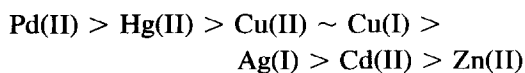


## Vapor Phase Hydrochlorination of Acetylene: Correlation of Catalytic Activity of Supported Metal Chloride Catalysts

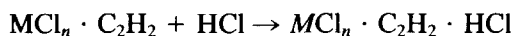
The heterogeneously catalyzed reaction of acetylene with hydrogen chloride is an important industrial reaction and is utilized to produce about 6% of the world annual production of vinyl chloride. Supported metal chlorides are used as catalysts for this process. Comparative studies on the hydrochlorination of acetylene using a range of metal chlorides supported on carbon or silica have been reported by a number of workers (1-3). The conversion of acetylene to vinyl chloride was found to decrease in the order:



At the reaction temperatures investigated the blank thermal reaction between acetylene and hydrogen chloride in the absence of catalyst is not significant and does not affect this relative order of activity. Since the metal chlorides were supported on high-area carbons or silicas the differential rates of sintering of the active components would not be expected to be significant in the time scale of the experiment and would not be expected to give a major contribution to the order of activity.

The order was not found to be significantly affected by the nature of the support. However, carbon is considered to be the preferred support (1) and when silica is utilized some polymerization products are observed (2) due primarily to surface acidity. The requirement for a basic support surface has recently been established of Panfilov *et al.* (4, 5). Studies on the mechanism of the hydrochlorination of acetylene have indicated that the rate-determining step involves the addition of HCl to a surface

metal acetylene complex (6-8):



It is therefore considered that the stability of these surface metal-acetylene complexes will be a major parameter in determining the catalytic activity and selectivity of the metal chloride. Infrared spectroscopy has been used by Smith *et al.* (2) to study the interaction of acetylene with the silica-supported metal chloride. A reduction in acetylene bond order was observed which gave a tenuous correlation with catalytic activity. Since the formation of an acetylene metal complex is thought to be involved in the reaction mechanism, only metals capable of forming compounds with acetylene, e.g., metastable acetylides, would be expected to form active catalysts. Metastable acetylides are known to be formed by Cu, Ag, Au, Na, K, Rb, Zn, Cd, Hg, Pd, Os, Ce, Al, Mg, Ca, Sr, Ba and are considered possible for Pt, Ru, Rh, Ir. It is interesting to note that the most active cations Pd(II), Hg(II), Cu(II), and Ag(I) can form metastable acetylides.

Smith *et al.* (2) proposed that catalytic activity could be correlated with the electron affinity of the cation for the series Cu(II) > Zn(II) > Mn(II) > Ca(II). Shinoda (3) considered that a correlation existed between the conversion of acetylene to vinyl chloride and the electron affinity of the cation divided by the corresponding metal valence (Fig. 1). Overall, the data demonstrate no significant correlation but it can be seen that cations that do not form metastable acetylides do not give active catalysts. However, Shinoda considered that the correlation consisted of two

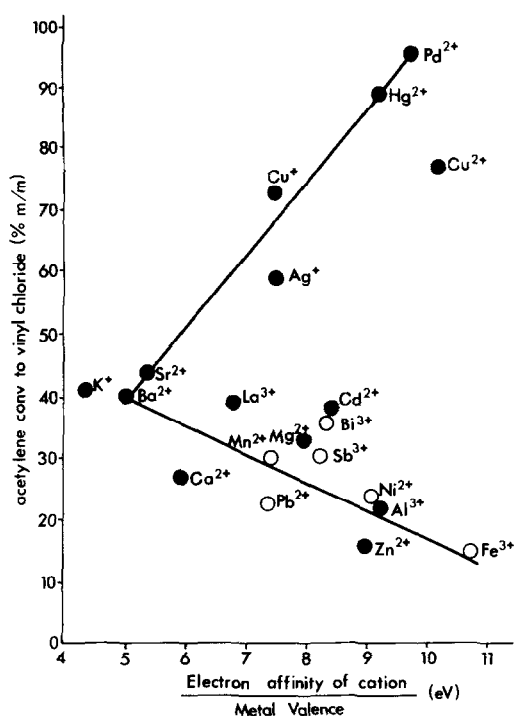
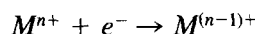


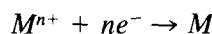
FIG. 1. Correlation of hydrochlorination activity of metal chlorides supported on carbon with the electron affinity of the metal cation divided by the metal valence (data from Ref. (3)).  $T = 200^{\circ}\text{C}$ , GHSV =  $150 \text{ h}^{-1}$ . (●) Metal capable of forming metastable acetylide.

