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Sintering of Supported Metal Catalysts

José Luis Contreras[1] and Gustavo A. Fuentes[2]
[1]Universidad Autónoma Metropolitana-Azcapotzalco, México City,
[2]Universidad Autónoma Metropolitana –Iztapalapa, México City,
México

1. Introduction

Supported metal catalysts are composed of small metal crystallites (nanoparticles) deposited on high surface area supports. As the size of the crystallites decreases, the dispersed metal is employed more efficiently because a larger fraction of the metal atoms can be made accessible at the surface of the crystallites. The supports are commonly metal oxides, but other materials can be used, such as carbides, carbon, silicates, clays, etc.

Use of a support allows the physical separation of the nanoparticles and thereby hinders their agglomeration into larger crystallites [Wanke & Flynn, 1975]. When it occurs, agglomeration causes a decrease in the number of surface metal atoms per unit mass of metal and therefore decreases the number of active sites of the catalyst. This phenomenon is called sintering or ripening, and it involves different processes that cause changes in the metal particle size distribution (PSD) over the support with an increase in the mean particle size. It is also possible to decrease the mean particle size, a phenomenon called redispersion, dealt with briefly in this work.

Although the support usually stabilizes the metal nanoparticles, in practice it is common to observe the shift of the PSD towards large particle sizes, especially when the catalyst is operated at elevated temperatures. Under those conditions the loss of active surface area by the agglomeration of small crystallites into larger ones is in some cases accompanied by the collapse of the pore structure and loss of internal surface area either for supported or unsupported catalysts [Butt & Petersen, 1988].

The loss of active surface area produced by sintering is an important cause of catalyst deactivation during industrial operation and this is very important in the case of noble metal catalysts. Textural or structural promoters, which modify either the support or the metallic phase to stabilize the metallic particles, are commonly employed in the development of industrial catalysts.

Sintering is a complicated phenomenon because it involves different mechanisms and the metal-support interaction plays an important role. There are several reviews about sintering

of supported metal catalysts but in this case we will refer to three of them when dealing with the older literature: the work of Wanke and Flynn [Wanke and Flynn, 1975], that of Lee and Ruckenstein [Lee H.H. & Ruckenstein ,1983], and the last one from Butt and Petersen [Butt & Petersen,1988].

The goals of the chapter are:

1. To review the experimental results about sintering of supported metal catalysts, restricted to supported Pt, Pd, Rh, Ni and bimetallic systems.
2. To present the methods used to correlate sintering data.
3. To briefly analyze the mechanistic models proposed to explain sintering of supported metal catalysts.
4. To discuss stabilization strategies of supported metal catalysts against sintering.

2. Experimental methods to measure the metal dispersion

The metal surface area and the average metal particle size are obtained as a function of treatment conditions of supported metal catalysts.

The metal particle size will can be expressed in terms of metal dispersion, which is defined as the ratio of active surface atoms to total metal atoms. Several experimental methods have been developed to measure this property, they are: (i) gas chemisorption, (ii) Transmission Electron Microscopy (TEM) (iii) X-Ray Diffraction and (iv) Other methods.

2.1 Gas chemisorption

This method measures the amount of gas chemisorbed by the metal on the surface of the support which can be converted to a metal dispersion by assuming an adsorption stoichiometry. This stoichiometry is defined as the ratio of the number of adsorbed atoms or molecules adsorbed per surface metal atom.

Before the review of this technique was made by Wanke and Flynn [Wanke & Flynn,1975] others reviews were made [Whyte,1973,Dorling,1971, Muller,1969, Schlosser, 1967, Gruber, 1966,Dorling,1970,Flynn,1974,Prestridge,1971,Paryjczak,1974,Maat,1965,Renuoprez,1974   as cited in Wanke & Flynn,1975] and therefore only important points will be cited here.

The conversion of gas chemisorption uptakes to metal dispersion requires an assumption of the adsorption stoichiometry and in order for the adsorption technique to be an absolute measure of the metal surface area, the "correct" adsorption stoichiometry has to be used. In this respect Wanke [Wanke & Flynn,1975] said that this was not a problem because as long as the adsorption stoichiometry is constant, it does not depend on metal particle size, catalysts pretreatment conditions, etc., the calculated surface areas are correct on a relative basis.

There is experimental evidence that adsorption stoichiometries may vary considerably with metal particle size [Wilson,1970, Wanke,1972,Dalla Betta,1972,Kikuchi, 1974, as cited in Wanke & Flynn,1975] and this could produce serious difficulties since the changes in adsorption uptake are not directly proportional to the changes in dispersion if the adsorption stoichiometry is function of the dispersion. It is known that the adsorption

stoichiometry for oxygen atoms on supported Pt catalysts has been reported to be less than 0.5 for small Pt crystallites (less than 15 Å) and approximately 1 for larger Pt crystallites (more than 20 Å) [Wilson,1970, Dalla Betta,1972, as cited in Wanke & Flynn,1975].

2.2 Transmission electron microscopy

According with Butt and Peterson [Butt &Petersen,1988] transmission microscopy is, the most direct method of examination and in recent years the resolution claimed has increased to observe individual particles (1 nm) and also the particle size distributions can be directly determined.

These distributions are based on three implicit assumptions: (i) The size of a particle is the same as its image recorded on the micrograph (corrected for magnification), (ii) Detection of a given size of particle implies that all particles of that size and larger are being detected and (iii) Contrast of the metal particles is distinguishable from the contrast arising from the support material.

The first assumption deals with the fact that the photographic image is two-dimensional, and of course crystallites which are not equiaxed will have apparent different dimensions depending on their orientation.

The second assumption is related with a question, is the sampling a valid representation of the true distribution in both size range and size frequency?. It is known that small metal particles are very difficult to see and sometimes these small particles are important for certain reactions.

The third assumption has to do with the contrast that is achieved between the support and the metal particles. As it is known [Anderson & Pratt,1985] the metal particles in a supported catalyst can be observed and measured directly by using an electron microscope in transmission. In most cases 100 keV electrons should be used and there is some advantage in using higher energies for thicker specimens.

It is important to keep in mind that particle size distributions determined by TEM are less reliable when the particle size extends below 1 nm.

2.3 X-Ray Diffraction (XRD)

Small crystalline particles on a catalyst, being analyzed by XRD, causes a broadening in the diffraction lines and this broadening can be related to the size of the particles [Wanke & Flynn, 1975]. This technique has been described by Klug and Alexander [Klug,1954, as cited in Wanke & Flynn,1975] and Dorling [Dorling, 1970, as cited in Wanke & Flynn,1975]

For the characterization of supported metal catalysts this technique has limited capacity to detect crystalline particles with a size below 2 to 4 nm [Spindler, 1972, Moss, 1967, as cited in Wanke & Flynn,1975] although Adams et al.,[Adams, 1962, as cited in Wanke & Flynn,1975] detected much smaller particles using a special spectrometer.

In general, for well dispersed catalysts the evaluation of dispersion with XRD can be erroneous because very small particles may go undetected.

Another technique, called Small-Angle X-ray Scattering (SAXS), sometimes is used. This technique has been used for several decades to determine particle size in the range of 10 to 50 Å [Guinier, 1969 as cited in Wanke & Flynn,1975].

Use of this technique with supported metal catalysts has been questioned because the low-angle scattering by the porous support obscures scattering by the metal particles. Somorjai [Somorjai,1968, as cited in Wanke & Flynn,1975] eliminated the support interference by compressing the catalyst samples at extremely high pressures to collapse the pores. Furthermore other technique use pore maskants of electron density similar to the support (for example CH_2I_2) in order to eliminate support interference [Renouprez, 1974, as cited in Wanke & Flynn,1975].

2.4 Others experimental methods

The benzene hydrogenation has been used to measure the metal dispersion [Narayanan & Sreekanth,1989] Oxides such as SiO_2, γ-Al_2O_3, TiO_2 (anatase and rutile), ZrO_2 and MgO with different properties have been used as supports for loading nickel by the pore volume impregnation method. Surface area and acidity measurements, X-ray diffraction and H_2 and O_2 adsorption measurements along with hydrogenation of benzene were used as tools for characterizing the catalysts.

The turnover number (TON) for benzene hydrogenation was dependent on the available metal area and on the crystallite size. A smooth correlation between TON and the Ni dispersion (S_{metal}/S_{BET}) was observed.

Within the limitation of X-ray Photoelectron Spectroscopy (XPS) sampling depth, this method is useful in studying sintering and redispersion of Pt on alumina. Pt/Al_2O_3 analysis by XPS is complicated by overlapping Al2p and Pt4f lines [Shyu, J.Z., Otto, K, 1988]. The interference problem is eliminated when the $Pt4d_{5,2}$ lines are used instead. Although these lines are relatively broad, they can be used to discriminate between particulate and dispersed phase Pt on alumina. The discrimination is based on the Pt binding energy measured after an oxidized sample has been exposed to hydrogen at 150°C.

3. Sintering of supported Pt/Al_2O_3 catalysts

The main factors affecting the rate of sintering of a specific supported metal are the temperature, time and type of atmosphere.

In some studies [Spindler, 1972, Mills, 1961,Armstrong,1972, Emelianova,1969, as cited in Wanke & Flynn,1975] thermal treatments were employed to change the metal crystallite size in order to determine the effect of metal crystallite size on adsorption uptakes and /or rates of reaction. In these studies, however, the rate of metal particle growth as a function of treatment conditions was not of interest, and hence the conditions used are often not described in detail.

In many studies the change of metal dispersion as a function of treatment conditions could be difficult to interpret because:

1. The experimental determination of metal dispersion may not be accurate.
2. The support may undergo changes such as collapse of the pore structure and the trapping of metal within the support.
3. The chemical state of the metal during the treatment may be ill-defined.

One of the first works to study sintering in Pt/Al_2O_3 catalysts was made in N_2 [Herrmann,1961, as cited in Wanke & Flynn,1975] at several temperatures and periods of time. H_2 chemisorption at 200°C and 9 torr was used to measure the Pt area. The H_2 uptakes were such that a dispersion greater than unity resulted for fresh catalysts if an adsorption stoichiometry of one H_2 atom per surface Pt atom was used.

3.1 Effect of air, O_2, H_2 and inert gases

After the previous study, Somorjai [Somorjai, 1968, as cited in Wanke & Flynn,1975] reported the effect of treatment in oxidizing and reducing atmospheres at 600 and 700°C for periods of up to 96 h on the average metal particle size for a $5\%Pt/Al_2O_3$ catalyst. The results of SAXS showed that the average Pt particle diameter increased as the treatment time increased and an inverse behavior for dispersion was found.

