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Reviews

Solvated Metal Atom Dispersed Catalysts

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Synthetically useful amounts of solvated metal atoms can be prepared by metal evaporation and low-temperature solvent trapping. When these solvates are warmed metal atom nucleation takes place followed by particle growth. In the presence of a high surface area catalyst support, such as SiO_2 or Al_2O_3, metal atom nucleation takes place at surface –OH groups, followed by particle growth. This procedure serves as an effective method for the preparation of very highly dispersed metallic heterogeneous catalysts, (solvated metal atom dispersed (SMAD) catalysts). Unusual particle structure and high dispersion allow these materials to be extremely active in many catalytic schemes. In addition, the SMAD procedure can be used to prepare new bimetallic particles that are not possible to prepare by conventional procedures. For example, layered bimetallic structures can be obtained whereby the more oxophilic metal reacts with the support –OH groups first, in a sacrifical way, followed by deposition and growth of the second, less oxophilic metal (e.g., $Co–Mn/Al_2O_3$). Catalytic properties are altered significantly by the effect of one metal on another, due to this layered structure. In other examples, highly dispersed alloy particles can be prepared by the SMAD procedure (e.g., Pt–Sn). The SMAD procedure represents a new approach to the direct preparation of supported small metal particles and allows the possibility of preparing hitherto unknown layered structures and metastable alloy particles.

Introduction

Some of the most important synthetic materials discovered in the past half-century are metallic, highly dispersed heterogeneous catalysts. The commercial importance can be gauged by the statement that "20% of our gross national product is dependent on such catalysts".[1]

The preparation of small zerovalent metallic particles on catalyst supports has been carried out by two general methods:

(1) For 60 years the **metal ion reduction** procedure has served the catalysis community well.[2] In this procedure metal salts, usually halides or nitrates, are dissolved in water and the solid catalyst support, usually SiO_2 or Al_2O_3, is impregnated by the metal salt. This impregnation is carried out by slurrying the catalyst support in the aqueous metal ion solution followed by water evaporation. Ion exchange has also been used to prepare the desired dispersed metal ions. The dispersed metal salt is then converted to a metal oxide by treatment at high temperature with oxygen/water. Finally, a hydrogen reduction step is carried out where the metal oxide is reduced to the metallic state. Very often metal atom clustering occurs during this step, and metal particles are thus formed and stabilized. Scheme I illustrates this process with $NiCl_2$ as an example. Note the formation of Ni(s), which is a metallic particle trapped on the surface of the SiO_2 support. The size of this metallic particle is quite variable and is often made up of hundreds or thousands of Ni atoms. Thus, during the reduction process, considerable atom agglomeration (sintering) takes place, and this step is often difficult to control due to the high temperatures that are employed. The particles obtained in this way are usually crystalline and spherical, although rafts and other similar structures have been observed. The reduction step is controlled mainly by thermodynamics, although kinetics certainly cannot be ignored.

Scheme I. Example of a Classical Metal Ion Reduction Scheme To Yield a Ni/SiO₂ Heterogeneous Catalyst[a]

$$NiCl_2 + H_2O \rightarrow Ni^{2+}(aq) + 2Cl^-(aq)$$

$$Ni^{2+}(aq) + 2Cl^-(aq) + SiO_2(s) \rightarrow \underbrace{Ni^{2+}\ Cl^-\ Cl^-}_{\substack{SiO_2 \\ \text{impregnated}}}$$

$$\underbrace{Ni^{2+}\ Cl^-\ Cl^-}_{SiO_2} + H_2O \xrightarrow[\text{heat}]{O_2} \underbrace{Ni^{2+}\ O^{2-}}_{SiO_2} + 2HCl$$

$$\underbrace{Ni^{2+}\ O^{2-}}_{SiO_2} + H_2 \xrightarrow{500\ ^\circ C} \underbrace{Ni(s)}_{SiO_2} + H_2O$$

[a] Ni(s) is generally a metal cluster particle made up of at least several hundred Ni atoms.

Scheme II. Example of a Coprecipitation Metal Ion Reduction Scheme

$$NiCl_2 + AlCl_3 + H_2O \rightarrow Ni^{2+}(aq) + Al^{3+}(aq) + 5Cl^-(aq)$$

$$Ni^{2+}(aq) + Al^{3+}(aq) + 3(NH_4)OH + 5Cl^- \rightarrow \frac{Ni^{2+}Cl^-Cl^-}{Al(OH)_3} + 3NH_4^+ + 3Cl^-$$

$$\frac{Ni^{2+}Cl^-Cl^-}{Al(OH)_3} + H_2O \xrightarrow[500\ ^\circ C]{\text{air}} \frac{Ni^{2+}O^{2-}}{Al_2O_3} + 2HCl$$

$$\frac{Ni^{2+}O^{2-}}{Al_2O_3} + H_2 \xrightarrow{500\ ^\circ C} \frac{Ni(s)}{Al_2O_3} + H_2O$$

A variation of metal ion reduction involves coprecipitation of the catalytic metal with the support. In this way, a more thorough and deeper impregnation can be accomplished, and this can be helpful for obtaining a higher dispersion[3] and to slow down the kinetic aspects of particle growth. Scheme II illustrates this method. Advantages of the metal ion reduction methods are (1) experimentally

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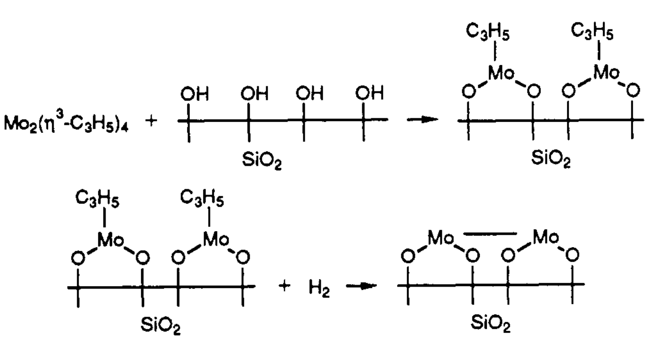
[1] Haensel, V.; Burwell, R. *Sci. Am.* **1971**, *225*, 46.

[2] Anderson, J. R. *Structure of Metallic Catalysts*; Academic Press: New York, 1975.

[3] Li, Y. X.; Hsia, Y. F. *Oil Gas (Chinese)* **1985**, *1*, 161.

Scheme III. Use of Stable Organometallic Compounds as Precursors to Heterogeneous Catalysts[7,8]



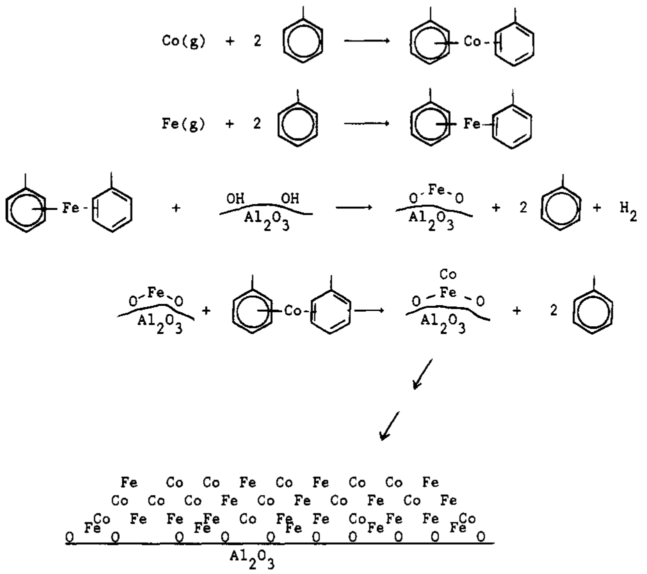
rather easy and can be readily scaled up and (2) relatively low cost. Disadvantages are (1) difficulty in obtaining complete reduction of the metal ions to the zerovalent state, (2) sintering during high temperature, salt decomposition, and reduction steps, and (3) difficulty in reducing two metals simultaneously or sequentially so that bimetallic clusters/particles are formed.

