Absence of High Methanation Activity of Titania-Supported Rhodium, Ruthenium and Iridium Catalysts in their Strong Metal–Support Interaction State

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From pulse surface reaction rate analysis measurements, it was found that the high intrinsic methanation activity of titania-supported rhodium, ruthenium, and iridium catalysts was absent in their strong metal–support interaction state.

For CO hydrogenation, some titania-supported metal catalysts exhibit an extremely high activity in their strong metal–support interaction (S.M.S.I.) state.[1] Although there has been controversy over the high activity of the S.M.S.I. catalyst,[2] its high methanation activity has been confirmed unambiguously both by Rieck and Bell for palladium[3] and by the present authors for palladium and platinum.[4] Since it is known that other metals supported on titania also show S.M.S.I. behaviour after high temperature reduction, this confirmation might lead us to expect that the S.M.S.I. of titania-supported noble metals always results in a high methanation activity. It is, therefore, desirable to examine whether or not the activity enhancement in the S.M.S.I. state is common to all titania-supported noble metals. By use of

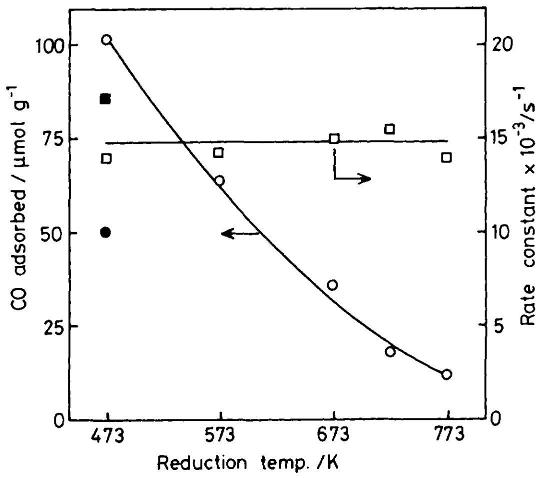

Figure 1. Amount of CO adsorbed (○) and rate constant per active site determined by P.S.R.A. for methanation on titania-supported Rh catalyst at 423 K (□) against reduction temperature. The filled symbols represent the amount of adsorbed CO and the rate constant determined after oxidation of the S.M.S.I. catalyst followed by reduction at 473 K.

Table 1. Amount of CO adsorbed and the rate constant per active site determined by P.S.R.A. for methanation on titania-supported Ru and Ir catalysts.

	CO adsorbed (μmol g⁻¹)		Rate constant (s⁻¹)	
Pretreatment[a]	Ru	Ir	Ru[b]	Ir[c]
I	12.8	15.2	0.470	0.226
II	2.80	0.315	0.390	0.158
III	8.29	9.79	0.399	0.250

[a] I, heated in flowing O_2 at 723 K for 2 h, followed by reduction at 523 K for 2 h; II, after I, reduced at 773 K for 1 h; III, after II, heated in flowing O_2 at 723 K for 2 h, followed by reduction at 523 K for 2 h. [b] At 433 K. [c] At 498 K.

pulse surface reaction rate analysis (P.S.R.A.), we have measured the intrinsic methanation activity of other noble metals supported on titania, in both normal and S.M.S.I. states. In the present S.M.S.I. catalyst system, P.S.R.A. has the following advantages: the rate constant per active site on the catalyst can be determined directly,[4,5] and the rate for the initial state can be measured with minimal influence of the H_2O produced, which destroys the S.M.S.I. state.[6]

Titania-supported rhodium, ruthenium, and iridium catalysts were prepared by impregnating TiO_2 (Nippon Aerosil, P-25) with an aqueous solution of the noble metal chloride ($RhCl_3$, $RuCl_3$, or $IrCl_4$), followed by drying at 383 K overnight. The metal loadings were 2.2 wt % for Rh and 1.0 wt % for Ru and Ir. Prior to the rate and adsorption measurements, the catalyst was subjected to reduction for 2 h in flowing H_2 at various temperatures. The amount of CO adsorbed on the catalyst was determined by a conventional pulse adsorption method at room temperature. The rate constant for methanation was determined by use of P.S.R.A. as described previously.[4,5]

For the titania-supported Rh catalyst, the amount of CO adsorbed and the rate constant for methanation are plotted in Figure 1 against the reduction temperature. As the reduction temperature increases, the amount of adsorbed CO decreases monotonically to 1/10 of the original. When the catalyst, which has already lost its chemisorption ability, is heated in flowing O_2, the chemisorption ability is considerably restored. These observations indicate that the drastic decrease in the amount of adsorbed CO results primarily from S.M.S.I., and that sintering of the supported Rh metal in the catalyst is a minor factor. Relative to its remarkable influence on the chemisorption ability, the reduction temperature scarcely affects the methanation rate; the rate constant is almost the same irrespective of the reduction temperature. Furthermore, the rate constant for methanation is not much altered by oxidation of the S.M.S.I. catalyst followed by reduction at 473 K.

Because P.S.R.A. can give directly the rate constant per active site on the catalyst,[4,5] the results shown in Figure 1 indicate unambiguously that the intrinsic methanation activity of titania-supported Rh catalyst is the same in both normal and S.M.S.I. states. This is in marked contrast to the results for titania-supported Pt and Pd catalysts, where the rate constant for methanation is about ten times larger in the S.M.S.I. state than in the normal state.[4]

Titania-supported Ru and Ir also exhibited the chemisorption behaviour similar to that for Pt, Pd, and Rh, as summarized in Table 1; as a consequence of S.M.S.I., high temperature reduction results in marked loss of chemisorption ability. However, the methanation activity variation appeared to be different; relative to the normal state, S.M.S.I. does not lead to activity enhancement but rather to a slight decrease in rate constant. This is again in marked contrast to the results for Pt and Pd[4] and even to that for Rh.

It is noteworthy that although all titania-supported noble metals examined show similar adsorption behaviour after high temperature reduction, the methanation activity variation between in the normal and S.M.S.I. states is different from one noble metal to another. This observation may throw light on the mechanism of S.M.S.I. The cause of this activity variation is now under investigation.

Received, 21st April 1987; Com. 521

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