Other study changing the support was made by Bett et al., [Bett,1974, as cited in Wanke & Flynn,1975]. They study the sintering of Pt/carbon catalysts in N_2 and H_2 at temperatures of 600,700 and 800°C. The dispersion decreased as the temperature and time increased. The experiments showed that for the samples with high concentration of Pt (20wt%) the dispersion was lower than the dispersion for samples with low concentration of Pt (5wt%).

In other study Hughes et al.,[Huges,1962, as cited in Wanke & Flynn,1975]measured the changes in Pt dispersion of a $0.4\%Pt/Al_2O_3$ catalyst which were caused by treatment in H_2 at 900 and 1000°F for treatment times up to 1000 h. They found that the CO adsorption uptake U as a function of treatment time, t could be correlated by an exponential function, as follows:

$$U = a\,(t)^b \tag{1}$$

Where a and b were constants at a fixed temperature. They found a correlation between Dispersion (D) and time (t) assuming a stoichiometry of 1 for CO/Pt.

$$D = 0.73\,(t)^{-0.13} \tag{2}$$

With (t) in hours, and these equations are valid for 2< (t) < 1000 h.

Again, Wanke and Flynn [Wanke & Flynn,1975] made a review of several investigations where the sintering was evaluated changing the temperature sintering of supported Pt when the time was constant. The effect of treatment temperature on dispersion of supported Pt catalysts showed that for Pt catalysts having low Pt concentration (less than 3.7wt%Pt) the dispersion decreased as treatment temperature increased under several atmospheres (vacuum, air and H_2) and both Al_2O_3 and SiO_2 supports were studied using H_2PtCl_6, $Pt(NH)_4(OH)_2$, colloidal PtS deposited on $Al(OH)_3$ in aqueous suspension.

In the case of Pt/SiO$_2$ at 1% Pt the dispersion decreased near 54% after air calcination from 400 to 700°C. In the case of Pt/Al$_2$O$_3$ the dispersion decreased 97 % after air calcination from 550 to 700°C[Jaworska- Galas, 1966, as cited in Wanke & Flynn,1975]. Other experiments with these type of catalysts showed similar results [Renouprez,1974, Benesi, 1968, Wilson, 1972, as cited in Wanke & Flynn,1975].

Another procedure to vary the metal dispersion of supported catalysts is to treat catalysts at an elevated temperature for various periods of time. Results of such studies using a Pt/η-Al$_2$O$_3$ catalyst showed that after 70 h in air at 700°C the dispersion of Pt decreased 97%, whereas in the case of H$_2$ reduction after 70 h at 500°C the dispersion decreased only 36% [Gruber, 1962, as cited in Wanke & Flynn,1975]. This last experiment was extended to 1200 h at 500°C and the Pt dispersion decreased 61%. Then the Pt dispersion decreased more with air than with H$_2$.

In the case of Pt/Al$_2$O$_3$ Gruber [Gruber, 1962, as cited in Wanke & Flynn,1975] carried out studies with two catalysts prepared with Pt(NH$_3$)$_4$(OH)$_2$ and with H$_2$PtCl$_6$ having 0.7% and 0.6%Pt respectively the Al$_2$O$_3$ has 200 m^2/g. The thermal treatment was carried out in H$_2$ at 500°C for 1 to 82 days. The Pt dispersion (D) in function of time (t) in hours was correlated by the following equations:

$$D = 0.38 \, (t)^{-0.1} \qquad\qquad \text{for 0.6\% Pt/η- Al}_2\text{O}_3 \qquad\qquad (3)$$

and

$$D = 0.465 \, (t)^{-0.073} \qquad\qquad \text{for 0.7\% Pt/η- Al}_2\text{O}_3 \qquad\qquad (4)$$

These equations are valid between: 24 < (t) < 2000 h.

In the case to study large Pt crystals supported on various crystal faces of Al$_2$O$_3$ by scanning electron microscopy (SEM) at 900°C in air at 0.5 and 1 atm, Huang and Li [Huang,1973, as cited in Wanke & Flynn,1975] measured Pt particle size changes as a function of treatment time. Treatment times of up to 4 days were studied and their results were well correlated by a power-law function as follows.

$$\overline{d}^4 - \overline{d}o^4 = k \, (t) \qquad\qquad (5)$$

Where $\overline{d}$ is the average Pt particle diameter at time (t) and $\overline{d}o$ is the average Pt particle diameter at (t) = 0. The rate constant k varied by more than a factor of 10, depending on which crystal face of the Al$_2$O$_3$ was used as the support. The rate constant decreased by as much as a factor of 3 when the sintering atmosphere was charged from air at 1 atm to air at 0.5 atm pressure.

From experiments run at varying temperatures for the same amount of time is the second type of experimental data. Examples of this were given for Wanke and Flynn (Wanke &Flynn,1975) for Pt/SiO$_2$ as can be seen in Fig. 1.

From these results, it appears that ion exchange provides a means of obtaining higher initial dispersions, however it is not clear from these data whether and to what extent the ion-exchange materials are more resistant to sintering. Perhaps the most common type of
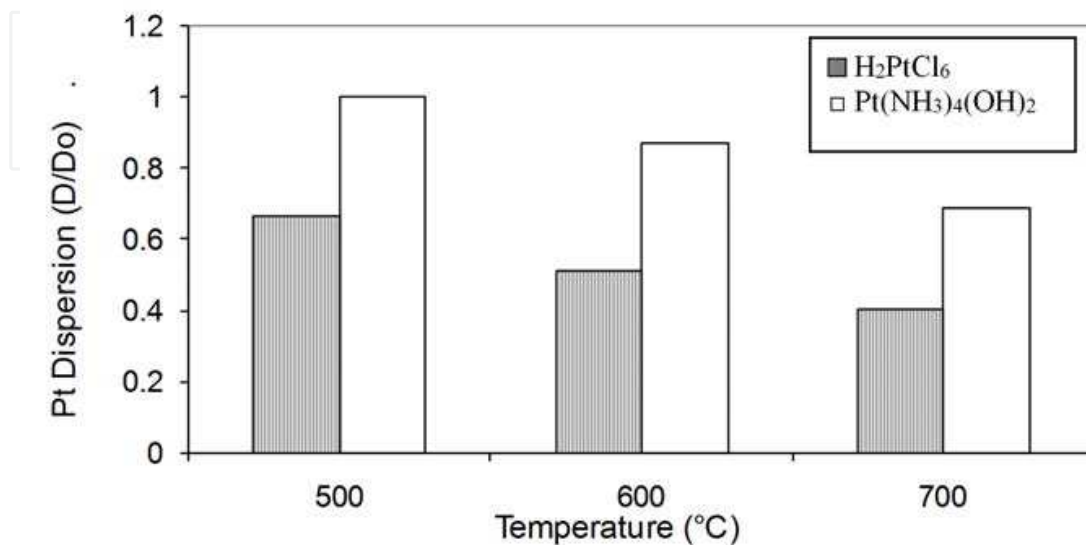
Fig. 1. Sintering of a catalyst of 1.6%Pt/SiO$_2$ in H$_2$ atmosphere (2 h) prepared by cationic and anionic precursor (Benesi et al.,1968).

experimental data on sintering comes from constant temperature-variable time studies (Fig. 2). In these experiments the Pt dispersion decreased very fast in air atmosphere (in less than 72 h), while in H$_2$ it did not decrease as much. Analysis of this type of sintering is simple, and gives immediate answers about the evolution of Pt particles.

In the literature there are many sintering studies of Pt on Al$_2$O$_3$ and other supports (MgO, SiO$_2$, zeolites, SnO$_2$, CeO$_2$, TiO$_2$, carbon, and others), but Al$_2$O$_3$ is the classical support, with the largest number of references.

The effect of different atmospheres, such as N$_2$, O$_2$, and H$_2$ on the sintering of diluted samples of Pt/Al$_2$O$_3$ reforming catalyst was studied in the temperature range 300-800 °C [Hassan,et al.,1976]. The results of sintering in these atmospheres at temperatures below 400 °C were very similar to those previously obtained in the case of unsupported platinum.

In the case of bimetallic catalysts we will group them taking into account the presence of Pt. Various samples of Pt-Al$_2$O$_3$-Cl reforming catalyst were subjected to a series of heat treatments and studied by several characterization techniques [Herrmann et al., 1961] and Pt was present in the original catalyst in a highly dispersed, perhaps ionic, form and that heat treatment causes the formation of Pt crystallites, and not merely their growth.
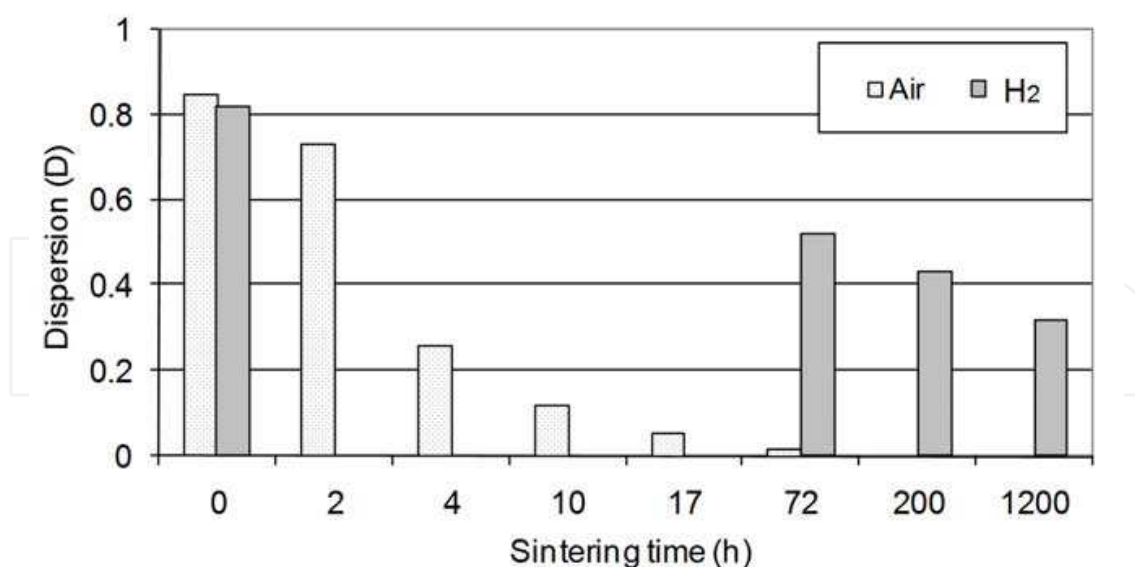
Fig. 2. Sintering of 0.6%Pt/Al$_2$O$_3$ in air (at 780°C) and H$_2$ (at 500°C) as a function of sintering time. [from Maat & Moscou,1965 and Gruber, 1962].

