Supported Palladium Catalysts

A COMPARISON OF SOLVATED METAL ATOM IMPREGNATED AND CONVENTIONALLY PREPARED CATALYSTS

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In the last fifteen years a promising new method for preparing highly dispersed supported metal catalysts, called solvated metal atom dispersion (SMAD), has been developed by Klabunde and co-workers (1-9). This method employs the metal vapour technique, where metal atoms, such as nickel, cobalt, iron and magnesium, are solvated at liquid nitrogen temperature, 77 K, in toluene or some other appropriate solvent. Upon being warmed, the solvate decomposes and metal clustering begins. The nucleation process competes with a "reaction channel" where the growing clusters react with the host solvent. These growing clusters incorporate carbonaceous fragments, resulting from the cleavage of organic solvent, and are stabilised as amorphous "pseudo-organometallic" powders. The powders represent a special new class of materials which behave as novel heterogeneous catalysts. The incorporated carbonaceous fragments do not poison the catalysts, but instead aid their catalytic activity (10) and apparently provide a better means of attaching the metallic particles to the catalyst support surfaces (5, 7, 11).

In the present work, which is based on the SMAD method, a modified technique, called SMAI – solvated metal atom impregnation – and described in the Scheme, has been used

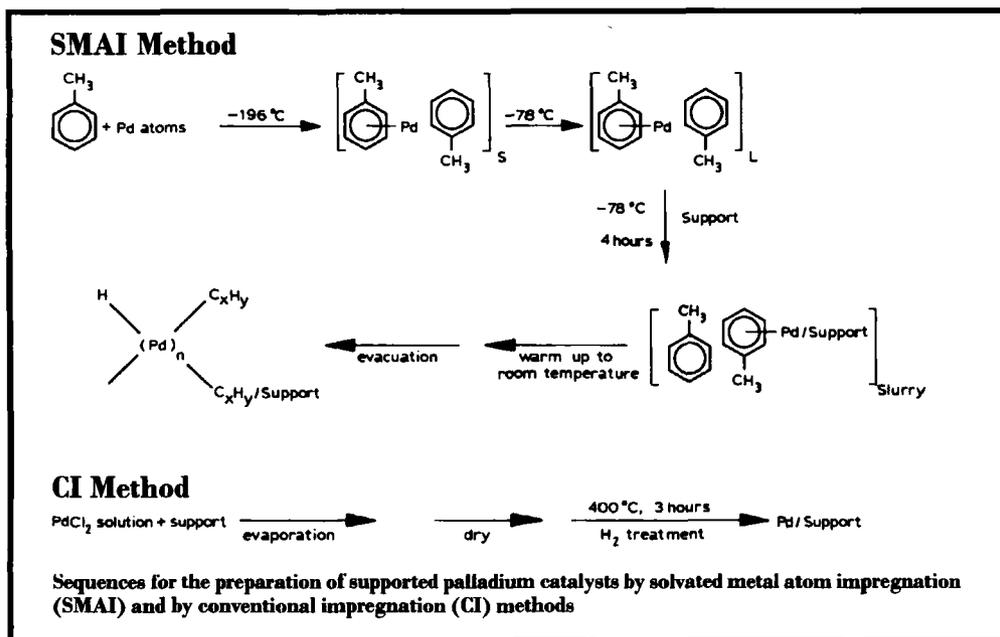[*] correspondence to Hangzhou Semiconductor Company, Hangzhou, Zheijiang, P. R. China

Sequences for the preparation of supported palladium catalysts by solvated metal atom impregnation (SMAI) and by conventional impregnation (CI) methods

Table I
Elementary Analysis of the Carbon and Hydrogen Content in the Samples

Sample	Carbon, per cent	Hydrogen, per cent
0.42% Pd/SiO₂ (SMAI)	0.9	0.8
0.42% Pd/SiO₂ (CI)	No	No
1.39% Pd/Al₂O₃ (SMAI)	2.0	1.5
1.39% Pd/Al₂O₃ (CI)	No	No
1.50% Pd/ZrO₂ (SMAI)	1.5	0.9
1.50% Pd/ZrO₂ (CI)	No	No
1.56% Pd/MgO (SMAI)	1.0	0.6
1.56% Pd/MgO (CI)	No	No
1.65% Pd/TiO₂ (SMAI)	1.2	1.0
1.65% Pd/TiO₂ (CI)	No	No

for preparing various supported palladium catalysts. The reactions chosen for study are the methanation of carbon dioxide in a flow system under a pressure of 10 atmospheres and the hydrogenation of benzene in an autoclave, the latter yielding mainly hexamethylene. For comparison corresponding supported palladium catalysts prepared by conventional impregnation, CI, are also shown in the Scheme.