(2) a. Decomposition of organometallic reagents on catalyst supports is a more recent innovation.[4,5] Stable organometallic compounds can be adsorbed from the vapor state or from solutions. Once adsorbed, controlled thermolysis can lead to loss of ligands and metal particle growth. If mononuclear organometallics are employed, adsorbed metal atoms can be formed and then they aggregate to larger metal particles (Scheme III).[6-8] If organometallic cluster compounds are employed, it may be possible to form a well-defined cluster of metal atoms on the support surface. In practice, however, stripping ligands to deposite well-defined clusters has not been easy, and rarely have successful experiments been reported. Cluster aggregation to larger particles frequently occurs under surprisingly mild conditions. And, at the other extreme, cluster decomposition by strong interaction with the support surface has also been encountered quite often.

An additional innovative approach in this area has been to decompose the organometallic in a plasma discharge, so-called plasma assisted decomposition of organometallics in the presence or very near an appropriate catalyst support.[9] When plasma and thermal decomposition are compared, it is usually found that quite different metallic particles are formed. Major advantages of the use of stable organometallics are (1) no need for high-temperature reduction steps, thereby avoiding one step where sintering can occur and (2) with cluster compounds, the possible advantage of producing well-defined (known cluster size) supported clusters. Major disadvantages of these organometallic processes are (1) limited selection of stable organometallics and cluster compounds that can be experimentally utilized, (2) difficulty in completely stripping ligands, (3) difficulty in preparing supported bimetallic particles.

b. Solvated Metal Atom Dispersed Catalysts (SMAD). A second approach to using organometallic reagents is to use weakly ligand stabilized metal atoms, or "solvated metal atoms".[10] One way of looking at such solutions is that the metals have been dissolved in organic solvents in a supersaturated state. The way this is done is to break down the crystalline/bonding forces in a solid metal by evaporating the metal and trapping the atoms in a cold solvent. Choice of solvent and choice of metal dictate how stable the metal solvate is.

Scheme IV. Solvated Metal Atom Dispersion (SMAD) Initiation and Growth of a Bimetallic Heterogeneous Catalyst[15]



Since such metal solvates are often thermally unstable, they can be used as precursors to metal particles. When the solvated metal atom solutions are warmed, metal cluster/particle nucleation takes place. In the presence of a catalyst support, nucleation and particle growth on the support surface can lead to highly dispersed heterogeneous catalysts, which has been termed "solvated metal atom dispersed" or SMAD.[11,12] Scheme IV outlines an example of the SMAD procedure. The advantages of this approach are (1) many metal–solvent combinations can be used, (2) very high dispersion of metal is achieved and no reduction step is necessary, thereby avoiding sintering, (3) since metal particle deposition occurs at low temperature, kinetics control the growth process, and unusual particle morphologies can be encountered that possess high reactivities,[13,14] (4) metal particles are securely anchored to catalyst supports by reaction of solvated atoms with surface hydroxyl groups in an initial oxidation–reduction step,[15] (5) bimetallic metal particles can be grown, sometimes with layered morphologies,[14-17] as metastable bimetallic particles or alloys, and (6) the handling of toxic organometallics, such as $Ni(CO)_4$, or other stable but

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(4) Ichikawa, M. *J. Chem. Soc., Chem. Commun.* **1976**, 26.

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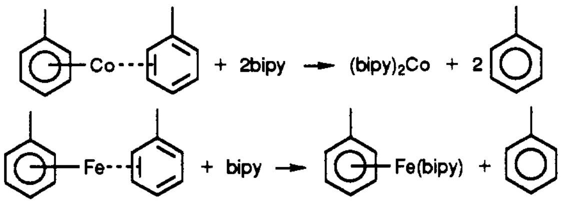
sensitive carbonyls is avoided. Disadvantages are (1) the need for metal vapor reactors,[18,19] (2) the SMAD procedure is not routine to carry out, and skillful experimentalists are needed, and (3) scaleup has not been demonstrated.

We will now take a closer look at the SMAD procedure and SMAD catalysts.

Solvated Metal Atoms

To be able to solvate metal atoms and thus trap them in liquid solvents for later use greatly facilitates the use of zerovalent metals in many ways. As early as 1976 toluene-solvated nickel atoms were used for preparation of a phosphitenickel(0) complex simply by addition of $(EtO)_3P$ to the Ni–toluene solution following by warming from −90 °C to room temperature.[10] These experiments confirmed that solvated nickel *atoms* were present in the toluene after toluene liquefaction. Later, new and unusual stable organometallic compounds were prepared from toluene-solvated atoms; for example, $(bipy)_2Co(O)$[20] and (η^6-arene)Fe(bipy).[21] By 1990 a large number of useful syntheses have employed solvated metal atoms as important precursors. Zennick has made excellent progress and has recently reviewed this area.[22]



Although in theory a large number of metal atom–solvent combinations could be proposed for further organometallic synthetic schemes, in practice only a limited number of combinations have found substantial use. Solvation implies a weak metal atom–solvent interaction. If it is too strong, a stable organometallic compound results, such as Cr or V with toluene to form bis(toluene) Cr, V compounds. Weaker interactions, in the present context more useful, are formed with Mn–, Fe–, Co–, and Ni–toluene combinations where one or both of the toluene ligands are labile, which has been demonstrated by the fact that they can be displaced by ligands that can bind more strongly (bipy, diphos, phosphites, etc.)

Generally, the requirements of the solvent are that it (a) is volatile, so it can be handled conveniently and removal is not a problem, (b) forms a weak-to-moderate bonding interaction with the metal atom in question, (c) has a low melting point so that thermally unstable solvates can be manipulated in solution form, and (d) is relatively unreactive.

Table I lists solvent–metal combinations that have been successfully employed and the approximate upper limit of temperatures where the metal atom solutions can be manipulated. Probable structures have also been indicated, and at this point it is useful to consider what is actually known about such structures.

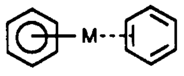
Table I. Metal Atom Solvent Combinations

metal	most appropriate solvents	probable struct	approx thermal stability, °C	ref
Mn	toluene	bisarene sandwich	−40	
Fe	toluene	bisarene sandwich	−30	
Co	toluene	bisarene sandwich	−50	
Ni	toluene THF	bisarene sandwich, tetra-THF, Ni–O binding	−80	10, 38
Zn	THF, diglyme, dioxane	tetra-THF, Zn–O binding		
Cd	THF, dioxane, toluene, diglyme			38
In				
Sn	THF, acetone, dioxane, toluene, ethanol, diglyme			
Pb	THF, diglyme, dioxane			
Ag	THF, toluene			11
Pd	THF, toluene			11
Pt	toluene	bisarene sandwich		59
Re	toluene	arene–metal hydride		51

Unfortunately, due to the lability of solvated metal atoms, isolation and characterization of the pure adducts has not been possible for the important metals such as Fe, Co, and Ni. Even demonstrating the proper stoichiometry of solvent:metal is difficult, for example, for arene = sol and M = Fe, Co, Ni. Andrews and Ozin[23] have nicely summarized what is known due to matrix isolation experiments on arene–metal atom matrices. They discuss a variety of clever approaches at trying to ascertain if arene:M ratios are 1:1 or 2:1 and discuss the most likely initial steps in metal atom nucleation.[23-27] Andrews and Ozin support an arene:metal atom ratio of 2:1.[23] However, Efner and co-workers[28] found that 1:1 stoichiometries are possible in very low temperature matrices. And Lamanna and co-workers[29] demonstrated that a triple-decker sandwich compound of arene:Cr:arene:Cr:arene can be isolated, which demonstrates the possibility of similar structures being present with "solvated" systems.