The treatment of the catalyst samples at temperatures higher than 400 °C in both N$_2$ and H$_2$ could lead to an activation; the phenomenon which was observed previously by heating in vacuum. However, the treatment in O$_2$ showed a continuous deactivation over the whole range of studied temperatures.

A model catalyst suitable for examination in the transmission electron microscope was used to study the sintering of Pt crystallites supported on Al$_2$O$_3$ [Chu & Ruckenstein,1976]. The model catalyst consisted of a thin layer of γ-Al$_2$O$_3$ upon which Pt was deposited. The samples were subjected to heating in various chemical atmospheres for various lengths of time and temperatures. The change in size, shape, and position of each Pt crystallite was followed by examining the same region after each step in the treatment. Crystallite migration was identified as a cause of sintering. Evidence for the migration of crystallites of size larger than about 10 nm over large distances was presented. The degree of mobility of Pt crystallites depended on sintering conditions. Increase in temperature, periodic oxidation and reduction, reaction of Pt with the substrate, and burning off of coke accumulated on the surface all enhanced crystallite migration. The authors found that phase transformation occurring in the Al$_2$O$_3$ substrate was also associated with severe sintering of Pt crystallites. Heating of the model catalyst in pure O$_2$ or wet N$_2$ did not promote Pt sintering appreciably and significant sintering occurred during heating in wet H$_2$.

In other interesting work, Lietz et al. [Lietz et al, 1983] studied several Pt γ-Al$_2$O$_3$ catalysts treated in O$_2$ between 100 and 600 °C and in H$_2$ at 500 °C using uv-vis reflectance spectroscopy. The formation of different oxidized Pt surface species previously indicated by temperature programmed reduction (TPR) studies was confirmed by characteristic uv-vis spectra. The results are used as the basis for a model describing the types of surface reactions and details of the Pt surface species formed in O$_2$ and in H$_2$, and for a model of the sintering in O$_2$. The amount of soluble Pt was found to correspond with the amount of highly dispersed Pt. Hence, only surface Pt atoms were soluble.

In other work related with the effect of several treatments of O_2 and H_2 on the Pt/Al_2O_3 catalyst the authors studied the sintering of these catalysts following ageing-regeneration cycles typical of industrial use and after extreme treatments in "oxidizing" or "reducing" environments [White, et al., 1983]. Details of particle morphology and the statistics of particle size distribution (PSD) were obtained by high-resolution electron microscopy, with complementary data from H_2 chemisorption measurements. It was found that catalyst sintering during a simulated industrial cycle was minimal, whereas "reducing" or "oxidizing" treatments at high temperature (600 °C) caused loss of accessible Pt surface area: the PSDs and particle geometries, however, then differed greatly, despite similar chemisorptive capacities. Conversely, it was also observed that no appreciable particle growths resulted from severe reducing treatment despite a reduced chemisorptive capacity.

Sintering and redispersion of Pt oxide on alumina have been the subjects of many studies. Some authors [Yao et al.,1980] showed experimental results on sintering and redispersion phenomena which are interpreted on the basis of a thermodynamic formalism and direct formation of Pt sintering during heating of Pt catalysts which have been observed by TEM [Harris, 1986] to investigate Pt particle sintering in specimens of a Pt/Al_2O_3 catalyst heat-treated under oxidizing conditions. The specimens were prepared by sol-gel process. It was found that heating in air at 700 °C produced very rapid sintering, the mean particle diameter increasing from 50 to 300 Å after 8 h. The form of the particle size distributions, and the types of particle structure observed in sintered catalysts, suggested that the mechanism involved a combination of migration and coalescence of whole particles and Ostwald ripening.

In other interesting investigation related with the Pt sintering, the authors used a model of Pt/Al_2O_3 catalyst after heat treatment in H_2, and alternately in H_2 and O_2 at different temperatures (300 and 800 °C) by means of TEM [Sushumna & Ruckenstein,1988]. At both relatively low (500 °C) and high temperatures (750 °C), short-distance migration (usually 1-3 particle diameters) and coalescence of particles was observed to contribute considerably toward sintering.

At 500 °C and following two or three cycles of alternate heating in H_2 and O_2, significant migration of particles (up to 8 nm particles migrating over 25 nm) was observed on exposure of the oxidized particles to H_2 and/or of the reduced particles to O_2. Sintering was fast and pronounced in the initial 4 to 6 h of heating of a fresh sample; then it becomes slow. However, further continuous heating for extended periods of 12 h or more causes additional significant sintering by particle migration and coalescence among other mechanisms.

This suggests that investigations based on only 1 or 2 h of heating, as often reported in the literature, yield incomplete information. The present results indicate that at both 500 and 750 °C, sintering by ripening (apparently only of a localized kind) also occurs.

In other investigation [Sushumna & Ruckenstein,1988] the authors showed evidences of the occurrences of a variety of phenomena such as short-distance migration and coalescence of particles, migration toward or away from another particle, decrease in size and disappearance of larger particles near unaffected smaller particles, decrease in size or disappearance of both small and larger particles, decrease in size or disappearance of small particles near larger particles (ripening), decrease in size and subsequent migration of

particles or vice versa, collision without coalescence, and collision-coalescence-separation into two particles again. The particles seem to feel the presence of other nearby particles via long-range inter-particle forces that induce the migration of a particle toward another or emission of atoms toward a nearby particle.

The two major mechanisms of sintering of supported metal crystallites appear to be (i) short-distance, direction-selective (in contrast to random) migration of particles followed by (a) collision and coalescence or (b) direct transfer of atoms between the two approaching particles, or (ii) localized ripening (direct ripening) between a few stationary, adjacent particles.

From literature, Pt sintering is produced mainly by temperature, type of atmosphere and time (Table 1). But there are other causes such as: type of support, impurities in the support and level of metal loading. Unfortunately, there is a disparity in the literature on such presumably factors in Pt/Al_2O_3 catalysts [Butt, 1988].

In the literature some authors have gave attention to the factors of strong H_2 adsorption and strong metal-support interactions (SMSI) as being potentially important effects in the determination of metal exposure of crystallite size as related to studies of sintering [Butt, 1988].

In this point, it is important that when metal dispersion results are discussed, it will be understood that possible influences of strong chemisorption or SMSI have not been considered, then some results can be suspect because interpretation of sintering was based on dispersion measurements following such treatments. Although there is some evidence that high-temperature treatment in H_2 does not promote sintering, this issue is not clear in terms of the effect of strongly bound H_2.

From Table 1, air calcination of the $0.5\%Pt/Al_2O_3$ catalyst at 500°C produced low dispersion (D=0.15). An increase of air temperature (600°C for 24 h) produced sintering, decreasing dispersion (D =0.06). The change of atmosphere from H_2 to O_2 in the $2.75\%Pt/Al_2O_3$ catalyst decreased the dispersion from 0.67 to 0.5. This behavior is similar in the next other types of catalysts.

The presence of HCl in the $2\%Pt/Al_2O_3$ catalyst after O_2 treatment at 520°C showed that the Pt dispersion increased from 0.75 to 1.08 and then HCl contributed to the Pt redispersion.

Some authors found that after heat treatments of Pt/Al_2O_3 catalysts in H_2 and O_2 at high temperatures, drastic changes both in H_2 and O_2 chemisorption occurred in spite of no change of Pt particle size.

The great effect of the type of atmosphere has been investigated by Guo et al.[Guo et al.,1988], they studied the influence of thermal treatments in O_2, H_2 and inert atmospheres on the dispersion of $Pt/\gamma-Al_2O_3$ and the Pt sintering was followed by H_2 chemisorption and wide-angle x-ray diffraction (XRD). Catalysts containing about 1.0 and 5.0 wt% Pt were treated in atmospheres containing H_2, He, N_2, O_2 and various chlorine compounds, XRD was used to obtain Pt crystallite sizes and size distributions.

The results showed that the treatment atmosphere had a significant influence on the Pt crystallite sizes and size distributions; treatment in He at 800°C resulted in relatively small

Pt crystallites, while treatment in O_2 usually resulted in bimodal size distributions. Treatment in chlorine-containing atmospheres resulted in sintering or redispersion of the Pt depending in the nature and concentration of the chlorine-containing species.

In other studies, the effect of an oxidative atmosphere is studied on fresh and sintered unchlorinated naphtha reforming catalysts containing 0.6-1% Pt.

Catalyst	Atmos-phere.	Tempera-ture (°C)	Time (h)	Pt Dispersion	Analytic Method	Reference
0.5%Pt/ Al$_2$O$_3$	Fresh Air	500	1	0.15	H$_2$ Chemi-sorption -TEM	(Harris,1983)
	Air	600	2	0.10		
	Air	600	8	0.09		
	Air	600	24	0.06		
2.75%Pt/ Al$_2$O$_3$	Fresh H$_2$	500	8	0.67	H$_2$ Chem.	(Apesteguia 1984)
	Air	590	0.5	0.35		
	Air	600	0.7	0.3		
0.93%Pt/ Al$_2$O$_3$	Fresh H$_2$	500	8	0.65	H$_2$ Chem.	(Apesteguia 1984)
	Air	600	5	0.48		
0.5%Pt/ Al$_2$O$_3$	Fresh H$_2$	500	1	1.1	H$_2$ Chem.	(Lieske,1983)
	O$_2$	800	Seq.	0.41		
	O$_2$	550	11	0.60		
2%Pt/ Al$_2$O$_3$	Fresh H$_2$	400	12	0.90	H$_2$ chem.	(Lee, 1984)
	H$_2$	700	3	0.39*		
	O$_2$	520	2	0.74		
	O$_2$+HCl	520	2	1.08		
	O$_2$+HCl	600	2	0.95		
	H$_2$+HCl	600	2	0.29*		
	O$_2$	300	2	0.69		
	O$_2$+HCl	520	2	0.92		
	O$_2$	800	2	0.07		

* The H/Pt ratios for these runs probably do not correspond to Pt dispersion

Table 1. Dispersion of Pt/Al$_2$O$_3$ catalyst in presence of several atmospheres, temperature and time using H$_2$ chemisorption to measure the Pt dispersion (stoichiometry H/Pt=1).

The TPR profiles show that only one of species is formed under given experimental conditions, regardless of the mean crystallite size of the metal particles [Borgna,et al.,1992]. The structural information supplied by extended X-ray absorption fine structure (EXAFS) compared with cuboctahedral particle modeling, implies that such species was a surface platinum oxide, the structure of which was close to that of PtO$_2$, (Figure 3) but largely distorted.

