

THE VAPOR-PHASE HYDROCHLORINATION OF ACETYLENE OVER
METAL CHLORIDES SUPPORTED ON ACTIVATED CARBON

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The hydrochlorination of acetylene over a series of metal chlorides supported on activated carbon was carried out at 200°C. The catalytic activity of metal chloride was correlated to the electron affinity of metal cation with two straight lines.

The vapor-phase hydrochlorination of acetylene over a series of metal chlorides supported on carbon and silica has been investigated by many previous workers.¹⁻⁴⁾ However, there were only a few kinds of metal chlorides which were examined for this reaction. The present investigation was undertaken to systematize the catalytic activities of many metal chlorides in the hydrochlorination of acetylene over metal chlorides supported on activated carbon. Metal chlorides in this work were obtained from Kanto Kagaku Co. The catalysts of metal chlorides supported by activated carbon were obtained by impregnating activated carbon (Takeda Shirasagi C) with an aqueous solution of metal chloride and then dried at 200°C in the atmosphere. A flow reaction system was used. A reactor of the Liebig condenser type was made of Pyrex glass tube. 50 ml of catalyst was placed in the middle of the reactor and the reaction temperature was measured in a thermowell placed in the catalyst bed. A mixture of acetylene and hydrogen chloride (mole ratio 1.00:1.03) was fed into the reactor which was indirectly heated by the boiling ethylene glycol in the outer tube and the reaction temperature was maintained at ca. 200°C. The space velocity of the mixed gas was 150 (hr⁻¹) throughout the experiment. After allowing one hour to reach a steady state, the gaseous reaction products were analyzed by gas chromatography.

A correlation between the conversion of acetylene to vinyl chloride and the electron affinities (eV) of metal ions is shown in Fig. 1. The numbers on the abscissa indicate the values of the electron affinities⁵⁾ of cations divided by the

corresponding metal valences. The correlation seems to consist of two straight lines. It has been suggested that the relative magnitudes of the electron affinities of the

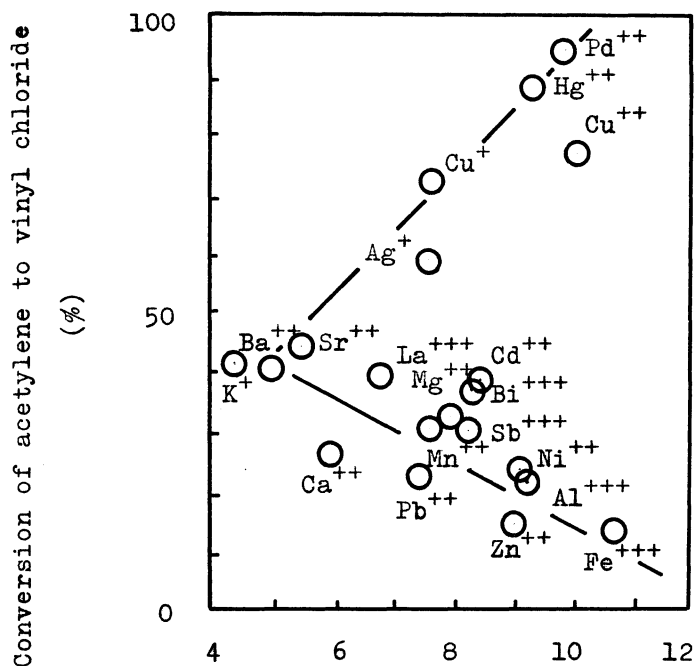


Fig. 1. The hydrochlorination activities of metal chlorides supported on activated carbon are correlated with the electron affinities of metal cations divided by the corresponding metal valences.

Electron affinity of cation / metal valence (eV)

cations and propyne (10.56 eV) makes the charge transfer from propyne to cation most reasonable.⁴⁾ Therefore, the acetylene-metal bond is a combination of μ - and π -bonding. The upper line indicates that the conversion of acetylene increases linearly with the electron affinities of metal cations. On the other hand, with a series of metal chlorides in lower line which are Friedel-Crafts type catalysts, the conversion decreases with the electron affinities. These metal chlorides form complexes with hydrogen chloride such as $[\text{FeCl}_4]^- \text{H}^+$. The attack of this type complex as an electrophilic agent to triple bond, as well known, does not take place. The complexing feasibility of metal chloride and hydrogen chloride slows down the hydrochlorination rate. In conclusion, the reactivity of metal chloride relates to the electron affinity of the metal cation and the correlation consists of two straight lines.

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