straight lines as shown in Fig. 1. The upper series of data indicates that acetylene conversion for these cations increases linearly with the electron affinity. The lower series of data demonstrate the opposite trend and this was considered to be due to cations forming complexes with HCl of the type  $\text{H}_m[\text{MCl}_{n+m}]$  which are Friedel-Crafts-type catalysts. However, close examination of the data indicates that Hg(II), Cd(II), and Zn(II) have similar electron affinities and are capable of forming metastable acetylides. In addition  $\text{HgCl}_2$ ,  $\text{CdCl}_2$ , and  $\text{ZnCl}_2$  all form complexes with HCl. The order of stability of these complexes is  $\text{Hg} > \text{Cd} > \text{Zn}$  (9) which is directly proportional to catalytic activity. Hence, the ability of the metal chloride to form both compounds with acetylene, e.g., metastable acetylides, and complexes with HCl may be prerequisites for an active catalyst. On this basis the

distinction Shinoda makes between the two sets of cations appears to be arbitrary and indicates that the electron affinity of the cation is not the correct correlation parameter. Electron affinity is based on a one-electron process:



However, the interaction of acetylene and the metal chloride may involve the transfer of more than one electron. Hence, the standard reduction potential is considered to be a more suitable parameter with which to correlate catalytic activity since this is an  $n$ -electron process:



The correlation of the conversion data obtained by Shinoda with this parameter is shown in Fig. 2. Since the relative proportions of Cu(I) and Cu(II) present are not known an average value of Cu is used. It is apparent that this gives an improved correlation with the data being approximated by a single line as shown. Initially, catalytic activity decreases with increasing reduction potential giving a minimum for Zn(II) and Fe(III). Subsequent increases in reduction potential significantly increase catalytic activity. On this basis, cations with a standard reduction potential greater than that of Hg(II) and Pd(II) would be expected to give more active catalysts. This has been confirmed for Au(III),  $E^0 = 1.42 \text{ V}$ , and Pt(II),  $E^0 = \sim 1.2 \text{ V}$ , which have been shown to be extremely active and selective catalysts for the hydrochlorination of acetylene to vinyl chloride (10-13). For example, a catalyst containing gold(III) chloride, 2% (m/m), and platinum(II) chloride, 2% (m/m), supported on carbon gave a conversion of acetylene of 85% and a selectivity to vinyl chloride >99.9% at a reaction temperature of  $61^{\circ}\text{C}$  (13). Under comparable conditions a catalyst containing 4% (m/m) mercury(II) chloride would be relatively inactive since reaction temperatures  $\geq 140^{\circ}\text{C}$  are required before any appreciable conversion is observed. In addition, it is

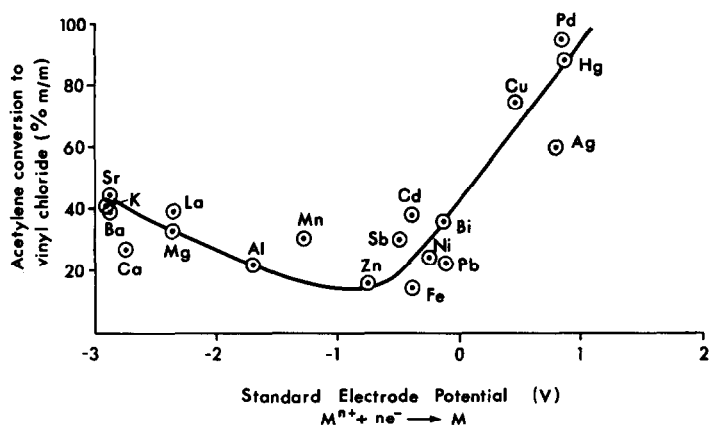


FIG. 2. Correlation of hydrochlorination of activity of metal chlorides supported on carbon with the standard reduction potential (conversion data from Ref. (3)).  $T = 200^{\circ}\text{C}$ ,  $\text{GHSV} = 150 \text{ h}^{-1}$ .

interesting to note that compounds of Ba (14) and La (15) have been reported to increase catalyst lifetime when these compounds are added to supported mercury(II) chloride catalysts. It is therefore possible that these materials which exhibit negative standard reduction potentials may act as promoters in supported mercury(II) chloride catalysts.

The correlation of catalytic activity with the standard reduction potential implies that the metal may in some cases be found as a transient species in the reaction. This is confirmed in the case of mercury(II) chloride catalysts when metallic mercury is observed in downstream reaction vessels.

Based on this correlation it is possible that active metal chlorides (e.g., Hg(II), Au(III), Pt(II)) interact in a different manner with acetylene and vinyl chloride than inactive chlorides of metals with standard electrode potentials less than zero. This is indicated by the action of Ba(II) and La(III) chlorides as promoters for mercury(II) chloride catalysts which may be an electronic effect due to their ionic nature. However, this area requires further detailed studies of the interaction of acetylene and vinyl chloride with supported metal chloride catalysts with a range of standard electrode potentials using modern surface analytical techniques.

In conclusion, it is therefore considered that the catalytic activity for the hydrochlorination of acetylene to vinyl chloride correlates significantly with the standard reduction potential of the metal cation for supported metal chloride catalysts. In addition, it is considered that such a correlation explains the catalytic data for this reaction reported to date.

#### ACKNOWLEDGMENT

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*Received December 19, 1984*

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