The same authors extended their study several years later and a main observation of their study is that chlorine was present in the first shell around platinum during the entire sintering process [Borgna et al., 1999]. The experimental data were well fitted only by including chlorine in the first coordination sphere of Pt. Since the oxidizing mixture used here did not contain chlorided compounds, this result indicates that chlorine originating from the support was always in the immediate surroundings of Pt during the metal

sintering. The authors used in situ EXAFS spectroscopy for identifying the surface species involved in the sintering of alumina-supported Pt catalysts under dried oxidizing atmospheres.

A Pt/Al_2O_3 catalyst (0.62 wt% Pt, 0.88 wt% Cl) was heated in a 2% O_2/N_2 gaseous mixture from 300 to 525°C for about 120 min and then kept at this temperature for up to 720 min. The main observation, which is in good agreement with ex situ TPR experiments, was that chlorine was always present in the surrounding of Pt during the oxidizing treatment. The metal sintering process involved three successive steps during which the chlorine and oxygen coordinations passed through a maximum, whereas Pt coordination exhibited a minimum. Formation of $Pt(OH)_4Cl_2$ species was detected at the end of the first step, i.e., when the temperature reached 500°C. After about 4 h of treatment, they deduced that Pt species are made up of a metal platinum core surrounded by a double coating of oxychlorinated species (Fig. 3).

More precisely, EXAFS experiments suggested that surface platinum oxide is made of rigid PtO_6 octahedra, but their assembly led to a largely disordered structure. The absence of a long-range order allows the location of residual chlorine species either between the PtO_6 octahedra or at the Pt-oxidized surface shell.
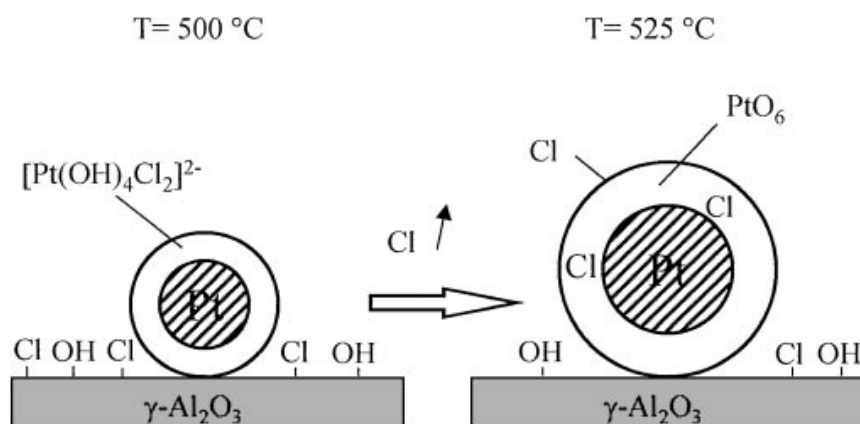

Fig. 3. Pt species are made up of a metal platinum core surrounded by a double coating of oxychlorinated species.

The effect of H_2O on the Pt sintering also has been studied by Barbier et al. [Barbier,et al.,1992]. They made a direct reduction by H_2, without precalcination, of Pt/Al_2O_3 activated by H_2PtCl_6. They studied several series of catalysts with different metal and chloride loadings. It appears that H_2O acts as a kinetic inhibitor of the reduction reaction but can also induce Pt sintering. HCl has no kinetic effect on the reduction but is able to increase the metallic accessibility. The higher the H_2 pressure, the lower the Pt dispersion. The extent to which the metal is accessible is considered to be resultant of two parallel reactions, namely polymerization and reduction of partly reduced Pt^{2+} complexes.

In other study, the sintering mechanism of Pt nanoparticles dispersed on a planar, amorphous Al_2O_3 support as a model system was studied by Simonsen,et al [Simonsen,et al.,2010] By means of in situ transmission electron microscopy (TEM), the model catalyst was monitored during the exposure to 10 mbar air at 650 °C. Time-resolved image series

unequivocally reveals that the sintering of Pt nanoparticles was mediated by an Ostwald ripening process.

A statistical analysis of an ensemble of Pt nanoparticles shows that the particle size distributions change the shape from an initial Gaussian distribution via a log-normal distribution to a Lifshitz-Slyozov-Wagner (LSW) distribution. Furthermore, the time-dependency of the ensemble-averaged particle size and particle density is determined. A mean field kinetic description captures the main trends in the observed behavior. However, at the individual nanoparticle level, deviations from the model are observed suggesting in part that the local environment influences the atom exchange process.

3.2 Effect of sintering over the catalytic activity

The Pt particle size has an important effect over the catalytic activity and selectivity for different reactions. For example, Maat and Moscou [Maat and Moscou ,1964, 1965], correlated the sintering of a commercial reforming catalysts of $0.6\%Pt/Al_2O_3$ with 0.5% chloride, with its activity for n-heptane reforming. Variable time-constant temperature sintering experiments were carried out at 780°C in an inert atmosphere and the resulting Pt surface areas determined by H_2 chemisorption and electron microscopy. Corresponding crystallite sizes (average) ranged from about 1 nm for the fresh catalyst to 45 nm for the most severely sintered case (780°C, 72 h) and good correlation of sintering kinetics was obtained via equation:

$$dD / dt = - k D^n \tag{6}$$

with n=2, where D is the Pt percentage exposed or Pt dispersion and k the sintering kinetic constant.

The integration of this equation yields:

$$k = 1/t \ln [D_o/D] \qquad \text{where n =1} \tag{7}$$

$$k = D_o^{1-n} /t(n-1) [(D_o/D)^{n-1} - 1] \qquad n=2 \tag{8}$$

where Do is the initial dispersion and D the dispersion at time t.

The authors found a significant change in activity, although it is not as large as one might have expected. The total change in surface area is from 233 to 5 m^2/g Pt a 98% decreases, yet total conversion decreases only from about 95 to 75%, roughly 25%. What is probably of more ultimate importance in these data is the change in product distribution. The selectivity for the various products changes markedly with sintering and the dehydrocyclization activity is severely affected, while the sum of isomerization plus cyclization remains approximately constant.

The isomerization selectivity increases, from 9 to 25 mol% product, with increasing sintering. Since the aromatics produced in dehydrocyclization reactions would be prominent in determining product octane, this change represents a severe decline in a desired selectivity. The reason for the alteration in selectivity is found in the bifunctional nature of the catalyst; aromatization reactions are strongly dependent on the metallic function, while the isomereization activity is predominantly a function of the acid Al_2O_3.

Maat and Moscou do not report any notable sintering of the support in these experiments, so presumably the acidic function is relatively unchanged and the apparent increase in isomerization activity on sintering is the result of increased reactant availability in competition with the metallic function.

In another type of catalysts, for catalytic reduction of NOx, the redox behavior of the fresh and sintered catalysts was investigated using a pulse reactor. A highly dispersed Pt/Al_2O_3 catalyst was used for the selective catalytic reduction of NOx using propene (HC-SCR) [Vaccaro et al.,2003]. Contact with the reaction gas mixture led to a significant activation of the catalyst at temperatures above 523 K. According to CO chemisorption data and TEM analysis, Pt particles on the activated catalyst had sintered. The authors observed that if Pt particles were highly dispersed (average size below ~2nm), only a small part (~10%) of the total number of Pt surface sites (as determined by CO chemisorption (Pt_{surf})) participated in the H_2/O_2 redox cycles ($Pt_{surf,redox}$). Then for a sintered catalyst, with an average particle size of 2.7 nm, the number of superficial Pt (Pt_{surf}) and $Pt_{surf,redox}$ sites were in good agreement.

In other work, volatile organic compounds (VOC) were burn by catalytic combustion using a Pt catalyst and the activity was promoted with the sintering of Pt crystallite, which was supported on the anodized aluminum plate with the electrolysis supporting method[Wang et al.,2005]. The effect of atmosphere and the sintering temperature were studied. Results of the pre-treatment under the respective combustion of toluene, benzene, or ethylbenzene showed that the linear relationship between the ultimate average particles size and VOC molecular weight could be concluded.

In order to make the link between sintering of a Pt/Al_2O_3 catalyst and its activity for the CO oxidation reaction Yang, et al., [Yang, et al., 2008] treated the catalyst (1.6% Pt) by thermal aging for different durations ranging from 15 min to 16 h, at 600 and 700 °C, under 7% O_2. It was observed a shift of the Pt particle size distributions due to sintering towards larger diameters. These distributions were studied by TEM. The number and the surface average diameters of Pt particles increase from 1.3 to 8.9 nm and 2.1 to 12.8 nm, respectively, after 16 h aging at 600°C.

The catalytic activity for CO oxidation under different CO and O_2 inlet concentrations decreases after aging the catalyst. The light-off temperature increased by 48 °C when the catalyst was aged for 16 h at 600 °C. The CO oxidation reaction is structure sensitive with a catalytic activity increasing with the platinum particle size.

Another investigation where the reforming reactions were used to know the state of metal particles was made with Pt/Al_2O_3. Consecutive oxidation-reduction cycles involving successive oxidation treatments of $0.3\%Pt/Al_2O_3$ catalyst were made at various temperatures, each followed by a reduction treatment in H_2 to produce an active catalyst, lead to changes in catalytic activity for the reactions of n-hexane with H_2. Decreased activity is paralleled by changes in selectivity brought about by the increased tendency of large Pt particles towards coking [Anderson,et al.,1989]. Results show that the reforming reactions of n-hexane can be used to gain information about the state of metal particles following sintering/redispersion of Pt on alumina.

In order to evaluate Pt catalysts using an accelerated test, a novel method was developed using a periodic pulse technique in which a catalyst is exposed to forced redox cycles. It was

applied to the oxidation of C_2H_4 on Pt/Al_2O_3 catalysts [Murakami,et al.,1991]. It was found that the catalysts are sintered at relatively low temperature, i.e., at 588 K, in reaction atmosphere, and that the periodic pulse technique actually accelerates the sintering. The sintering in the continuous flow reaction for ca. 1000 h could be reproduced within ca. 100 h, indicating the possibility of rapid estimation of catalyst life. It is suggested that the sintering in reaction atmosphere is governed by the chemical factors rather than the thermal ones.

In another interesting study of effect of Pt sintering was made using a Pt/Al_2O_3 catalyst which was sintered in O_2 and H_2 atmospheres using two metal loadings of the catalyst: 0.3% and 0.6% Pt [Susu & Ogogo,2006]. After sintering, the aromatization selectivity was investigated with the reforming of n-heptane as the model reaction at a temperature of 500 °C and a pressure of 391.8 kPa. The primary products of n-heptane reforming on the fresh platinum catalysts were methane and toluene, with subsequent conversion of benzene from toluene demethylation. To induce sintering, the catalysts were treated with O_2 and temperatures (500 and 800°C). The $0.3\%Pt/Al_2O_3$ catalyst exhibited enhanced aromatization selectivity at various sintering temperatures while the $0.6\%Pt/Al_2O_3$ catalyst was inherently hydrogenolytic.