If it is assumed that two arene solvent molecules are involved, each as a six-electron-donor molecule, the valence electron counts are very high for Fe, Co, and Ni. Thus, it seems likely, at least in low-temperature liquid arenes, that the arenes (benzene, toluene, or mesitylene)

M	valence electrons	M	valence electrons
Cr	18	Co	21
Mn	19	Ni	22
Fe	20		



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would be labile for Fe, Co, and Ni. Indeed, with (arene)$_2$Fe one arene is readily displaced,[21] while for (arene)$_2$Co[20] and (arene)$_2$Ni[10] both arenes are readily displaced.

Thus, it is usually tacitly assumed that the later transition metals are solvated by two arene molecules, with perhaps one being bound as η^2 or η^4, and are quite labile, perhaps rapidly exchanging with other arene molecules. However, further work on structural elucidation is warranted, and the possibility of rapid, reversible C–H activation also being dynamic processes cannot be discounted.[30]

Furthermore, the initial steps in metal atom nucleation to yield $(sol)_xM_2$, $(sol)_xM_3$, etc., are not understood and could be the subject of interesting further research.

Monometallic SMAD Catalysts

A. Preparation. Most SMAD catalysts have been prepared as follows: Metal is evaporated under vacuum and codeposited with solvent vapor on the inside cold walls of the metal vapor reactor.[18,19,31,32] After deposition is complete, the frozen matrix is warmed until the solvent melts. This solution can then permeate a pretreated catalyst support, whereupon metal atoms nucleate on the support surface.

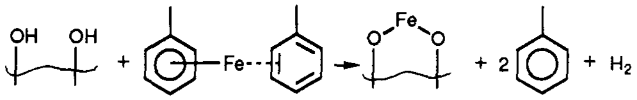
A modification of this method is to evaporate the metal directly into a cold liquid solvent in a rotating metal vapor reactor.[33,34] The resultant metal solvate can contact a slurry of the support in the reactor or can be removed for further manipulation such as filtering at low temperature in order to ensure a homogeneous metal solvate, which can then be used to impregnate the solid support.[34]

Of course the metal concentration can be varied as well as the temperature and time of impregnation, all of which can have an effect on the final metal particle size and, perhaps, morphology.

B. The Impregnation Step. Much remains to be learned about the impregnation mechanism. The surface area of the support definitely affects metal particle size. Presumably higher surface area supports possess more nucleation sites, and more such sites would dictate the formation of smaller metal particles in the final product. It appears that both Lewis and Bronsted acid sites can serve as nucleation sites. For example, Ni–toluene impregnations of Al_2O_3, SiO_2, SiO_2–Al_2O_3, and SiO_2–ZrO_2 supports yielded SMAD catalysts that were more active as the acid strength of the support increased.[33] This observation can be explained by surface area effects; more nucleation sites yield a larger number of smaller particles and therefore more nickel particle surface.

It was also found that very low loadings of metal on a support (<1% by weight) yielded catalysts of low activity. The most active catalysts, on the per gram of metal basis, were found when about 2–4% loadings were employed. Thus, it seemed that either sufficiently large particles were necessary for good catalytic activity and/or that the first metal atoms were sacrificed in some way.[33,35]

Further studies showed that metal nucleation, at least with Fe, Co, and Ni, occurred on support hydroxyl groups and that the first metal atoms to deposit were indeed sacrificed by being oxidized by the hydroxyl groups.[15,36]



C. Effect of Solvent. Choice of solvent is quite important. During the growth stage the forming metal particles exhibit high reactivities with the host solvent, even at temperature below −100 °C. Both C–H and C–C cleavage of the solvent can occur.[13,14,35,37,38] Such high reactivity is believed to be due to the unusual morphology of the growing particles, with many reactive defect sites being available for such reactions.[14] Carbonaceous fragments are thus incorporated into the metal particles.

In one series of experiments metal particles were formed from M–solvent pairs, where solvent = toluene, pentane, perfluorocyclohexane, and xenon.[33] No catalyst support was used in these experiments. The goal was to determine what solvent polarity and complexing power had on catalytic activity. In general it was found that the M–pentane powders (no catalyst support) showed the highest activities for hydrogenation of 1-butene and 1,3-butadiene. Similar results were found for perfluorocyclobutane, except in the case of cobalt where a great deal of C and F were incorporated into the particles, and low catalyst activities resulted.[33]

Interestingly, xenon as a "solvent" yielded very large metal crystallites with low surface area and little comparative catalytic activity.

The conclusion from these studies is that the most selective catalysts could be obtained by using the more strongly complexing solvents such as THF or toluene. Halogenated solvents are to be avoided.

Another series of experiments were carried out with Ni/Al_2O_3 SMAD catalysts where the solvents were varied from toluene, mesitylene, α,α,α-trifluorotoluene, and *m*-bis(trifluoromethyl)benzene.[39] Highly dispersed, small particles were formed on the Al_2O_3 support. However, the fluorinated solvents allowed a great deal of C and F incorporation into the growing metal particles, and this led to surface nickel fluorides that greatly diminished catalyst activity.[39]

Studies such as these have led to the following conclusions about solvent choice: (1) Avoid heteroatom-containing solvents if possible (O, F, Cl, S, etc.). (2) Employ solvents that can form weak complexes with the metal atoms—alkanes and inert gases do not work as well as aromatics, especially when preparing supported catalysts. (3) Incorporation of C, H from the solvents cannot be avoided, but this is not necessarily a disadvantage.

D. Effect of Support. Nickel/support SMAD samples prepared from toluene-solvated Ni atoms were tested as catalysts for hydrogenolysis of methylcyclopentane, hydrogenation of toluene, dehydrogenation of isopropyl alcohol, and methanation of carbon monoxide.[35] Supports employed were MgO, Al_2O_3, SiO_2, and carbon. Conventional catalysts were compared with the SMAD systems. Generally, support effects were not very significant for the SMAD catalysts, except in the case of methanation reactions over Ni/MgO. In this case a bifunctional effect may be important.[35]

Overall, support effects are not pronounced except for two findings: (1) surface area tends to allow better dispersion, and (2) acid sites also allow better dispersion.

Zeolites have also been employed as supports in SMAD procedures. For example, Fe–toluene and Co–toluene

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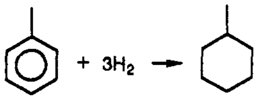
solvates have been allowed to permeate NaY zeolite. It was reported, on the basis of Mossbauer data, that very small metal particles were deposited within the zeolite cages.[40] It is somewhat surprising that such selective deposition would be encountered, however, and definitive data concerning the question of whether the metal is actually in the cages are needed.

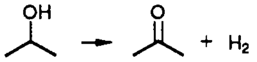
Characterization and Catalytic Properties of SMAD Metal Particles

A. Monometallic SMAD Catalysts. A wide variety of spectroscopic methods (XPS, XRD, Mossbauer, EXAFS), gas adsorption methods, and catalytic probe reactions (toluene hydrogenation, CO reduction, isopropyl alcohol dehydrogenation, and methylcyclopentane hydrogenolysis) have been employed for the study of SMAD catalysts (eqs 1–5).