Results and Discussion

Catalysts were prepared by the solvated metal atom impregnation method using purified toluene as the solvating medium. The purified supports, of silica, γ-alumina, magnesia, zirconia and titania were introduced into the system by a specially designed Schlenk Operating Line. The occurrence of carbonaceous fragments in the supported palladium SMAI catalysts was confirmed by elementary analysis and by the pyrolysis of a catalyst under a stream of hydrogen. The carbon and hydrogen contents in the SMAI samples are given in Table I. It can be seen that the SMAI catalysts contain a small amount of organic fragments which were formed during the preparation, and result from the decomposition of toluene. Furthermore, Figure 1 shows methane release upon pyrolysis of a 1.39 per cent palladium supported on alumina (SMAI) catalyst under hydrogen, as a function of temperature. This indicates that the supported palladium SMAI catalyst is rich in carbonaceous species

which are mainly in the form of C₁ species, such as C, CH, CH₂, etc. These C₁ species contribute to the formation of methane only under a hydrogen stream. Thus at this stage the small palladium crystallites in the SMAI samples are surrounded by a layer of residual carbonaceous species, and then the tiny crystallites combine to form clusters of metal particles which then attach to the support surface through carbonaceous linkages. Therefore as a catalytic centre, the small palladium cluster is pseudo-organometallic in nature, as well as being present in a highly dispersed form.

The average size of palladium particles in SMAI catalysts is less than 2.0 nm, which is about ten times smaller than those in the corresponding CI catalysts, see Table II. Such high dispersions of metallic particles (clusters) in SMAI
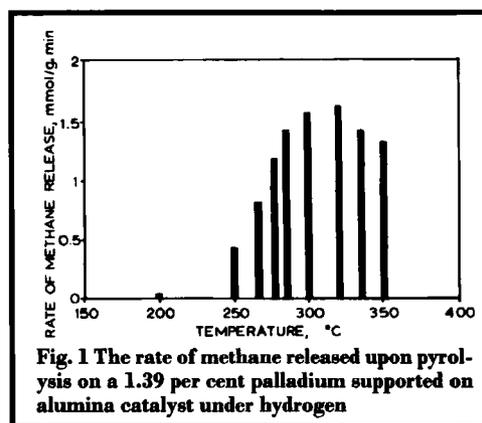

Fig. 1 The rate of methane released upon pyrolysis on a 1.39 per cent palladium supported on alumina catalyst under hydrogen

Table II

Comparison of Palladium Particle Sizes and Extent of Reduction for Supported SMAI and CI Catalysts

Catalyst	Particle size, d, nm		Extent of reduction, per cent Oxygen titration
	Hydrogen adsorption	TEM	
0.42 % Pd/SiO$_2$ (SMAI)	1.8	1.4	95
0.42 % Pd/SiO$_2$ (CI)	19	15	58
1.39 % Pd/Al$_2$O$_3$ (SMAI)	1.6	1.6	98
1.39 % Pd/Al$_2$O$_3$ (CI)	14	11	45
1.56 % Pd/MgO (SMAI)	1.8	1.7	95
1.56 % Pd/MgO (CI)	6.9	6.8	52

samples are attributed to their extremely mild preparation conditions, whereas the metallic particles on CI samples are formed under high temperature hydrogen treatment conditions and only achieve a low dispersion. In addition to the dispersions, Table II also shows another important feature, which is the extent of the reduction of the supported metal in the SMAI samples. The percentage reduction of palladium particles on these SMAI catalysts, measured by oxygen titration, reaches 95 per cent, which is almost twice that of the corresponding CI catalysts.