3.3 Redispersion of Pt on Al_2O_3

Changes in the dispersion of supported Pt/Al_2O_3 catalysts following reduction and a variety of thermal treatments have been monitored by gas uptake and electron microscopy [Flynn & Wanke,1975]. Evidence of redispersion was found after sintering of one catalyst in oxygen at 450 to 600 °C. Sintering was found to be sensitive to gas atmosphere and metal loading. Addition of a portion of presintered catalyst containing large Pt particles increased the rate of sintering of a catalyst. From electron micrographs of the same catalyst area before reduction and after reduction and various thermal treatments, it was concluded that Pt agglomeration occurs during all these steps. Some Pt crystallites remain in a fixed location during reduction and thermal treatments.

Other investigation of redispersion of Pt of thermally sintered Pt/Al_2O_3 catalysts used in the simultaneous oxidation of CO and propene has been achieved by an oxychlorination treatment [Cabello Galisteo et al.,2005]. The catalyst can be considered to model the active component of the catalytic converter fitted to diesel driven cars. Platinum crystallites redispersion was verified by XRD, H_2 chemisorption, TEM and Fourier transform infrared spectroscopy (FTIR). The extent of regeneration reflects the platinum particle redispersion achieved by such a treatment. Oxychlorination also introduced electronic effects in the Pt particle caused by the presence of chlorine at the $Pt-Al_2O_3$ interface but no detrimental result of this was observed in the oxidation reactions. The results indicate that the deactivation of the diesel oxidation catalysts can be reverted by this simple treatment resulting in a remarkable recovery of the catalytic activity.

4. Sintering of supported Pd catalysts

In the literature most of the sintering studies reported are for Pt catalysts. Less information is available on the sintering of other noble metal catalysts, such as Pd, Rh, Ni etc. Wanke and Flynn [Wanke & Flynn,1975] made a review of the sintering of these metals.

In the case of Pd, it was observed an unexpected growth rates of Pd particles supported on charcoal at temperatures below 50°C [Pope, 1971, as cited in Wanke & Flynn,1975]. In that study, it was observed a 30% loss of Pd surface due to reduction of a 10%Pd/charcoal catalysts at 25°C for 2 h. The reduction temperature required for the H_2 reduction of Pd precursors was very low.

In other case, Brownlie et al., [Brownlie, 1969, as cited in Wanke & Flynn,1975] prepared a Pd/charcoal catalysts by vapour deposition of Pd, for the hydroisomerization of 1-butene. The authors observed by TEM a change in average Pd crystallite size from 140 Å for the fresh catalyst to 1300 Å for the catalyst used for reaction and the reaction temperature was 43°C. Little particle growth was observed for another Pd/charcoal sample which was prepared by impregnation with palladous chloride and exposed to the same reaction condition.

In the case of Pd/Al_2O_3 at 5% Pd the dispersion decreased near 85% after H_2 reduction from 400 to 800°C[Aben, 1968, as cited in Wanke & Flynn,1975]. The same authors studied the Pd/SiO_2 catalyst and the dispersion decreased 80 % after H_2 reduction from 400 to 900°C.

In relation of the metal-support interaction in the Pd/SiO_2 system some authors [Lamber et al, 1990] have studied the effect of support pretreatment using TEM and electron diffraction. The authors found that heating of the Pd/SiO_2 system in a H_2 atmosphere may lead to chemical (strong) interaction between metal and support and growth of palladium salicide (Pd_2Si). Microdiffraction analysis showed an oriented growth of the Pd_2Si precipitate with respect the Pd matrix. The magnitude of metal-support interaction, the agglomeration of metal particles and the formation of an intermetallic compound are strongly influenced by the thermal pre-treatment of the SiO_2 substrate.

In other investigation, catalysts, containing Pd and Pt on a carbon support, were studied by the temperature-programmed reduction, in situ X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy (XAFS)[Stakheev et al.,2004]. The reduction of Pd and Pt species in samples 2%Pd/C and 2%Pt/C calcined in an air flow at 370°C was studied. Reduction of the 2%Pd/C sample begins at 50 - 60°C and is completed at 250 - 300°C. Particles of various dispersions are formed during reduction. Long-distance peaks observed in the EXAFS spectra point to the presence of a fraction of relatively large crystallites. The average Pd - Pd coordination number (~5) at 200°C gives evidence that a number of very small Pd nanoparticles, oligomeric clusters, is present. Reduction at T > 200°C results in sintering of a small fraction of the Pd particles. Reduction of Pt in 2%Pt/C sample begins at 120 - 150°C and is completed at 300 - 350°C. The sintering-resistant monodispersed Pt particles are formed under these conditions.

5. Sintering of supported Rh catalysts

In the case of Rh, several samples supported on Al_2O_3 and SiO_2 were prepared and reduced in H_2 prior to the treatment in air [Wanke, 1972, Hughes,1962,Wanke, 1969, as cited in Wanke & Flynn,1975].

For a 5%Rh/Al_2O_3 catalyst, the dispersion of Rh decreased 25% at 600°C after 3 h in air (initial dispersion 0.79), when the temperature increased at 800°C for 8 h the dispersion decreased 84% [Wanke, 1969,1972, as cited in Wanke & Flynn,1975].

In the case of a catalyst of 5%Rh/SiO_2 the dispersion decreased 84% (initial dispersion 0.53) after calcinations in air at 800°C for 4 h[Yates, 1967, as cited in Wanke & Flynn,1975].

In the case of a catalyst of 0.3%Rh/Al_2O_3 the dispersion decreased 67% (initial dispersion 0.77) in presence of N_2 at 900°C [Hughes, 1962, as cited in Wanke & Flynn,1975]. The Rh in the 5%Rh/SiO_2 catalyst [Yates, as cited in Wanke & Flynn,1975] was present as $RhCl_3$ prior to the air treatment since the dried impregnated catalyst was not reduced prior to the sintering. The comparison between the catalysts supported on Al_2O_3 was difficult because the authors did not know the state of the metal prior to the treatment in N_2.

In a comparative study made by Fiedorow, et al[Fiedorow at al.,1978] changes in dispersion of alumina supported Pt, Ir, and Rh catalysts due to thermal treatment (250-800 °C) in O_2 and H_2 atmospheres were measured. In O_2 atmospheres the sequence of thermal stability was found to be Rh > Pt > Ir, while in H_2 atmospheres the sequence was Ir > Rh > Pt. Increases in dispersion due to treatment in O_2 were observed for Pt and Ir catalysts. The observed relative stabilities are compared to qualitative predictions based on sintering mechanisms. The extent of the changes was found to be quite different among the Al_2O_3 supports used.

6. Sintering of supported Ni catalysts

The Ni in the 10%Ni/ Al_2O_3-SiO_2[Carter, 1963, as cited in Wanke & Flynn,1975] and 6.7%Ni/SiO_2[Van Hardeveld, 1966, as cited in Wanke & Flynn,1975] catalysts was present as the nitrate at the beginning of the treatment. Complete reduction was obtained after H_2 reduction at 370°C.

Low Ni dispersion was found for the 3%Ni/Al_2O_3 catalyst (initial dispersion 0.021) and after 900°C in N_2 for 72 h the dispersion was 0.002 [Hughes, 1962, as cited in Wanke & Flynn,1975]. The sintering of Ni in these catalysts was difficult to measure.

The sintering of Ni in H_2 was evaluated in the 6.7%Ni/SiO_2 catalyst [Van Hardeveld,1962, as cited in Wanke & Flynn,1975]. The dispersion of Ni decreased from 0.11 to 0.028 after 1 h at 700°C, the dispersion decreased 74%. In these catalysts the methods used for measuring the dispersion were: H_2 chemisorption (static system at -78°C), CO adsorption (in He flow system) and X-ray line broadening.

7. Sintering of supported bimetallic catalysts

Some studies of supported bimetallic catalysts have been made using Pt,Pd Ir, Rh and Ru, for example: Pd-Ru, Pd-Pt, Pd-Ir, Pt-Ir, Pt-Ru and Pt-Rh. The characterization studies were difficult to interpret using the metal dispersion since significant alterations in the supports occurred at the elevated treatment temperatures [Armstrong, 1972, as cited in Wanke & Flynn,1975]. In this study it is interesting to note that in some of the catalysts (Pt-Rh and Pt-Ru) the use of steam between 1000 and 1200°C resulted in an increase in activity.

The sintering in bimetallic catalysts as Pt-Ir/Al_2O_3 has been studied [Graham & Wanke, 1981] with focus on the effects of thermal treatments in O_2 (300 to 600 °C) and H_2 (500 to 800 °C) on the metal dispersions of 1% Pt, 1% Ir, and 1% Pt-1% Ir catalysts. Treatment in O_2 at 400 to 600 °C resulted in an increased dispersion for the Pt catalyst. Small increases in

dispersion for the Ir catalysts were observed after treatment in O_2 at 300 °C; at higher temperatures the Ir dispersion decreased significantly. Segregation of the metals occurred in the bimetallic Pt-Ir catalysts during treatment in O_2. The largest decreases in dispersion due to treatment in H_2 were observed for the Pt catalyst. Surprisingly, H_2 treatment of the Ir and Pt-Ir catalysts resulted in essentially the same relative decreases in metal dispersions

One of the beginning investigations of Pt-Ir catalyst was made by Graham &Wanke [Graham &Wanke,1981] They studied the effect of parameters such as temperature, gas flow rate, O_2 concentration and oxychlorination on the sintering of an industrial bimetallic reforming catalyst (Pt-Ir/ Al_2O_3). The time taken for carbon removal decreased with increasing gas flow rate (from 0.75 to 3 l/h/cc. cat.) and good metal dispersion and high BET surface area were achieved at a flow rate of 3 l/h/cc.cat. Increasing the initial combustion temperature from 370 to 450° C led to considerable sintering of the metal. However, it did not significantly change the BET surface area. Better metal dispersion and higher BET surface area were restored using O_2 concentrations in the range 0.3 to 0.6% above which value considerable sintering of both metal and support occurred. In sintered catalysts, metal redispersion could be improved to some extent by oxychlorination treatment. Dispersion of the metallic phase was found to be higher at higher chlorine levels in the catalyst.

Bimetallic catalysts have shown good catalytic stability. The research on bimetallic catalysts has had a major impact in the reforming of petroleum naphtha fractions to produce high octane number components for gasoline [Sinfelt, 1983]. Two industrial catalysts for naphtha reforming were developed in 1969 for different companies (Exxon and Chevron). Pt-Ir and Pt-Re supported on Al_2O_3 [Jacobson et al., as cited in Sinfelt , 1983]. During the 1970´s bimetallic catalysts largely replaced traditional Pt catalysts in reforming.