(1)

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2)$$



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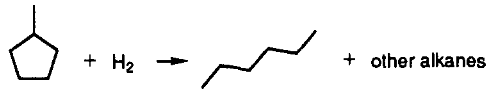

(4)

$$CO + 2H_2 \rightarrow (CH_2)_n + H_2O \quad (5)$$

With nickel as the catalytic metal, properties were examined by toluene hydrogenation and methylcyclopentane hydrogenolysis, and examples of structure-sensitive reactions (particle size effects) were encountered.[32] That is, maximum rates of conversion were encountered at metal loadings of about 2% on MgO. Since lower loadings should lead to small particles, it was proposed that optimum particle sizes were encountered at the 2% loading on this particular support.

Unfortunately, the real size of the particles could not be determined. Supported SMAD particles never exhibit powder X-ray patterns, and this is due to their very small crystallite sizes. However, CO and H_2 chemisorption studies combined with O_2 titration studies showed that the Ni particles were nearly fully metallic with high metallic surface areas (50–150 m^2/g), compared with conventionally prepared (Ni^{2+} reduction) Ni/MgO catalysts. The catalytic activities of the Ni/MgO SMAD catalysts outstripped by many times the activity of conventionally prepared systems.[32] Furthermore, the Ni particles were very stable toward sintering, even up to 500 °C in a stream of H_2. Similar findings for Ni/Al_2O_3 catalysts were also reported.[39]

It was also found that relatively low loadings of Fe or Co/SiO_2 SMAD catalysts could be used in Fischer–Tropsch reactions, and high activities were encountered.[41] Conventionally prepared analogous catalysts were not active at such low loadings (3–4% by weight).

Fischer–Tropsch reactions of SMAD Fe/NaY zeolite and Co/NaY zeolite catalysts have also been studied.[40] Some selectivity toward the formation of C_4 hydrocarbons was encountered, and this was attributed to the possibility that the zeolite cavities accommodated the growth of very small Fe or Co particles. The purposeful growth of large particles on the zeolite surface (not within the cavities) led to changed catalytic properties whereby higher methane yields resulted.[40] Overall, numerous studies of monometallic SMAD systems have allowed the following conclusions: (1) The solvated atoms nucleate, probably at surface O–H groups or at Lewis acid sites. The growth of the particles proceeds until metal in the solution is depleted. In this way, paricle size can be affected by metal concentration. For Ni/MgO optimal particle sizes for certain catalytic reactions were obtained at 2% by weight metal loadings. For Ni/Al_2O_3 slightly lower loadings were optimal. (2) The deposited SMAD particles are very small when these light loadings were used, probably <25 Å. And they show *no crystalline nature* according to XRD analysis.

Table II. Metal Surface Areas of Metal Powders (Unsupported) Derived by the SMAD Procedure

metal	solvent	surf. area, m^2/g	av cryst size, Å	av particle diam (calc from surf. area), Å	ref
Ni	pentane	47, 60, 80	25–36	143	11, 13, 32
	hexane	45, 70		96	10, 12
	heptane	37		182	13
	octane	53		127	13
	perfluorocyclobutane	90			33 33
	xenon	20			33
	toluene	30, 100			10, 33
	THF	400			10
Co	pentane	90	18–23		33
	perfluorocyclobutane	100			33
	xenon	40			33
Fe	pentane	170			33
	perfluorocyclobutane	130			33
	xenon	10			33

Table III. Metal Surface Areas of Monometallic SMAD Catalysts (Supported on SiO_2, Al_2O_3, or MgO)[a]

metal (% loading)	support (surf. area, m^2/g)	metal surf. area, m^2/g	av cryst size, Å	ref
Ni (22)	Al_2O_3 (170)	30		33
Ni (5)	Al_2O_3 (170)	55	<40	11, 33
Ni (70)	SiO_2 (270)	31		33
Ni (8)	SiO_2 (270)	37	<40	11, 33
Co (17)	Al_2O_3 (170)	49		32
Co (4)	Al_2O_3 (170)	52		32
Co (9)	SiO_2 (270)	59		32
Co (4)	SiO_2 (270)	76		32
Ni (0.4)	MgO (90)	39		32
Ni (0.6)	MgO (90)	67		32
Ni (1.6)	MgO (90)	19		32
Ni (2.7)	MgO (90)	110		32
Ni (2.8)	MgO (90)	53		32
Ni (6.2)	MgO (90)	145		32
Ni (8.9)	MgO (90)	37		32

[a] All in toluene solvent.

A SMAD particle growth scheme is depicted in Scheme IV (in this case for two metals), and Tables II and III summarize much of the data.

Catalytic activites of SMAD systems were invariably extremely high compared to analogous conventionally prepared catalysts. The reasons for this include the unusual morphology of the particles, high dispersion, high percentage of metal in the reduced state, preservation of high dispersion and small particle size (since no high-temperature reduction step is necessary), and very little oxide surface coating on the particles; in SMAD particles some protection from adventitious oxidation is operative, due to the presence of carbonaceous fragments.

B. Bimetallic SMAD Catalysts. (1) Co–Mn: The more recent work with SMAD catalysts has involved bi-

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(40) Nazar, L. F.; Ozin, G. A.; Hugues, F.; Godber, J.; Rancount, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 624.

(41) Meier, P. F.; Pennella, F.; Klabunde, K. J.; Imizu, Y. *J. Catal.* **1986**, *101*, 545.

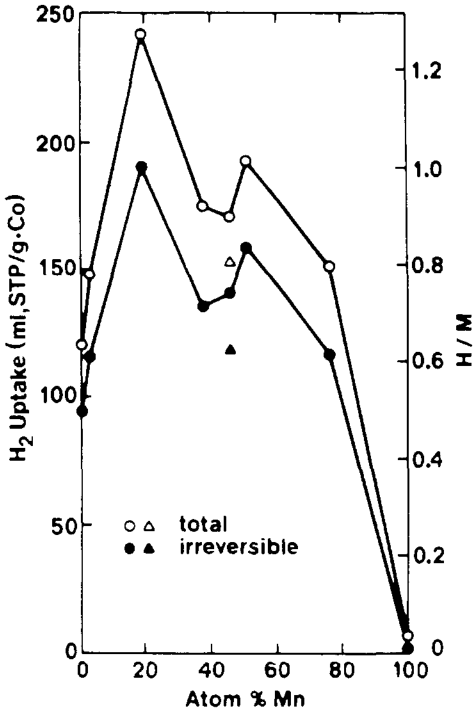

Figure 1. Total and irreversible H_2 adsorption at room temperature over a bimetallic SMAD Co–Mn/SiO_2 catalyst as a function of composition. Triangles: the catalyst was prepared by sequential codeposition instead of simultaneous codeposition.

metallic systems. The concept is to solvate the atoms of two different metals simultaneously. Upon exposure of this solution to a catalyst support, nucleation of one metal or both metals could take place, so layered structures or bimetallic particles might be deposited. Furthermore, since particle growth takes place at low temperature, bimetallic metastable particles could be formed with two metals that do not form thermodynamically stable alloys (immiscible metals).

Questions abound as to what morphologies and catalytic properties might be encountered. Since there is no way to predict such things, numerous experiments with several bimetallic combinations needed to be carried out.

When Co- and Mn-toluene solvates were prepared by simultaneous evaporation of Co and Mn from separate crucibles and then allowed to deposit on SiO_2, remarkable properties were encountered.[42] About 4% metal loadings were used. Interestingly, when the Co:Mn mix was 20 atom % Mn, hydrogen chemisorption more than doubled, in spite of the fact that Mn/SiO_2 did not chemisorb much H_2 (Figure 1).[43]

Correspondingly, striking increases in catalytic activities were also observed. For hydrogenation of 1-butene, initial rates increased by 100-fold when Mn was present at only 2.5 atom %. Further increases were observed by continuing addition of Mn up to 51 atom %. The activity of Mn/SiO_2 (without Co) for this reaction was 10^2 lower than Co/SiO_2 and at least 10^4 lower than that of Co–Mn/SiO_2 (based on 100% Co dispersion; molecules/Co atom·s).