Since the supported palladium SMAI catalysts possess such novel characteristics they behave differently, for example during carbon dioxide methanation and benzene hydrogena-

tion, in their catalytic activity and selectivity. Comparisons of these catalytic behaviours are illustrated in Tables III and IV, respectively. From Table III it can be seen that the rates of methane formation on the SMAI catalysts are much higher than those on CI catalysts, especially for palladium supported on titania. The existence of a support effect on the reactivity for methane formation is observed, with the order titania > zirconia > magnesia > silica. For benzene hydrogenation, however, no obvious support effect is observed and the supported palladium SMAI catalysts exhibit unusual reactivity and selectivity compared with the corresponding CI catalysts.

In short, comparing the catalytic behaviours

Table III

Comparison of Catalytic Activity of Supported Palladium Catalysts Prepared by SMAI and CI for Carbon Dioxide Methanation[a]

Catalyst	Treatment	Rate of methane formation, mmol/g of Pd/h	Carbon dioxide conversion, per cent
0.42% Pd/SiO$_2$ (SMAI)	No	44	5
0.42% Pd/SiO$_2$ (CI)	H$_2$, 400°C, 3 h	6	–
1.50% Pd/ZrO$_2$ (SMAI)	No	482	18
1.56% Pd/MgO (SMAI)	No	143	16
1.56% Pd/MgO (CI)	H$_2$, 400°C, 3 h	30	6
1.65% Pd/TiO$_2$ (SMAI)	No	1712	21
1.65% Pd/TiO$_2$ (CI)	H$_2$, 400°C, 3 h	42	8

[a] Reaction Conditions: total flow rate = 80 ml/min, H$_2$/CO$_2$ = 4, reaction pressure = 10 atm, reaction temperature = 300°C

Table IV

Comparison of the Reactivity of Supported Palladium SMAI and CI Catalysts for Benzene Hydrogenation[a]

Catalyst	Rate of benzene hydrogenation, per cent/h/g of Pd	Conversion of benzene, per cent
1.39% Pd/Al₂O₃ (SMAI)	696	13.5
1.39% Pd/Al₂O₃ (CI)	0	0
1.50% Pd/ZrO₂ (SMAI)	66	1.3
1.50% Pd/ZrO₂ (CI)	0	0
1.56% Pd/MgO (SMAI)	498	9.8
1.56% Pd/MgO (CI)	20	0.4
1.65% Pd/TiO₂ (SMAI)	599	12.0
1.65% Pd/TiO₂ (CI)	0	0

[a] Reaction Conditions: initial hydrogen pressure 30 atm, reaction temperature 140°C, reaction time = 4.5 h, Reactor: autoclave (170 cm³)

of SMAI and CI catalysts leads to the conclusion that the SMAI catalysts exhibit a much higher reactivity and selectivity than CI catalysts for the hydrogenation of benzene and the methanation of carbon dioxide. The highly active properties of the SMAI catalysts can probably be attributed to the presence of residual carbonaceous fragments which surround the small metallic crystallites, highly dispersed particles in metallic form and a higher degree of reduction of the supported palladium. However, for carbon dioxide methanation, a study of catalytic stability shows that the highly active SMAI catalysts have very poor stability compared with the corresponding CI catalysts. The explanation for the shorter life of the SMAI catalysts remains obscure; however, it may be related to the adsorbed acidic carbon dioxide species which affect the decomposition of metallic form particles (clusters) during the reactions.

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Aluminium-Ruthenium High-Temperature Alloys

In a continuing search for materials that combine strength, toughness and oxidation resistance at high temperatures, a variety of intermetallic compounds have been considered. A simple screening test identified aluminium-ruthenium, iridium-niobium, ruthenium-scandium and ruthenium-tantalum as worthy of investigation and some of the properties of these tough binary alloys were presented here in July 1992.

A further communication on the properties of aluminium-ruthenium alloys has now been published (R. L. Fleischer and D. W. McKee, "Mechanical and Oxidation Properties of AlRu-Based High-Temperature Alloys", *Metall. Trans. A*, 1993, **24**, (3), 759–763).

The authors confirm the interesting properties of Al₄₇Ru₅₃ and Al₄₈Ru₅₁Y, which combine low oxidation rates at 1100°C with good mechanical properties at room temperature. Al₄₃Ru₅₂Sc₅ has good high-temperature mechanical properties, and at 1350°C the oxidation rate is only marginally unacceptable, indicating that the alloy may be useful at lower temperatures.