# Mercury Adsorption on Chromium Oxide Gels

It seems to have been assumed in most studies of physical adsorption that adsorption of mercury vapour is unimportant. In only a few cases has any attempt been made to study the adsorption of mercury or its influence on the adsorption of other vapours. Coolidge[1] found that the adsorption of mercury vapour at 298 K on charcoal is negligible and more recently Miles[2] has shown that the presence of mercury vapour did not affect the adsorption isotherms of hydrocarbon vapours on charcoal. A similar result has been obtained in our laboratories for the adsorption of nitrogen at 77 K on aluminas and silicas. With certain chromium oxide gels, however, we have now established that a significant amount of mercury vapour adsorption takes place at temperatures around 298 K.

Our attention was first directed to anomalous increases in weight observed by our co-workers, J. D. Carruthers and L. J. Stryker, during the outgassing of chromium oxide gels. In prolonged outgassing of these gels at 298 K, the weight of the sample decreased to a minimum (after 2–3 h) and then underwent a slow but uniform rate of increase. The weight change was arrested by the introduction of a small pressure of a permanent gas, but the same rate of increase was restored on further outgassing. When a similar experiment was performed using a microbalance (in place of the spring balance) and a mercury-free adsorption system, no increase in weight could be observed. It seemed likely that the weight increase was due to the adsorption of mercury vapour, which originated from various exposed mercury surfaces in the system (for instance the manometer). To test this hypothesis the mercury vapour pressure was increased three-fold by increasing the temperature of a mercury reservoir; immediately, the rate of increase in weight of the adsorbent was accelerated (initially two-fold). In another experiment, the sample was outgassed in the absence of mercury vapour and when the stable minimum weight was attained it was exposed to mercury vapour; in this case the weight of the sample increased in much the same way as had been observed earlier.

In the case of chromium oxide[3] (gel *E*) which had been calcined in air at 560 K for 18 h, it was found that exposure to mercury vapour at $P/P_0=0.8$ resulted in an uptake of 0.6 mg of mercury/g sample after 2 h. This uptake seemed to be close to the equilibrium value. No detectable desorption of mercury occurred on outgassing this sample at 298 K, but after exposure to air and further evacuation additional amounts of mercury were adsorbed; at $P/P_0=0.8$, an uptake of about 0.5 mg of Hg/g sample was observed. This effect could be repeated a number of times until an apparent saturation value was reached of 5–6 mg of Hg/g sample. The BET-nitrogen surface area of this sample was 165 $m^2/g$ and therefore the saturation uptake of mercury vapour appeared to correspond to an area per Hg atom of about 250 $Å^2$.

In another experiment, it was found that when an uncalcined chromium oxide[3], gel *A*, was outgassed at 298 K in the presence of mercury vapour no detectable uptake was observed; the same sample calcined in air *in situ* at 500 K for 16 h adsorbed appreciable quantities of mercury in a similar manner to gel *E*. It is interesting to note that chromium oxide gels calcined at temperatures around 500 K contain appreciable proportions of Cr(VI) in their surface layers[4,5].

Further work is now in progress to ascertain the cause of the significant mercury vapour adsorption on certain chromium oxide gels. Recent mercury adsorption measurements on a nickel-on-pumice catalyst[6] and thermal desorption studies on a platinum–asbestos catalyst[7] may help to explain the apparent mobility of the adsorbed mercury on chromium oxide gels that is indicated by the stepwise uptake of mercury vapour following exposure of the gel to air. Adsorption measurements are being made on gels, before and after exposure to mercury vapour, using a microbalance and a transducer as the pressure-sensitive device.

It is evident that in adsorption studies of vapours on chromium oxide, and perhaps other transition metal oxide gel systems, one cannot tacitly assume that mercury vapour adsorption is negligible.

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[1] Coolidge, A. S., *J. Amer. Chem. Soc.*, **49**, 1949 (1927).

[2] Miles, A. J., thesis, University of Bristol (1964).

[3] Baker, F. S., Sing, K. S. W., and Stryker, L. J., *Chem. and Ind.*, 718 (1970).

[4] Carruthers, J. D., Fenerty, J., and Sing, K. S. W., *Reactivity of Solids*, 127 (John Wiley and Sons, Inc., 1969).

[5] Carruthers, J. D., Sing, K. S. W., and Fenerty, J., *Nature*, **213**, 66 (1967).

[6] Campbell, K. C., and Hislop, J. S., *J. Catalysis*, **13**, 12 (1969).

[7] Affrossman, S., and Erskine, W. G., *Trans. Faraday Soc.*, **62**, 2922 (1966).

# Effect of Carbiding on the Hydrogenolysis Activity of Molybdenum

We have been investigating the catalytic hydrogenolysis of hydrocarbons on metals, and in particular the hydrogenolysis of ethane on the metals of group VIII of the periodic table and on rhenium and the group IB metals[1–5]. Further investigations on molybdenum catalysts showed that hydrogenolysis proceeded readily only at temperatures high enough to cause carbiding of the molybdenum—about 375°–400° C. Moreover, the rate of ethane hydrogenolysis increased progressively with carbiding of the molybdenum. The nature of the effect is described in this communication.

The experiments were conducted in a flow reactor system at atmospheric pressure. The apparatus consisted of a U-shaped assembly comprising two vertical tubular sections of fused silica approximately 10 mm in diameter and 60 mm in length. The two sections were joined at the bottom by a piece of U-shaped capillary tubing. By means of stopcocks at either end, the apparatus could be closed for easy transfer between a high vacuum adsorption system and the flow system used for the catalytic measurements. One of the tubular sections was packed with catalyst down to the juncture between the section and the capillary. This juncture served as an adequate support for the catalyst. The catalyst bed depth was about 15 mm. Incoming gas passed down through a mass of quartz wool in the tubular section not containing the catalyst, then through the U-shaped capillary, and finally up through the bed of catalyst in the other tubular section. The entire cell assembly was surrounded by an electric heater. In the catalytic runs the ethane and hydrogen reactants were mixed with helium before contacting the catalyst. Gas flow was measured by capillary-type flow meters and reaction products were analysed by a chromatographic column connected to the reactor outlet. The molybdenum catalyst used in the experiments was prepared by reduction of $MoO_2$ in flowing hydrogen (500 ml./min) for 16 h at 600° C. Although lower reduction temperatures have been used before[6], we found 600° C preferable. The reduction of the $MoO_2$, which had a surface area of 12.9 $m^2\ g^{-1}$ (S. J. Tauster, personal communication), took place in the reactor. A charge of approximately 1.0 g of $MoO_2$ with a particle size of 10–20 mesh was used.