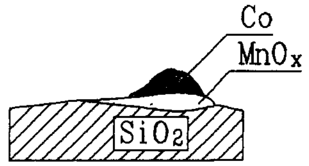

Figure 2. Proposed particle structure for Co–Mn/SiO_2.

To ascertain if such increases in activity were due to ensemble effects, a series of experiments with cyclopropane were carried out. Ponec and co-workers[44] have reported that cyclopropane hydrogenolysis is structure sensitive, while hydrogenation (one-bond cleavage) is not:

$$\Delta + H_2 \xrightarrow{\text{cat.}} CH_4 + CH_3CH_3$$

(hydrogenolysis, structure sensitive)

$$\Delta + H_2 \xrightarrow{\text{cat.}} CH_3CH_2CH_3$$

(hydrogenation, not structure sensitive)

Therefore, by studying Co–Mn catalysts of varying Co:Mn ratios, an ensemble effect (Mn dilution of Co particle surface) should be detected by a change in selectivity from CH_4 and CH_3CH_3 formation to more $CH_3CH_2CH_3$ formation as Mn is increased. (These considerations are based on the findings that Mn is an inactive catalyst, while Co is active). The results of these experiments showed no evidence for an ensemble effect; however, Mn addition up to 20 atom % caused progressive increases in overall activity for *both* hydrogenolysis and hydrogenation. Higher atom % of Mn caused lowering in activities, although at 80 atom % Mn another increase was observed, followed by complete loss in activity at 100 atom % Mn.

At this stage of the work it appeared that surface dilution of Co by Mn (ensemble effect) was not operative, and yet catalytic properties were dramatically affected by Mn.[43] To better define particle struture, EXAFS[16] and XPS[17] studies were carried out. The EXAFS data showed, surprisingly, that the Mn component was in an oxidized state (MnO_x) and that the presence of manganese enabled more cobalt to remain metallic. This suggested a sacrifical role of Mn such that support –OH groups were interacting with Mn atoms first and thus not able to oxidize Co atoms. The EXAFS data also showed that the second, third, and fourth shells around cobalt were progressively less important; thus, the particles were exceedingly small.[16]

The EXAFS results suggested that a layered structure may be forming as Mn deposited first, and Co second. XPS studies confirmed this layered structure.[17] Indeed, taking all the data together, there is strong evidence that the Co–Mn particles were in a layered form. The particles were rich in Mn at the surface of the SiO_2 while being rich in Co on the upper surface. Figure 2 depicts the proposed structure. This morphology can explain why: (1) addition of Mn caused more Co to be exposed to the surface, thereby increasing the amount of H_2 chemisorbed by the Co present (better Co dispersion); (2) the Mn atoms behave sacrificially so that surface –OH groups oxidize solvated Mn atoms; thereby the –OH groups are used up so that Co cannot be oxidized and instead remains metallic and catalytically active. The Mn so deposited also apparently presents a good nucleation site for Co atoms, thus leading to the layered structure.

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(42) Klabunde, K. J.; Imizu, Y. *J. Am. Chem. Soc.* **1984**, *106*, 2721.

(43) (a) Imizu, Y.; Klabunde, K. J. In *Catalysis of Organic Reactions*; Augustine, R.L., Ed.; Marcel Dekker: New York, 1985; pp 225–250. Also see: Klabunde, K. J.; Imizu, Y. U.S. Patent 4,588,708, 1986. (b) Private communications with Professor W. Sachtler have pointed out the danger in proposing an electronic effect to explain these findings, and mixed-ensemble effects need to be considered; see: Haining, I. H. B.; Kemball, C.; Whan, D. A. *J. Chem. Res.* **1977**, 2056; *J. Chem. Res. Symp.* **1978**, 364. Augustine, S. M.; Sachtler, W. M. H. *J. Phys. Chem.* **1987**, *91*, 5953. Augustine, S. M.; Sachtler, W. M. H. *J. Catal.* **1987**, *106*, 417. Augustine, S. M.; Sachtler, W. M. H. *J. Catal.* **1989**, *116*, 184. Augustine, S. M.; Nacheff, M. S.; Tsang, C. M.; Butt, J. B.; Sachtler, W. M. H. *Proc. 9th Int. Congr. Catal., Calgary, Canada* **1988**, *3*, 1190.

(44) Beelen, J. M.; Ponec, V.; Sachtler, W. M. H. *J. Catal.* **1973**, *28*, 376.

However, one point must still be considered: this particle morphology could explain moderate increases in catalytic activity since more metallic Co is deposited and exposed. However, explaining over 100-fold increases in activity is still difficult based on this model. Further work is still needed in order to fully clarify this interesting system.

These results do point to the novel features of bimetallic SMAD catalysts; namely, that layered, well-anchored particles can be formed. It is difficult to imagine other catalyst preparation schemes being capable of such syntheses.

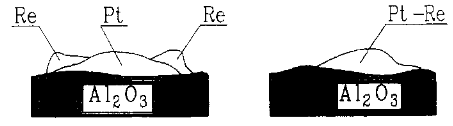
(2) Fe–Co, Fe–Mn, and Co–Mn: In an attempt to take further advantage of such layered catalyst structures, additional Fischer–Tropsch (F–T) catalytic studies were carried out.[45] It was reconfirmed that low loadings of either Fe or Co yielded highly active F–T catalysts[41] and that no hydrogen pretreatment step was necessary to achieve such high activities. Also, these catalysts were very selective for production of *terminal alkenes*.[45] When Mn was added to Fe or Co, F–T activities went *down*, but selectivities stayed the same. Such behavior suggests an electronic effect, and it was proposed that the strength of binding of CO to Co was affected by the presence of Mn.

Returning to the question of bimetallic particle structure, experiments were devised so that two metals of nearly equal oxophilicities could be examined as SMAD deposits on Al_2O_3. Thus, to more closely equalize the oxophilicities of the two metals in question, Fe and Co combinations were examined.[15] XPS and Mossbauer were the main tools used, and these investigations showed that a partial layering took place, where mainly iron (from Fe–toluene) deposited first, whereupon Co and more Fe then nucleated on the iron-bearing surface sites (see Scheme IV).[15] These results point out that toluene solvated iron and cobalt atoms do not deposit according to their thermal stability (Fe–toluene about −30 °C and cobalt-toluene about −50 °C). Since iron preferentially deposited first, the reaction of the iron–toluene solvate with surface –OH groups must be the dominant driving force for deposition and thereby nucleation of particle growth.

In a similar way, layered Fe–Mn/support particles could be prepared from Mn and Fe–toluene solutions; here again the more oxophilic metal Mn deposited first, followed by iron.

As Ozin and co-workers have pointed out[36] and we have confirmed,[15] the nucleation step appears to be reaction of solvated metal atoms with surface –OH groups. Our results show that this reaction is somewhat selective though, with the more oxophilic metal reacting first.