The research in bimetallic catalysts has received particular attention: (a) the investigation of selectivity effects in catalysis by such bimetallic materials, (b) the preparation and characterization of highly dispersed bimetallic catalysts and (c) the metallic stability.

Since the ability to form bulk alloys was not a necessary condition for a system to be of interest as a catalysts, it was decided not to use the term alloy in referring to bimetallic catalysts in general. Instead, terms such as bimetallic aggregates of bimetallic clusters have been adopted in preference to alloys. Bimetallic clusters refer to bimetallic entities which are highly dispersed on the surface of a carrier.

In an investigation of Pt-Ir catalysts, the effects of thermal treatments in O_2 (300 to 600 °C) and H_2 (500 to 800 °C) on the metal dispersions of 1% Pt, 1% Ir, and 1% Pt-1% Ir catalysts were studied by Graham & Wanke [Graham & Wanke,1981] . Treatment in O_2 at 400 to 600 °C resulted in increases in dispersion for the Pt catalyst. Small increases in dispersion for the Ir catalysts were observed after treatment in O_2 at 300 °C; at higher temperatures the Ir dispersion decreased significantly. Segregation of the metals occurred in the bimetallic Pt- Ir catalysts during treatment in O_2. The largest decreases in dispersion due to treatment in H_2 were observed for the Pt catalyst. Surprisingly, H_2 treatment of the Ir and Pt-Ir catalysts resulted in essentially the same relative decreases in metal dispersions.

Studying the same bimetallic catalyst, Bishara et al., [Bishara et al.,1983] investigated the effect of temperature, gas flow rate, O_2 concentration and oxychlorination on the sintering of

an industrial bimetallic reforming catalyst (Pt-Ir/Al$_2$O$_3$). The time taken for carbon removal decreased with increasing gas flow rate from 0.75 to 3 l/h/cc. cat. and good metal dispersion and high BET surface area were achieved at a flow rate of 3 l/h/cc.cat. Increasing the initial combustion temperature from 370 to 450° C led to considerable sintering of the metal. Better metal dispersion and higher BET surface area were restored using O$_2$ concentrations in the range 0.3 to 0.6% above which value considerable sintering of both metal and support occurred. In sintered catalysts, metal redispersion could be improved to some extent by oxychlorination treatment. Dispersion of the metallic phase was found to be higher at higher chlorine levels in the catalyst.

In other study by Deng et al., [Deng et al.,1988] the effect of addition of Ba on sintering of Pt clusters on Pt/γ-Al$_2$O$_3$ catalysts was examined. During the preparation and thermal treatment of the catalysts, two new species - BaCO$_3$ and BaAl$_2$O$_4$ - were formed from Ba acetate (Ba(AC)$_2$). Ba acts as an inhibitor for sintering at either a low Ba/Pt atomic ratio range or a high ratio range, whereas in-between those two ranges it acts as a promoter. The inhibiting effect of Ba (AC)$_2$ on sintering of Pt clusters cannot be related to the neutralization of support acidity. The inhibiting and promoting effects of Ba can be ascribed to the presence of BaCO$_3$ at a low Ba/Pt atomic ratio and BaAl$_2$O$_4$ at a high Ba/Pt atomic ratio, respectively.

One of the most common bimetallic catalyst is Pt-Re. Pieck et al. [Pieck et al., 1990] studied the influence of temperature and gas flow rate on total metallic dispersion and specific surface area of Pt-Re/Al$_2$O$_3$ reforming catalyst during the burning of coke deposited on its surface. A laboratory catalyst coked to different coke concentrations and a commercial catalyst coked in a commercial plant were used. The chloride level during oxychlorination and its influence on total metallic dispersion were also studied. The actual temperature inside the catalyst during coke burning is the main parameter affecting the total metallic dispersion. During catalyst oxychlorination the metallic phase is redispersed and the total dispersion at values of 0.9-1% chloride on the catalyst is the same, independent of the initial dispersion. The total metal dispersion of Pt-Re/Al$_2$O$_3$ is fixed by the platinum complexes in either sintering or redispersion. This is because, on reduction of Pt complexes, metallic Pt forms crystallites where Re is reduced producing the Pt-Re clusters.

Shinjoh et al.,[Shinjoh et al.,1991] studied both sintering and activity behaviors over noble metal catalysts aged in oxidative atmospheres with various O$_2$ contents at 1000°C for 5 h. With increasing O$_2$ contents, catalytic activities over aged Pt, Rh, and Pt/Rh catalysts decreased, and, in contrast, those over aged Pd and Pd/Rh catalysts increased. While, an order of sintering for the noble metal particles on aged catalysts agreed closely to that of the each percentage conversions as well as to that of vapor pressures of respective catalyst species, such as noble metals or their oxides. It is confirmed through the above results that the performance of aged catalysts are tightly governed by the properties of noble metals and the selectivity data are also important for exploring the catalytic activities, in particular, over multi-functional catalysts such as automotive exhaust ones.

In other study, a series of Pt-Rh/Al$_2$O$_3$ catalysts designated PtRhx, where x is the atomic percentage %Rh/Rh+Pt were prepared by successive impregnation of Al$_2$O$_3$ pretreated in H$_2$ at 850°C, with aqueous solutions of H$_2$PtCl$_6$ and RhCl$_3$[Kacimi & Duprez,1991]. They were calcined at 450°C (fresh catalysts) and then sintered (2% vol. O$_2$/Ar for 2h) at 700, 800

and 900°C. The catalysts were dechlorinated at 400°C. This treatment induces a decrease of the metal area of Pt while there is no change for Rh. It was observed a significant change in the surface composition of Pt and Rh for the sintered catalysts which are strongly enriched in Rh at high Rh content and in Pt at low Rh content. Two models are proposed to explain their results, they take into account the structural and morphological changes of Rh and Pt in oxidizing atmosphere as well as the degree of interaction between the two components of the bimetallics.

The same authors [Kacimi, et al., 1993] studying the sintering of Pt-Rh/Al_2O_3 catalysts in O_2 atmosphere at 700 and 900°C, found a strong enrichment in Rh at high Rh content while, at low Rh content, the bimetallics would be enriched in Pt. All the states of Rh (including Rh^{3+} in strong interaction with Al_2O_3) were analyzed by XPS $^{18}O/^{16}O$ and oxygen storage capacity (OSC) techniques and also they analyzed Rh° and Rh_2O_3.

In other investigation on Pt-Sn/Al_2O_3 reforming catalysts Yaofang et al, [Yaofang et al.,1994] studied the kinetics of coke combustion, platinum sintering in a nonhydrogen atmosphere, and redispersion on Pt-Sn catalyst. Using kinetic results the authors carried out mathematical simulation of coke burning in a radial continuous regenerators. Good agreement was obtained between the temperatures calculated from the simulation and measured values. Gaseous O_2 may enhance resistance against sintering at high temperatures. The platinum sintered in the catalyst without a decrease in support surface area and it could be completely redispersed through chlorination and oxidation.

The same authors [Yaofang, et al.,1995] studied the kinetics of coke combustion, Pt sintering in a non-H_2 atmosphere, and redispersion on Pt-Sn reforming catalyst. By using the kinetic results, mathematical simulation of coke burning in a radial continuous regenerator was established. Good agreement was obtained between simulation-calculated and measured temperatures. The O_2 in the gas may enhance resistance to sintering at high temperatures in the presence of water. The sintered Pt on the catalyst, if there had been no decrease of the support surface area, can be completely redispersed through chlorination and oxidation..

Platinum sintering and redispersion were systematically investigated with Pt-Re and Pt-Sn reforming catalysts by Yaofang et al.,[Yaofang, et al.,1995]. It was found that platinum might sinter both in catalyst dehydration during the start-of-run and in coke burning during regeneration and had the same sintering mechanism as the following: $PtO_2 \rightarrow Pt + O_2$, except melt of alumina supporter. The sintered platinum could be completely redispersed through regeneration if the alumina had no decrease in its surface area. Otherwise the loss in the platinum dispersion or dehydrogenation activity of the catalyst after regeneration would be proportional to the loss in surface area of alumina. The sintered Pt redispersed quite fast, taking about 10 minutes of chlorination and 30 minutes of oxidation.

In other investigation of Pt-Rh/Al_2O_3 and Pt-Rh/CeO_2-Al_2O_3 bimetallic catalysts (Pt+Rh≈60 µmol g^{-1}) the samples were prepared via chlorine-free precursors[Martin et al.,1995]. Oxygen storage capacities (OSC) were measured on the fresh (calc. 723K) and on the sintered catalysts (1%O_2+10%H_2O, 2h, 973K and 1173K). On Al_2O_3 catalysts, only Rh can promote OSC which is extremely sensitive to sintering. OSC values are higher on Al_2O_3-CeO_2 catalysts, but do not depend on the composition of the bimetallics. Moreover CeO_2

renders the catalysts resistant to sintering. $Pt-Rh/Al_2O_3$ and $Pt-Rh/CeO_2-Al_2O_3$ were modified by Cl, SO_4^{2-} and K. On Al_2O_3, OSC variations due to the additives follow the same trend as the variations of O_2 mobility (deduced from $^{18}O/^{16}O$ isotopic exchange). Chlorine and sulfur are inhibitors of OSC while K, at low content, is a promoter.

The addition of W to 0.3 wt % $Pt/\gamma- Al_2O_3$ catalysts has been found to stabilize and even increase Pt dispersion after high reduction temperature (up to 1073 K)[Contreras &Fuentes,1996]. This effect appears to be caused by formation of Pt species bound to WOx during drying and calcination and by strong interaction between Pt crystallites and the mixed oxide surface after H_2 reduction. UV-vis spectra show the formation of WOx and PtOy species on the surface of alumina in the calcined state. Interaction between Pt^{4+}- and W^{6+}-bearing structures seems to enhance UV absorption with minor variations in the location of the band maxima. $Pt/WO_3- Al_2O_3$ were in general more stable towards deactivation than monometallic Pt catalysts (reduced at 773 K) during hydrogenation of benzene. Reduction at 1073 K produced catalysts with lower initial activity but with increased resistance towards deactivation. Impregnation of Pt on $WOx-(\gamma- Al_2O_3)$ gave the best overall catalysts, apparently because of an improved interaction of crystallites with the modified surface of Al_2O_3. This result is important in order to control deactivation and sintering of the metallic phase if high operation temperatures are involved.

