI in AgI, a solid solution can be

made to have any lattice spacing from 4.58 to 4.28 Å measured in the (111) plane. This range in lattice spacings corresponds to lattice disregistries with respect to ice ranging from 1.5 percent to  $-5.2$  percent. Since CuI and AgI are not appreciably soluble in water ( $10^{-5}$  and  $10^{-8}$  mole/liter, respectively), they have a negligible effect in depressing the freezing point of the water.

To determine their relative effectiveness as nucleation catalysts, powdered samples of about 0.5 g of CuI-AgI were sealed in dilatometers containing approximately 1 g of distilled water, and the freezing temperature was observed when they were cooled in a vigorously stirred bath. The temperature was measured with a Beckman thermometer with an accuracy of  $0.01^\circ\text{C}$  and was lowered at a rate of  $0.5^\circ\text{C min}^{-1}$  (3). The water was singly distilled and had a conductivity of  $3 \times 10^{-6}$  ohm $^{-1}$  cm $^{-1}$ .

Figure 2 shows the observed thresh-

old nucleation temperature as a function of composition for ten samples of both the fusions and the precipitates. The fusions were tested after having been in water for about 1 month. The precipitates were tested immediately after having been immersed in water. Reduction of the cooling rate from  $0.05^\circ$  to  $0.01^\circ\text{C min}^{-1}$  produced no observable differences in threshold nucleation temperatures.

Figure 3 shows the smallest observed supercooling for the CuI-AgI fusions and precipitates, as a function of lattice disregistry with respect to ice. The disregistry is computed for the (111) plane of the CuI-AgI solid solution and the (0001) plane of ice. Vonnegut and Chessin's data for the AgI-AgBr solid solutions are also shown, along with Turnbull and Vonnegut's theoretical curve for coherent nucleation.

The fact that the temperature of  $-2.5^\circ\text{C}$  we measured for nucleation in the presence of pure CuI is appreciably higher than the value of  $-15^\circ\text{C}$  reported by Mason and Hallett (4) probably can be attributed to the very different conditions under which the observations were made. That the CuI-AgI catalysts precipitated from HI were generally more active than the fused CuI-AgI catalysts could be due to particle size, decay of the fused samples, or the effect described by Bigg (5) where small concentrations of HI can raise the nucleation temperature. Although the reasons for the difference are not clear, the parallel nature of the data in Fig. 3 suggests that the difference is uniform.

Turnbull and Vonnegut (2) advanced

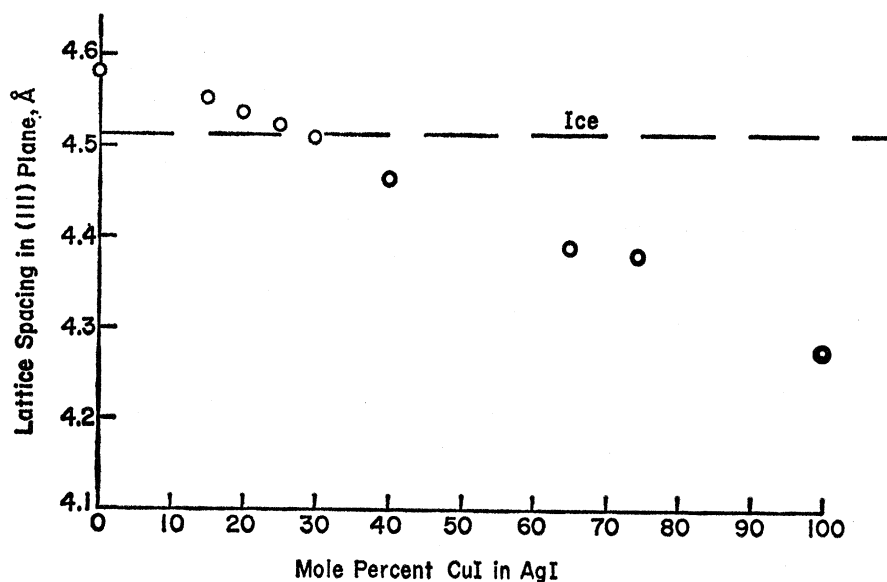


Fig. 1. Lattice parameter as a function of mole percent CuI in AgI.