(3) Pt–Re: Some bimetallic catalysts are of vital importance in the fuels industry. Examples include Pt–Re[46] (and S),[47] Pt–Ir,[48] and Pt–Sn[49,50] combinations. In an attempt to compare SMAD bimetallic catalysts with well-known conventional catalysts, bimetallic combinations of Pt–Re were prepared. Two types of preparative procedures were used.[51] (1) Half SMAD: a conventional catalyst was prepared, such as Pt/Al_2O_3, and this catalyst was treated with solvated Re atoms (in toluene). In this way the preformed Pt particles would receive Re on their surface as a surface coating, but a homogeneous Pt–Re alloy should not form. (2) Full SMAD: here both metals were evaporated and solvated simultaneously and allowed to nucleate together; thereby layered structures or homogeneous alloy particles could form. The full SMAD method was most frequently employed for all bimetallic SMAD combinations (i.e., Co–Mn, Fe–Co, Fe–Mn, etc., discussed earlier).



Half-SMAD Full-SMAD

Figure 3. Proposed models for Pt–Re half SMAD and full SMAD particles.

The activities of the SMAD Pt–Re/Al_2O_3 and /Z-13x (zeolite) catalysts for hydrogenolysis reactions were striking.[51a] Turnover frequencies (N_t (s^{-1})) for alkane conversions to smaller and cyclic hydrocarbons were extremely high, sometimes near 100. Direct comparisons with literature N_t values for conventional Pt–Re systems showed that the most active half SMAD catalyst exhibited N_t values 6-fold higher.[51b] Both the half SMAD and full SMAD Pt–Re catalysts were extremely reactive, and this activity seemed to be enhanced by more acidic support surfaces.

These data support earlier conclusions; namely, that acidic support surfaces possessed many nucleation sites, and thereby very good metal dispersion was possible. Also, since both the half SMAD and full SMAD methods yielded extremely active catalysts, it is likely that partially Re-covered Pt particles were formed. Such a picture serves as a good model for a catalytic Pt–Re particle. Perhaps Pt and Re atoms at the interface of the Pt–Re surface alloy would be the most likely active site[51] (Figure 3).

(3) Pt–Fe: The half SMAD modification was also used to prepare Pt–Fe/Al_2O_3 combinations. In this process a Pt/Al_2O_3 catalyst was prepared by conventional means and then treated with solvated iron atoms in toluene.[52,53] A series of Pt–Fe/Al_2O_3 samples were prepared and studied by Mossbauer and XPS, which showed that the iron was partly metallic and partly Fe_2O_3. It is likely that some surface Pt–Fe alloy formed since catalytic properties were significantly altered compared with the conventional Pt/Al_2O_3 catalyst (without iron). Thus, *n*-heptane and methylcyclopentane conversions in the presence of Pt–Fe/Al_2O_3 yeilded more hydrogenolysis products C_1–C_2 as well as high yields of C_3–C_4. Neither conventional Pt/Al_2O_3 or SMAD Fe/Al_2O_3 behaved as did the combination of Pt–Fe.[52]

(4) Pt–Sn: One of the dominant commercial bimetallic catalysts is the Pt–Sn/Al_2O_3 system.[48–50,54,55] It has proven to be more selective and longer lived for hydrocarbon reforming than Pt/Al_2O_3 by itself. The Pt–Sn system is particularly interesting since, unlike Re or Ir (which form active Pt–Re and Pt–Ir) combinations), Sn is inactive by itself in reforming reactions. Thus, in Pt–Sn there is an active metal combined with an inactive metal for mutual benefit.

Although many studies of conventional Pt–Sn catalysts have been reported, there remains considerable disagreement about the oxidation state of tin and how the platinum

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(45) Kanai, H.; Tan, B. J.; Klabunde, K. J. *Langmuir* **1986**, *2*, 760.
(46) Biloen, P.; Helle, J. N.; Verbeek, H.; Dautzenberg, F. M.; Sachtler, W. M. H. *J. Catal.* **1980**, *63*, 112.
(47) Kluksdahl, M. E. U.S. Patent 3,415,737, 1968.
(48) Sinfelt, J. H. U.S. Patent 3,953,368, 1976.
(49) Davis, B. H. *J. Catal.* **1976**, *42*, 376.
(50) Roberti, A.; Ponec, V.; Sachtler, W. M. H. *J. Catal.* **1973**, *28*, 381.
(51) (a) Akhmedov, V.; Klabunde, K. J. *J. Mol. Catal.* **1988**, *45*, 193. (b) Betizeau, C.; Leclereq, G.; Maurel, R.; Boliver, C.; Charcossett, H.; Frety, R.; Tournayan, L. *J. Catal.* **1976**, *45*, 179.
(52) Li, Y. X.; Klabunde, K. J. *New J. Chem. (Fr.)* **1988**, *12*, 691.
(53) Li, Y. X.; Klabunde, K. J. *Hyperfine Interact.* **1988**, *41*, 665.
(54) Bacaud, R.; Bussiere, R.; Figueras, F. *J. Catal.* **1981**, *69*, 399.
(55) Sinfelt, J. A. *AICHE J.* **1973**, *19*, 678.

and tin interact with each other.[56,57] Nearly all spectroscopic investigations have indicated that tin is in a 2^+–4^+ state (not metallic). However, some authors believe that during the catalytic reforming process in the presence of hydrogen, some of the tin is reduced to metallic tin so that a small amount of surface Pt–Sn alloy may be present and perhaps important in the catalytic process.

Thus, an important project presents itself: to prepare bimetallic Pt–Sn particles in a highly dispersed form on a typical support such as Al_2O_3 and to examine catalytic properties. Since conventional catalyst preparation procedures are not successful in this way, the SMAD method was used. Both half SMAD (solvated Sn atoms deposited on preformed Pt particles on Al_2O_3), and full SMAD (both metals solvated and allowed to nucleate simultaneously) were employed.[19,31]

(i) Half SMAD: A conventional Pt/Al_2O_3 catalyst was prepared (0.6 wt % Pt loading) and treated with at Sn–THF solvate solution. Tin loadings were varied from 0.3, 0.5, 1.0, 1.5, and 3.0 wt. %. For comparison two conventionally prepared $Pt–Sn/Al_2O_3$ catalysts were also tested. With all catalysts a commercial Al_2O_3 (207 m^2/g, pore volume 0.45 mL/g, density 0.62 g/cm^3) was employed, calcined at 500 °C, cooled, inpregnated with Pt salt, and treated at 500 °C with flowing H_2 for 4 h prior to the SMAD procedure.[19,31]

A series of alkanes (cyclohexane, methylcyclopentane, *n*-hexane, *n*-heptane, and cyclopentane) were studied with flowing H_2 by using a pulse microreactor. The catalyst bed temperature varied from 360 to 500 °C.

The results of these experiments showed that the half SMAD $Pt–Sn/Al_2O_3$ catalysts were slightly more active than the conventional catalysts for dehydrocyclization and isomerization–dehydrocyclization reactions. But even more importantly, multiple hydrogenolysis (C–C cleavage) reactions to give smaller alkanes were suppressed.[19]

Since the Pt particles were preformed in the half-SMAD catalysts, it is unlikely that Pt–Sn alloy particles formed. More likely, surface patches of Sn^0 on Pt^0 formed, and in some way affected the catalytic process. Since large changes in activities were not encountered, but selectivities were changed, an ensemble effect may be operable. That is, Sn^0 may partially cover the Pt^0 particles, altering the platinum atom ensembles and thereby suppressing multiple C–C bond cleavages, which are structure-sensitive reactions.[31]