In other investigation bimetallic $Pd-Pt/Al_2O_3$ catalysts were prepared by controlled surface reactions [Micheaud et al.,1996] . The reduction of $PtCl_6^{2-}$ can be made by using as reductant hydrogen preadsorbed on a parent monometallic Pd/Al_2O_3 catalyst nothing or metallic palladium itself (direct redox reaction). Two precursors ($Pd(NH_3)_4Cl_2$ and $Pd(Acetate)_2$) were used to prepare the (1 wt % Pd) parent catalyst. The platinum loading was within the range of 0.13-0.14 wt %. The two preparation methods lead to different kind of Pt deposit, whatever the Pd parent catalyst. By using preadsorbed H_2, Pt can be deposited in decoration on low coordination sites (corners, edges) of Pd particles. By direct redox reaction, the deposit of Pd atoms occurs preferentially on the (111) faces of Pd particles. However some sintering can occur, especially during hydrogen treatment in aqueous medium and that sintering is enhanced by chloride ions.

In other study made by Sakamoto et al.,[Sakamoto, et al.,1999], the addition of Fe to the Pt/Al_2O_3 catalyst was made, with focus on the catalytic activities of stoichiometric and lean mixture simulated exhaust from automotive engines on bimetallic $Pt-Fe/Al_2O_3$ catalysts after the O_2, O_2-H_2, and $O_2-H_2-O_2$ treatments and compared to that of Pt/Al_2O_3 catalysts. The state of the Pt particles of the $Pt-Fe/ Al_2O_3$ catalysts was also investigated for several techniques. The activity of the $Pt-Fe/Al_2O_3$ catalyst was greater than that of the Pt/Al_2O_3 catalyst after the $O_2-H_2-O_2$ treatment for the stoichiometric mixture. Also, the activity of the $Pt-Fe/Al_2O_3$ catalyst after the O_2-H_2 treatment was greater than that after the O_2 and $O_2-H_2-O_2$ treatments. Pt particles were found to react with Fe additives to form homogeneous Pt-Fe alloy particles on Al_2O_3 under reducing conditions. Also, the Pt-Fe alloy particles on Al_2O_3 were found to segregate into Pt and Fe_2O_3 and to form a Fe_2O_3 coverage layer on Pt particles so that Pt particles were prevented from sintering when heated at 800 °C for a lean mixture. On the other hand, the activity of the Pt/Al_2O_3 catalyst was greater than that of the $Pt-Fe/Al_2O_3$ catalyst after the $O_2-H_2-O_2$ treatment for lean mixture. The layer of Fe_2O_3 on Pt is responsible for the low activity.

Hayashi et al., [Hayashi et al.,2002] investigated the sintering behavior of Pt metal particles by supporting them on silica-coated alumina. Silica coating was found to be effective for the retention of a large surface area of alumina even after calcination at elevated temperatures. Before sintering, the size of Pt metal particles on all the silica-coated aluminas, including the uncoated alumina, was identical, while the particle size was larger on silica than on alumina. After sintering the Pt catalyst at 1073 K, the particle size increased on uncoated alumina as well as on alumina coated with thicker silica layers, especially on the supports previously calcined at > 1473 K. On the other hand, the size of Pt metal particles did not increase much on alumina coated with monolayer silica. The observed suppression of sintering of Pt metal particles resulted from the retention of a large surface area of alumina with a thinner silica layer. In the case of a thicker silica layer, although a large surface area was maintained after calcination at elevated temperatures, the existence of a bulk silica-like property of the support did not favor the suppression of sintering of Pt metal particles.

In other investigation made by Mazzieri et al. [Mazzieri, et al.,2008] the deactivation, by coke deposition and sintering, and the regeneration of the metal function of Pt-Re-Sn/ Al_2O_3-Cl and Pt-Re-Ge/Al_2O_3-Cl catalysts were studied. The analysis of the carbon deposits and of the final state of the metal and acid functions were performed by means of temperature programmed oxidation, temperature programmed reduction and temperature programmed pyridine desorption (TPO, TPR and TPD-Py) respectively. The degrees of deactivation and activity recovery of the metal function were measured by means of the cyclohexane dehydrogenation and cyclopentane hydrogenolysis reactions. It was found that the Pt-Re-Sn catalysts were more stable than the Pt-Re-Ge ones. Regeneration produced a segregation of the metal phase on both kinds of catalysts. Metal particle sintering at 650 °C modified the metal function severely and Pt was segregated from the other components. All the rejuvenation treatments (Cl, air and high temperature) were unable to restore the original state of the metal function.

In other work of bimetallic catalysts, Kaneeda et al.[Kaneeda, et al.,2009] studied the Pt-Pd/Al_2O_3 catalysts for the NO oxidation after severe heat treatments in air. For this purpose, the addition of Pd has been attempted, which is less active for this reaction but can effectively suppress thermal sintering of the active metal Pt. Various Pd-modified Pt/ Al_2O_3 catalysts were prepared, subjected to heat treatments in air at 800 and 830 °C, and then applied for NO oxidation at 300 °C. The total NO oxidation activity was shown to be significantly enhanced by the addition of Pd, depending on the amount of Pd added. The Pd-modified catalysts are active even after the severe heat treatment at 830 °C for a long time of 60 h. The optimized Pd-modified Pt/Al_2O_3 catalyst can show a maximum activity limited by chemical equilibrium under the conditions used. From their characterization results as well as the reaction ones, the size of individual metal particles, the chemical composition of their surfaces, and the overall TOF value were determined for discussing possible reasons for the improvement of the thermal stability and the enhanced catalytic activity of Pt/Al_2O_3 catalysts by the Pd addition. The Pd-modified Pt/Al_2O_3 catalysts should be a promising one for NO oxidation of practical interest.

In other investigation, Contreras et al., [Contreras et al.,2009] found that W^{6+} ions inhibited sintering of the Pt crystallites once they were formed on the Al_2O_3 after reduction at 1073 K. Sequential samples impregnating Pt on WOx-Al_2O_3 were more active and stable during

benzene hydrogenation. W^{6+} ions promoted high thermal stability of Pt crystallites when sequential catalysts were reduced at 1073 K and decreased their Lewis acidity. The same authors studied the thermal stabilization of γ-Al_2O_3 using W^{+6} ions, which has been found useful to the synthesis of Pt/Al_2O_3 catalysts [Contreras et al.,2010].

The sequential impregnation method was also used by the same authors to study the n-heptane hydroconversion. They found that the W^{6+} ions delayed reduction of a fraction of Pt^{+4} atoms beyond 773 K and that W^{6+} ions inhibited the sintering of the metallic crystallites once they were formed on the surface. After reduction at 1073 K, sequential samples impregnating Pt on WOx/Al_2O_3 were more active and stable during n-heptane hydroconversion than monometallic Pt/Al_2O_3 catalyst. Selectivities for dehydrocyclization, isomerization and hydrocracking changed significantly when the W/Pt atomic ratio and reduction temperature increased. Initial and final reaction rates were more sensitive to reduction temperature. W^{6+} ions promoted high thermal stability of Pt crystallites when sequential catalysts were reduced at 1073 K and deactivation of bimetallic catalysts reduced at 773 K and 1073 K was less than the deactivation of Pt/Al_2O_3 catalyst.

In other paper of Pt-Rh catalyst Fernandes et al., [Fernandes et al.,2010] studied the influence of thermal ageing effects on catalytic activity for a Pt-Rh three-way catalyst. Deep textural, structural and physicochemical changes in the catalyst washcoat were caused by exposure to high temperatures (900 °C and 1200 °C). The catalytic activity was evaluated in terms of CO and propane oxidation and the reduction of NO by CO. In general, the conversions were lower after the ageing.

In other paper of Pt-Rh catalyst Hirata et al.[Hirata et al.,2011] studied the behaviors of sintering and reactivation of Pt and Rh on various metal oxide supports by TEM, CO pulse chemisorption and XAFS analysis. The results suggested that the phenomenon of reversible sintering and re-dispersion to reduced active metallic sites is related to the electron density of O atoms in support and to the crystal structure of support. As a result of in situ XAFS and in situ TEM analysis, Pt reversible sintering and re-dispersion phenomenon was observed on CeO_2 based metal oxide.

In a new investigation of Pt-Ni, and Ru-Ni bimetallic catalysts, Guo et al.,[Guo et al., 2011] studied that a trace amount of noble metal (Ru or Pt <0.1 wt%) was doped onto an anodic Al_2O_3-supported Ni catalyst, to know its performance in the steam reforming of methane, especially during the daily startup and shutdown operation. Although the steam purge treatment at high temperatures seriously deactivated the Ni catalyst because of the oxidation of metallic nickel with steam into Ni^{2+}, trace Ru assisted the regeneration of active metallic nickel by hydrogen-spillover. And, the Ni sintering was largely alleviated by the addition of Ru, and it was probably due to the formation of Ru-Ni alloy. In comparison with the Ru-doped Ni catalyst, the Pt-doped Ni catalyst showed a more favorable tolerance to steam oxidation, even at 900 °C.

8. Proposed models of the sintering process

In accordance with Wanke and Flynn [Wanke & Flynn,1975] the factors that influence the sintering of supported metal catalysts are: temperature, type of atmosphere, nature of the

support and the degree of metal loading appear to be of secondary importance.The experiments have shown that the rate of loss of dispersion increases with increasing temperature even in absence of O_2. In the case of presence of O_2 some investigators have observed an increase in metal dispersion at certain temperatures [Wanke & Flynn,1975].

Redispersion in O_2-containing atmospheres appears to be restricted to temperatures between 400 and 620°C. The Pt dispersion decreases at temperatures above this interval or for long periods of time.

The rate of loss of dispersion is larger in O_2 atmosphere than in H_2 atmosphere [Somorjai,1968, as cited in Wanke & Flynn,1975] and the rate of loss in dispersion decreased with decreasing O_2 partial pressure [Huang,1973, Wynblat,1973, as cited in Wanke & Flynn,1975].

The rate of sintering in N_2 atmosphere is approximately similar to the rate in H_2 atmospheres and the rate of sintering in vacuum is lower than if a gas phase is present [Boudart, 1968, as cited in Wanke & Flynn,1975].The effect of the support on the rate of sintering has a strong dependence however is difficult to establish. Some authors [Huang, 1973, as cited in Wanke & Flynn,1975] showed strong dependence on the support but the applicability of these results to supported metal catalysts is questionable because the size of metal crystallites in this work was much larger than those encountered in supported metal catalysts.

Wanke and Flynn [Wanke & Flynn,1975] compared sintering data for Al_2O_3, SiO_2 and carbon-supported catalysts and they did not find that it was not a possibility to determine the effect of the support on the sintering rate since sintering conditions, initial metal dispersions and metal loadings are different for all these samples.

