Another Strong Metal–Support Interaction: High Intrinsic Methanation Activity of an Alumina-supported Platinum Catalyst after High Temperature Reduction without Loss of Chemisorption Ability

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It has been found from pulse surface reaction rate analysis measurements that the intrinsic methanation activity of an alumina-supported platinum catalyst was increased by high temperature reduction without a marked reduction in its chemisorption ability.

Strong metal–support interaction (S.M.S.I.) is recognised as a phenomenon that causes reducible oxide-supported noble metals to lose much of their ability for chemisorption of H_2 or CO without agglomeration of the supported metal after high temperature reduction (H.T.R.; reduction at 773 K).[1] We found that although all titania-supported noble metals examined lost their chemisorption ability after H.T.R., as a consequence of S.M.S.I., the effect of S.M.S.I. on methanation varied from one noble metal to another. In the S.M.S.I. state the intrinsic methanation activity increased for Pt and Pd, while it did not for Rh, Ru, and Ir.[2] This difference in the effect of S.M.S.I. between the processes of CO chemisorption and methanation suggests that the activity enhancement after H.T.R. may be caused by a metal–support interaction different from that causing the reduction in chemisorption ability; that is, an additional metal–support interaction is operating. Here, we report evidence for existence of another strong metal–support interaction.

Pulse surface reaction rate analysis (P.S.R.A.) used for activity measurements has the following advantages: i, the rate constant per active site can be determined directly without any information about the number of active sites,[3] and ii, the methanation rate for the initial state of the catalyst can be measured with minimal influence of the H_2O produced, which is known to destroy the S.M.S.I. state.[4] These advantages exclude the uncertainty which arises over the determination of the exact number of active sites on the S.M.S.I. catalyst and therefore controversy about its high methanation activity.[5]

The alumina-supported Pt (Pt loading, 0.5 wt%) used was a reference catalyst of the Catalysis Society of Japan, JRC-A4-0.5Pt(1). After the catalyst had been heated in an O_2 stream at 723 K for 2 h, it was reduced with H_2 at 523 K for 2 h and subsequently reduced at elevated temperatures for 1 h. The catalyst, which had been reduced at 773 K for 1 h, was heated in flowing O_2 at 723 K for 1 h and then reduced at 523 K for

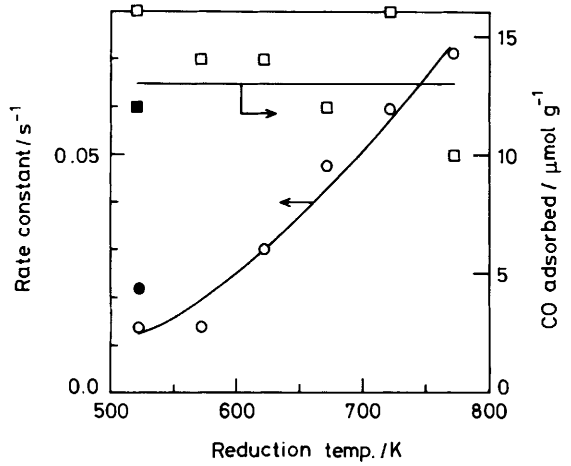

Figure 1. Rate constant per active site determined by P.S.R.A. for methanation on the alumina-supported Pt catalyst at 498 K (○) and the amount of CO adsorbed (□) against reduction temperature. The closed symbols (● and ■) were determined after oxidation of the S.M.S.I. catalyst followed by reduction at 523 K.

2 h. After each reduction, the methanation activity was measured at 498 K using P.S.R.A. in a manner described elsewhere.[3] After each rate measurement, the amount of CO adsorbed on the catalyst was determined by a conventional pulse adsorption method using He as a carrier gas.

Figure 1 illustrates the rate constant for methanation and the amount of CO adsorbed against the reduction temperature. In accord with the literature,[6] the reduction temperature has little influence on CO chemisorption, while it markedly affects the methanation rate; the rate constant after H.T.R. is about five times as large as that after reduction at 523 K (low temperature reduction, L.T.R.). Heating the catalyst exhibiting the high methanation activity in flowing O_2 followed by L.T.R. causes the rate constant to decrease to near the original value. The rate constant determined by P.S.R.A. is not affected by the number of active sites on the catalyst; therefore the results in Figure 1 clearly indicate that H.T.R. increases the intrinsic methanation activity of alumina-supported Pt catalyst, and moreover, that the change in the methanation activity caused by H.T.R. is reversible but not permanent.

High temperature heat treatment often causes sintering of the supported metal, resulting in its low dispersion. It is known that the methanation rate is larger on a low-dispersed catalyst than on a highly-dispersed catalyst.[7] However, the enhanced activity observed after H.T.R. should not be ascribed to this dispersion effect, since the methanation activity was restored almost completely by heating the catalyst in O_2 followed by L.T.R. The minimal effect of the reduction temperature on CO chemisorption also excludes the dispersion effect as a possible cause for the activity enhancement after H.T.R.

A similar variation in the intrinsic methanation activity, *i.e.*, a great increase after H.T.R. and a decrease to near the original value after heating in O_2 followed by L.T.R., was also observed on titania-supported Pt and Pd catalysts.[2] The activity enhancement on these titania-supported catalysts was ascribed to S.M.S.I., since after H.T.R., both titania-supported Pt and Pd were in the S.M.S.I. state.[2] Since a conventional definition of S.M.S.I. is that after H.T.R., a supported metal catalyst loses its chemisorption ability without any metal agglomeration,[1] the present alumina-supported Pt is a non-S.M.S.I. catalyst. The enhanced activity should, therefore, be ascribable to a metal–support interaction different from the conventional S.M.S.I.; that is, after H.T.R., another S.M.S.I. is operating on the present alumina-supported Pt catalyst, by which the intrinsic methanation activity is greatly increased.

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