To physically elucidate the Pt–Sn particle structure and morphology, X-ray diffraction, X-ray photoelectron spectroscopy, and Mossbauer spectroscopy techniques were applied.[31] These results showed that the tin was present as Sn^0, as expected, regardless of the percent loading of tin. Very small amounts of surface oxides were detected by XPS, but Mossbauer confirmed that the oxides made up less than 5% of the total tin. Although this may seem like a trivial point, it clearly differentiates the half SMAD $Pt–Sn/A_2O_3$ catalyst from the conventionally prepared catalysts, and this is illustrated in Figure 4, which shows the Mossbauer spectra of the conventional and half-SMAD materials. Mossbauer spectra of the SMAD fresh catalysts, or of those treated at 500 °C with flowing H_2, or of those after catalytic reaction with hydrocarbons/H_2, did not change. The spectra show that the conventional catalysts are made up of SnO_2 (coprecipitated) and SnO_2/SnO (coimpregnated), while the half SMAD material only shows Sn^0 (note: SnO in Figure 4 shows up as a doublet for Sn^{2+} (IS = 3.23 mm/s, QS = 1.09 mm/s). It was not possible to resolve an adsorption for a Pt–Sn alloy.[58]

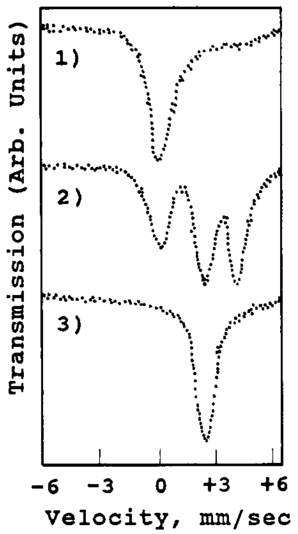

Figure 4. Tin-119 Mossbauer spectra for $Pt–Sn/Al_2O_3$ catalysts after treatment at 500 °C with flowing hydrogen: (1) coprecipitated (conventional); (2) coimpregnated (conventional); (3) half SMAD.

These spectral investigations tended to support our earlier suggestion; Sn^0 must deposit on the preformed Pt^0 particles and thereby influence in a geometrical way (ensemble effect) the catalytic reactions.[19,31] It is possible that a surface alloy forms, but no spectroscopic evidence for this was found. Nevertheless, the formation of small amounts of such a surface alloy may be possible, even with the conventional catalysts.

The most important conclusion from the work on the half SMAD $Pt–Sn/Al_2O_3$ system was that Sn^0 can affect catalytic selectivities in a beneficial way. However, studies of Pt–Sn alloy type particles would be of interest and could help sort out such subtle effects.

(ii) Full-SMAD $Pt–Sn/Al_2O_3$: Platinum and tin were coevaporated from separate crucibles and solvated in toluene in THF.[59] Upon exposure to a pretreated Al_2O_3 or SiO_2 support, nucleation took place to yield highly dispersed metallic particles. According to X-ray diffraction the metal particles were extremely small and/or amorphous. This was in contrast to conventionally prepared $Pt–Sn/Al_2O_3$ or $Pt–Sn/SiO_2$ systems where Pt crystallites were clearly evident.

To determine if alloy-like Pt–Sn particles were formed, several experiments were carried out.[59] First, a bulk Pt–Sn alloy crystal was examined by XPS. Comparisons of Sn(3d) XPS peaks for the standard alloy vs bulk tin metal showed no noticeable shift. Therefore, XPS was not useful in demonstrating the presence of Pt–Sn alloy particles in the full SMAD catalysts. However, it was possible to measure Sn^0, Sn^{2+}, and Sn^{4+} ratios by XPS. The fresh catalysts contained more than 84% of the total tin as Sn^0. Interestingly, even after vigorous oxidation steps, Sn^0 remained as a major component. Such oxidative stability of the full SMAD catalysts was unique and perhaps due to the presence of alloy.

Direct evidence for such alloy particles was provided by ^{119}Sn Mossbauer spectra. Although Sn^0 and Pt^0–Sn^0 have similar Mossbauer absorptions, they can be differentiated.

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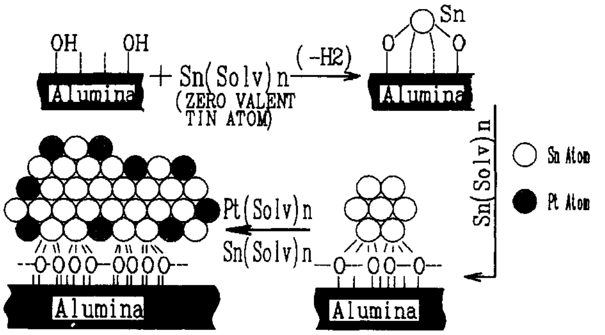
[56] (a) Adkins, S. R.; Davis, B. H. *J. Catal.* **1984**, *89*, 371. (b) Srinivasan, R.; De Angelis, R. J.; Davis, B. H. *J. Catal.* **1987**, *106*, 449.

[57] (a) Sexton, B. A.; Hughes, A. E.; Foger, K. *J. Catal.* **1984**, *88*, 466. (b) Lieski, H.; Volter, J. *J. Catal.* **1984**, *90*, 96.

[58] Kanekar, C. R.; Rao, K. R.; Rao, V. *Phys. Lett.* **1965**, *19*, 95.

[59] Li, Y. X.; Klabunde, K. J. *J. Catal.* **1990**, *126*, 173.

Scheme V. Proposal Sequence for the Formation of a Full SMAD Pt–Sn Bimetallic Particle on Al_2O_3 (Sn/Pt Atomic Ratio of 2.5 Is Illustrated[59])

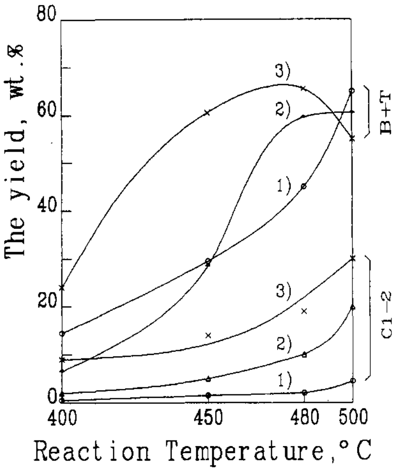


Thus, Sn^0 has IS = 2.55 mm/s, QS = 0.00 mm/s, and line width 0.57 mm/s, whereas Pt–Sn alloy has IS = 1.84 mm/s, QS = 0.68 mm/s, and line width 0.59 mm/s. In the full SMAD catalysts these absorptions overlap to give a broad peak. However, computer fitting allows the conclusion that for a series of SMAD catalysts, the Pt–Sn alloy accounts for 5–15% of the total tin present.[59]

Further evidence for Pt–Sn alloy particles was gleaned from EXAFS data collected at the Cornell synchrotron facility.[59,60] The Sn K-edge spectra for two full SMAD catalysts were compared with standard samples. The main absorptions for the SMAD samples were located at 2.86 and 2.84 Å and can be best assigned to Pt–Sn bonds in bimetallic particles. Smaller absorptions were also found that were assigned to Sn–O and Sn–Sn bonds.

These data, taken together, are convincing and allow the conclusion that Pt–Sn alloy particles were formed in the full SMAD process.[59] But it is also possible that unmixed Pt^0 and Sn^0 particles formed. In an attempt to learn more about the relative importance of these various possibilities, the results from the various spectroscopies techniques were carefully compared. For example, the XPS data showed that Sn^0 (plus Pt^0–Sn^0 alloy) accounted for 84–89% of the total tin, while Pt^0 (plus Pt–Sn alloy) accounted for 91–100% of the total platinum. Mossbauer results, however, suggested that only 5–15% of the zerovalent tin could be accounted for as Pt–Sn alloy, with larger amounts (66–82%) of tin as Sn^0 not associated with Pt–Sn alloy. It must be noted that XPS is a surface analysis technique and Mossbauer is a bulk analysis technique. The XPS detection of Sn^0/Pt^0 was about 1/1, while Mossbauer detected much larger ratios of Sn/Pt. Two possibilities seem to exist to explain these data: (1) most of the Pt^0 and Sn^0 nucleate and deposit as individual Pt and Sn particles along with smaller, individual Pt–Sn alloy particles; (2) most of the Pt and Sn deposit together but as partially segregated phases with a small amount of Pt–Sn bimetallic phase on the top. With the first scenario, it might be predicted that catalytic properties would not be altered (compared with Pt/Al_2O_3 alone), since Pt particles would be present as in conventional catalysts. With the second scenario, catalytic properties should be altered. Indeed, catalytic properties were altered, so the second scenario seems to be the best one, as depicted in Scheme V. In this scheme, solvated tin atoms are proposed to interact with surface O–H groups and can then serve as nucleation sites for additional Pt and Sn atoms.

