

Catalytic Activities of TiC, WC, and TaC for Hydrogenation of Ethylene

The transition metal carbides have been studied extensively because of their interesting properties such as extremely high melting point, metal-like thermal and electric conductivities, and superconductivity. These unique properties are thought to be closely connected with their electronic structure and chemical bond characters for which many experimental and theoretical works have been performed. Catalytic properties of the metal carbides for chemical reactions, however, have not yet been sufficiently investigated, whereas tungsten carbide is known as the catalyst for hydrogenation, isomerization, or electrocatalytic oxidation reactions (1). In particular, the conditions under which the carbides are catalytically activated have not been elucidated.

In earlier papers (2), it was reported that the catalytic activity of powdered tantalum monocarbide for hydrogenation of benzene was negligible at the evacuation temperatures lower than 900°C; however, it was highly activated when the sample was evacuated above 1000°C. An additional study by gas adsorption suggested that such activation was related to the removal of oxygen from the surface since the temperature at which the carbide activated was identical to the temperature at which the surface oxygen was removed (2).

In the present paper, we report the results of similar experiments carried out for the hydrogenation of ethylene on a series of metal monocarbides such as TiC, WC, NbC, HfC, as well as TaC to determine

the conditions of activation and also the possibility that these form a group of new catalysts.

The powdered metal monocarbides (300-350 mesh) were obtained from Furu-uchi Chemicals Ltd. and are of $\geq 99\%$ purity; all these carbides contain 0.03 to 0.1 iron and 0.05 to 0.3% free carbon as impurities, and in addition, TaC contains 0.5% niobium. For each material the characteristic sharp diffraction patterns of the corresponding metal monocarbide were confirmed from X-ray diffraction measurement. A 0.04- to 0.5-g amount of each sample was set as a catalyst in a reaction tube connected with a conventional closed system incorporating a gas-circulation pump and with a high-vacuum system (5×10^{-6} Torr, 1 Torr = 133.3 N m⁻²). Prior to each run the catalysts were evacuated *in situ* at various given temperatures for 30 min and then cooled at the reaction temperature, 0°C. A mixture of ethylene and hydrogen in a 1:2 mole ratio was used as the reaction gas and the total pressure was 30 Torr throughout the experiments. The reaction products were analyzed by mass spectrometry and gas chromatography. The product was found to be ethane only in the gas phase; hence the catalytic activities were measured from the initial decrease in total pressure. Surface area of the catalysts was measured by BET isotherms obtained from the adsorption of Kr gas at 78 K. In addition, a ESCA spectrometer with a monochromatic AlK α X ray (Hewlett-Packard 5950A) was used for examining the catalyst surfaces.

Figure 1 shows the dependence of the catalytic activities per gram of powdered TiC, WC, and TaC on evacuation temperature. With TiC, no activity is exhibited on evacuation at temperatures lower than 900°C; however, it is drastically generated at an evacuation temperature of 1000°C. With WC, the activity is negligible when evacuated at temperatures lower than 500°C, but it is greatly increased on evacuation above 600°C and remains almost constant on evacuation up to 1000°C. With TaC, the activity is less than that with TiC or WC by a factor of about 10; however, the shape of this "activation curve" is quite similar to that of the TiC and also to the previous results for hydrogenation of benzene (2) on TaC activated by evacuation above 1000°C. Some activity is, however, observed on evacuation at 800°C in the present case.

On the other hand, the changes in surface area of the carbides with evacuation temperature are shown in Fig. 2; these carbides have surface areas of 0.5 to 2 m² g⁻¹, decreasing in the order WC > TaC

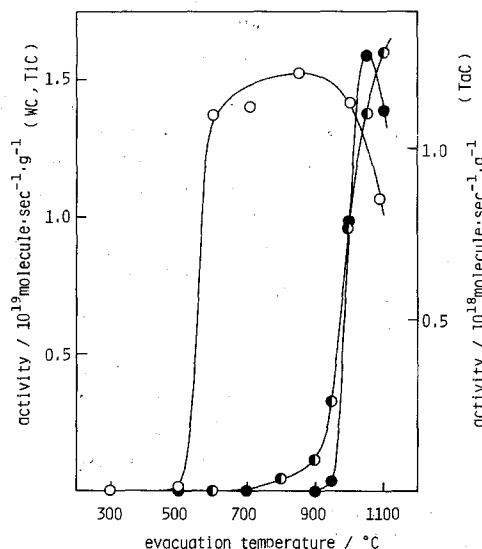


FIG. 1. Changes in activities for ethylene hydrogenation with evacuation temperature. O, WC; ◐, TaC; ●, TiC.