Scheme VI. Yields of Benzene and Toluene (B + T) and C_{1-2} vs Reaction Temperature for (1) Full SMAD Pt-Sn/Al_2O_3, (2) Coprecipitated Pt-Sn/Al_2O_3 (0.5 wt % Pt; 1.0 wt % Sn), (3) Half SMAD Pt-Sn/Al_2O_3 (0.6 wt % Pt, 1.0 wt % Sn)[59]



Catalytic performance of the full SMAD Pt–Sn/Al_2O_3 was evaluated by using *n*-heptane. Dehydrocyclization to toluene was of particular concern, while benzene and hydrogenolysis products (smaller hydrocarbons) were also analyzed; see Scheme VI. Catalyst performance was quite sensitive to Sn and Pt loadings. Optimum loadings were about 0.6 wt % Pt and 1.0 wt % Sn, which represents a Sn/Pt atomic ratio of about 2.7 (which is depicted in Scheme V).

Hydrogenolysis reactions were significantly depressed on the full SMAD catalysts, much more so than with the conventional or the half SMAD catalysts. This result lends further support to the idea that an ensemble effect is important and that Sn atoms on the surface of Pt particles suppressed the most structure-sensitive catalytic reactions.

An interesting facet of this work, where half SMAD, full SMAD, and conventional Pt–Sn/Al_2O_3 catalysts were compared, is that there is no doubt zerovalent tin does affect catalytic performance in beneficial ways. Thus, although zerovalent tin is rarely detected spectroscopically in conventional Pt–Sn catalysts, it may be the important chemical state of tin that causes such beneficial changes in this very important class of re-forming catalysts.[61]

On the basis of this work with SMAD Pt–Sn catalysts coupled with knowledge gained over the years about conventional systems, some useful generalizations can be suggested:[59] (1) for conventional coprecipitated catalysts, tin oxides may play a role in improving lifetime/stability, perhaps by blocking Pt particle sintering; (2) the presence of small amounts of Sn^0 on the surface of the Pt particles can affect catalytic activity and selectivity; (3) the presence of Pt–Sn alloy particles can significantly depress hydrogenolysis while still maintaining good activity for dehydrocyclization.

Conclusion

The ability to synthesize new materials by SMAD procedures provides a new dimension in the catalysis field. Very high dispersions are possible, and no high-temperature reducing steps are necessary, thereby avoiding possible sintering problems. Furthermore, reaction of solvated metal atoms with support –OH groups allows a strong

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(61) The concept that Pt–Sn alloy particles are important in determining activity and selectivity of supported Pt–Sn catalysts has been presented by earlier workers: (a) Biloen, P.; Helle, J. N.; Verbeek, H.; Dautzenberg, F. M.; Sachtler, W. M. H. *J. Catal.* **1980**, *63*, 63. (b) Verbeek, H.; Sachtler, W. M. H. *J. Catal.* **1976**, *42*, 257. (c) Dautzenberg, F. M.; Helle, J. N.; Biloen, P.; Sachtler, W. M. H. *J. Catal.* **1980**, *63*, 119.

anchoring mechanism and provides a nucleation site for further atoms. And, perhaps most importantly, the SMAD method allows versatility in preparing bimetallic catalyst particles, sometimes in layered structures and sometimes as alloy-like particles. Such novel bimetallic small particles would be difficult if not impossible to prepare by conventional synthetic schemes.

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Articles

Decomposition Mechanisms of Trimethylantimony and Reactions with Trimethylindium

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The decomposition of trimethylantimony (TMSb) was studied in a flow tube apparatus by using a variety of carrier gases and a mass spectrometer to analyze the products. Radical sources and scavengers were added to elucidate the mechanisms. In He, the main reactions are postulated to be a reversible homolytic scission of the first $Sb-CH_3$ bond followed by well-known radical reactions. This conclusion was supported by adding $(CH_3N)_2$ as a source of CH_3 groups: The effect was to retard the decomposition rate. Abstraction of H from TMSb apparently does not occur. In D_2 (H_2) the pyrolysis occurs at much lower temperatures than in He. A chain reaction is postulated in which CH_3 radicals react with the ambient to give D (H), which then reacts with TMSb to give CH_3D (CH_4) and additional CH_3. The existence of both CH_3 and D is shown by the products when toluene is added. The addition of trimethylindium (TMIn) results in lower decomposition temperatures for TMSb. The effect of TMIn is only indirect, with TMIn acting as a generator of D atoms (via reaction of CH_3 radicals with the D_2 ambient), which then accelerate TMSb decomposition. The presence of TMSb retards TMIn pyrolysis, presumably by depleting the concentration of D atoms, which are known to accelerate TMIn pyrolysis.

Introduction

Trimethylantimony (TMSb) is a well-known precursor for growth of group III/V semiconductors. It has been used successfully to produce the binary compounds GaSb[1,2] and InSb[3,4] as well as the ternary alloys InAsSb,[3,5] GaAsSb,[6] GaPSb,[7] and InPSb[8] and the quaternary alloys GaInAsSb[9] and InAsSbBi.[10] One of the surprising results from using OMVPE (organometallic vapor-phase epitaxy) has been in the ability to grow novel alloys such as GaAsSb, GaPSb, InPSb, GaInAsSb, and InAsSbBi. The large difference in atomic radii between As or P and Sb results in miscibility gaps at OMVPE growth temperatures. Nevertheless, it is possible to grow these materials over the entire composition range. In general, OMVPE growth with TMSb seems to be a remarkably useful method for achieving compositions that cannot be obtained in other ways.

Investigations of the pyrolysis mechanisms of TMSb serve as a useful complement to the growth studies listed above. Immediate questions include the role of carrier gases and the effects of surfaces. Studies of the combined TMIn–TMSb system have direct relevance to the actual growth process. An improved understanding of the elementary steps in the decomposition has several practical applications, including a more realistic basis for numerical models of OMVPE growth. These studies may also assist with the development of other Sb precursors for special requirements such as lower growth temperatures.

Previous Studies of TMSb Decomposition

To date only four papers have been published on TMSb decomposition. In 1958, Price and Trotman-Dickenson[11] reported on the pyrolysis in a toluene carrier. The results were somewhat confusing and ambiguous. In a later paper[12] it was reported that some of the conclusions in ref 11 were erroneous. The second study postulated the main steps in the process to be

$$(CH_3)_3Sb \leftrightarrow (CH_3)_2Sb + CH_3 \qquad (1)$$

$$(CH_3)_2Sb \rightarrow CH_3Sb + CH_3 \qquad (2)$$

$$2(CH_3)_nSb \leftrightarrow (CH_3)_{n-1}Sb + (CH_3)_{n+1}Sb \quad (n = 1, 2) \qquad (3)$$

$$mCH_3Sb \rightarrow (CH_3Sb)_m \quad (m \geq 2) \qquad (4)$$

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