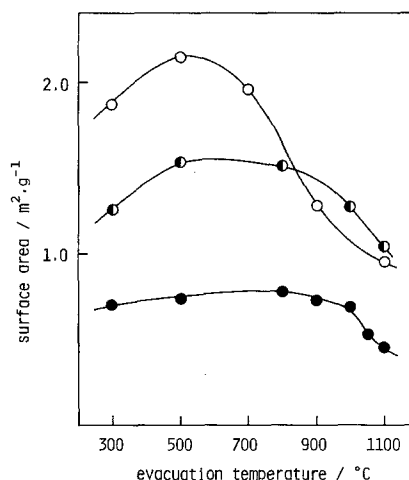


FIG. 2. Changes in surface area with evacuation temperature. O, WC; ◐, TaC; ●, TiC.

> TiC.³ The WC shows a maximum area after evacuation at 500°C which is the same temperature at which it was catalytically activated (Fig. 1). The shape of the surface area curve for TaC is similar to that for TiC, which is correlated with the similarity between their activation curves as described above. It is also of note that the surface areas of TiC and TaC decrease rather sharply at the catalytical activation temperature, 1000°C. However, these changes in surface area with evacuation temperature are quite small compared with the drastic changes in catalytic activity, indicating that the activation of these materials does not arise from the increase in their surface areas but results from generation of the active sites on the surfaces. X-Ray photoelectron spectroscopy measurement confirmed this point of view, i.e., the temperatures at which metal oxide oxygen is removed from the surfaces coincide with the respective activation temperatures; as shown in Fig. 3, only peaks corresponding to the respective metal monocarbides (solid lines in Fig. 3) were observed when the samples were heated *in vacuo* at temperatures higher than the above activation temperatures, whereas

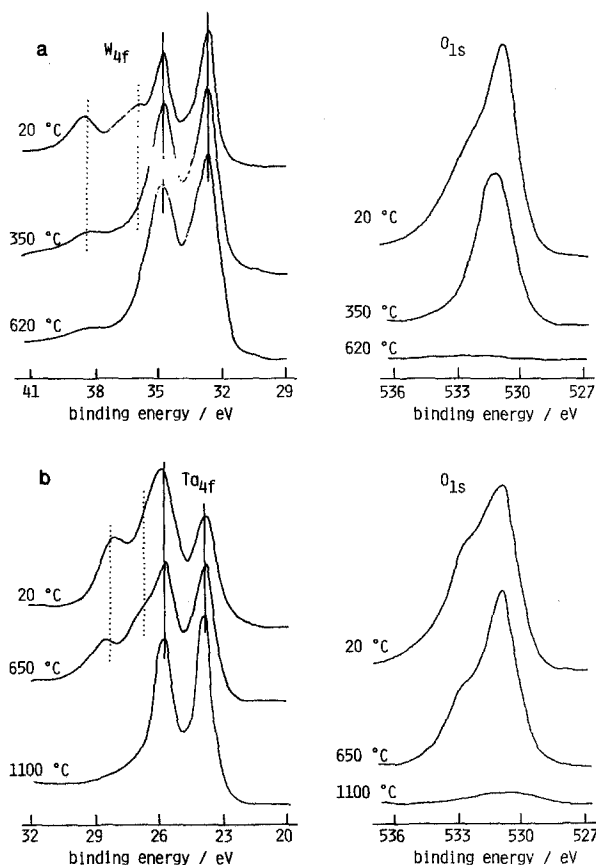


FIG. 3. Changes in XPS spectra of W_{4f} , Ta_{4f} , and O_{1s} regions of (a) WC and (b) TaC with evacuation temperature. —, Peaks due to carbides. ···, Peaks due to oxides.

oxidized states (dotted lines) of the metals were observed in the lower temperatures. Correspondingly O_{1s} peaks due to the oxides disappeared at the respective characteristic temperatures of activation.

The conditions for activation on other metal monocarbides such as HfC, ZrC, and NbC were also examined. However, so far we have not found such activation for the same reaction by evacuation up to 1100°C; nevertheless, surface oxygen was completely removed by evacuation at this temperature. These results suggest that other factors besides surface oxygen must be responsible for the catalytic activation for these carbides. Further studies on this point are in progress.

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Received January 24, 1979