The mathematical models based on postulated mechanism for the sintering of supported metal catalyst have appeared in the literature. The model developed by Ruckenstein and Pulvermacher [Ruckenstein & Pulvermacher,1973a, 1973b, as cited in Wanke & Flynn,1975] envisages the sintering of supported metal catalysts to occur by migration of metal crystallites over the surface of the support and the resulting collision and fusion of metal particles causes the loss in dispersion (crystallite migration model).

The second model proposed by Flynn and Wanke [Flynn,1974a, 1974b, as cited in Wanke & Flynn,1975] considers the sintering to occur by dissociation of atomic or molecular species from the metal crystallites. These atomic or molecular species migrate over the support surface and become incorporated into metal crystallites upon collision with the stationary metal crystallites (atomic migration model).

The crystallite migration model is similar to the mechanism proposed by Smoluchowski [Smoluchowski, 1917, as cited in Wanke & Flynn,1975] for the coagulation of colloidal suspension by Brownian motion. The atomic migration model is similar to the model proposed by Ostwald (Ostwald ripening) [Ostwald,1900, as cited in Wanke & Flynn,1975] for the change in mercury oxide particle sizes in solution. The transport of metal or metal compounds through the vapor phase is a third possible mechanism for the sintering of supported metal catalysts. The transport of metal by this mechanism in non-oxidizing atmospheres is negligible for Group VIII metals at temperatures below 1000°C.

Some authors have mentioned that the growth of supported metal crystallites are related with the interaction metal-support [Wynblatt, 1975, as cited in Wanke & Flynn,1975], in fact it could be so important to determine which mechanism will predominate.

In other studies, Fuentes & Salinas [Fuentes & Salinas,2001] have showed that apparent inconsistencies between leading models and experimental data were caused by the use of limited solutions to the models. In particular, the authors have studied solutions to the Ostwald ripening model and they found that the classical analytical solution, known as the Lifshitz, Slyazov and Wagner solution (LSW), is only a particular solution of a family of solutions. The important implication of that analysis is the observation that the particle size distribution predicted by their solution can fit adequately in the experimental distributions observed during sintering of Pt, Pd and Ni supported in a variety of supports.

8.1 Atomic migration model

The model presented by Flynn and Wanke [Flynn &Wanke, 1974a, 1974b, as cited in Wanke & Flynn,1975] envisages sintering to occur as a three-step process: (i) Escape of metal atoms or molecules such as metal oxides in an oxygen atmosphere from the metal crystallite to the support surface, (ii) Migration of these atoms along the support surface and (iii) Capture of these migrating atoms by metal crystallites upon collision of these migrating atoms with stationary metal crystallites.

These processes result in the growth of the large metal crystallites and in a decrease in size of the small metal crystallites since the rate of loss of atoms is smaller than the rate of capture for large crystallites, while for small crystallites the rate of loss is greater than the rate of capture. This occurs because large crystallites are in equilibrium with a lower concentration of migrating atoms than small crystallites (this is the two-dimensional analogy of Ostwald ripening).

8.2 Crystallite migration model

The crystallite migration model postulates that metal crystallites migrate as entities along the surface of the support. Rapid diffusion of metal atoms on the surface of a metal crystallite will cause metal atoms to accumulate on one side of the crystallite by random fluctuations. This rapid, random surface diffusion will cause Brownian type motion of the particles on the support [Wynblatt, 1975, as cited in Wanke & Flynn,1975].

Direct evidence of this crystallite migration is difficult to obtain. The usually cited references in support of crystallite migration [Phillips, 1968,Thomas, 1964, Sears,1963, as cited in Wanke & Flynn,1975] use microscopy to investigate this phenomenon, and the results show either very slight crystallite motion, such as small rotations, or they are anomalous in that large particles appeared to move faster than small particles.

If appreciable particle migration occurs, it is restricted to metal crystallites smaller than 50 Å in diameter [Whnblatt,1975, as cited in Wanke & Flynn,1975]. The model presented by Ruckenstein and Pulvermacher [Ruckenstein and Pulvermacher,1973, as cited in Wanke & Flynn,1975] is hence restricted to the early stages of sintering when crystallites are < 50 Å in size. Two limiting cases of the crystallite migration model were developed: (i) Surface

diffusion controlled (i.e. the rate of migration of crystallites is the rate-determining process) and (ii) Sintering controlled (i.e. the merging of two metal crystallites coming into physical contact by collision is the rate-determining process).

For both of these cases the authors were able to reduce the kinetic equations of the sintering process to power-law equations where the value of the power-law order, n depends on the rate-determining step. For the sintering controlled case (i.e. merging of particles), n is equal to 2 or 3 and for the surface diffusion controlled case n > 4. The magnitude of n for the surface diffusion controlled case is related to the dependence of the surface diffusion coefficient on the average metal crystallite size.

The authors Pulvermacher [Pulvermacher, 1974, as cited in Wanke & Flynn,1975] described mathematical techniques for differentiating between sintering and diffusion controlled cases. The application of these techniques to sintering data obtained by TEM, SAXS, X-ray broadening and chemisorption was presented.

Other authors [Wynblatt 1975, as cited in Wanke & Flynn,1975] showed on the basis of theoretical predictions that the merging of metal crystallites cannot be the rate-determining process at temperatures above 500°C, i.e., the sintering controlled case is generally not realizable under normal sintering conditions. This is supported by observations that metal blacks sinter is appreciable (fusion of particles in physical contact) at temperatures below 200°C [McKee, 1963, Khassan, 1968, as cited in Wanke & Flynn,1975].

It is important to notice that during the latter stages of sintering a mechanism other than crystallite migration causes the observed growth of metal crystallites.

Experimental attempts to determine which of the two mechanisms (atomic migration model and crystallite migration model) is predominantly responsible for the sintering of supported metal catalysts have not been conclusive. In large part this inconclusiveness arises from the complexity of the sintering process.

In another study, Handa & Matthews, [Handa & Matthews,1983] proposed a model, which utilizes a Monte Carlo simulation, of the sintering and the redispersion of supported metal catalysts is presented and compared with experimental data from a Pt/Al_2O_3 system. The model is based on an atomic migration mechanism, but includes instantaneous diffusion and coalescence of crystallites of size less than 1 nm in reducing and inert atmospheres. It was found that behavior in reducing, oxidizing and inert atmospheres could be predicted.

9. Metal stabilization

The stabilization of Pt/Al_2O_3 catalysts by addition of other oxides, preparation methods or metals has great importance in the preparation of catalyst because the sintering of Pt particles is reduced. One example of stabilization of Al_2O_3 by addition of oxides was done by Mizukami et al.,[Mizukami et al, 1991].

In this study thermostable high-surface-area Al_2O_3 was obtained by investigating the influence of preparation procedures, raw materials and additives on sintering of Al_2O_3. The complexing agent-assisted sol-gel method to obtain Al_2O_3 with large surface area and high durability at around 1000°C as compared with those prepared by conventional methods.

Upon addition of BaO, La$_2$O$_3$ and SrO to Al$_2$O$_3$, the sintering of Al$_2$O$_3$ was furthermore retarded and the effect was maximum when 10wt% BaO was incorporated to alumina. The activity order of the three catalysts for the CO oxidation was as follows: (commercial Al$_2$O$_3$) < (sol-gel Al$_2$O$_3$) < (sol-gel BaO-Al$_2$O$_3$). This sequence could be explained by the differences in the Pt crystal growth and α- Al$_2$O$_3$ appearance rates in the three catalysts.

In other study of stabilization, Pt/SiO$_2$ catalysts with well defined pore size distributions and metal particle sizes were prepared by the sol-gel method [Zou & Gonzalez, 1993]. Tetraethoxysilane (TEOS) and Pt(Acetyl acetonate)$_2$ were used as precursors. Pore size distributions were controlled by varying the H$_2$O/TEOS ratio during synthesis. It was found that when the particle size was matched to coincide with the average pore diameter the resulting Pt/SiO$_2$ catalysts were resistant to sintering in O$_2$ at temperatures up to 675°C.

In other work, catalysts of Pt supported on MgO, with Pt loadings of 0.5 to 5.9 wt%,[Ademiac, et al., 1993] were characterized by H$_2$ chemisorption, wide-angle x-ray diffraction and TEM after various high temperature treatments in O$_2$ and H$_2$. It is concluded that the H/Pt ratios for Pt/MgO do not, correspond to the Pt dispersion, even for catalysts with very low levels of impurities. Reduction at temperatures ≥400°C (HTR), of sulfur-containing Pt/MgO causes large decreases in H$_2$ adsorption, but the H$_2$ adsorption capacity can be restored by O$_2$ treatment at 500 - 550°C followed by reduction in H$_2$ at 250 to 300°C (LTR). Treatment of Pt/MgO in O$_2$ at 550 to 800°C results in decreases in average Pt crystallite size (redispersion); no significant Pt particle growth (sintering) occurs during O$_2$ treatment at temperatures as high as 800°C. Chlorine increases the rate of Pt redispersion, but chlorine is not required for redispersion of Pt on MgO

In other investigation, Pt clusters smaller than 1.5 nm on γ-Al$_2$O$_3$ support were stable against thermal sintering in H$_2$ at temperatures as high as 500°C[Zhang & Beard,1999]. The stability of small Pt clusters against thermal sintering can be ascribed to the anchoring effect of Pt by the acid sites on the surface.

The linearly adsorbed CO on Pt is characteristic of small Pt clusters. A band at 2112cm^{-1} suggests the presence of charged Pt atoms. Bridged CO infrared bands, 1825 and 1661cm^{-1}, which are absent from bulk Pt, are also evidence for the formation of small Pt carbonyl clusters. It was discovered in this work that the small Pt clusters coalesce readily upon H$_2$ reduction at 320°C when the catalyst is pretreated with a solution of a chloride salt such as NH$_4$Cl. The agglomeration of small Pt clusters in the presence of a chloride salt under a reducing environment is ascribed to the deanchoring effect of the chloride, which weakens the interaction of Pt with the anchoring Lewis acid sites. As temperature increases, the formation of mobile Pt chloride complexes that leads to Pt particle agglomeration is proposed .

The Pt particle sizes after the reductive agglomeration are distributed within a narrow range of 5-8 nm. The electronic character of the large Pt particles is identical to that of bulk Pt metal. It was further demonstrated that Pt cluster agglomeration is independent of the heating rate and the length of heating period, indicating that the predominant mechanism of Pt particle agglomeration is due to rapid coalescence of chlorinated primary small Pt particles under an H$_2$ atmosphere.

In other study of stabilization by supported bimetallic catalysts, highly dispersed Pt-W structures were formed on γ- Al_2O_3 from bimetallic cluster precursors with Pt-W bonds[Alexeev, et al.,2000]. The interactions of W cations with O_2 atoms of the support, on one hand, and with Pt clusters, on the other, stabilized Pt dispersion in clusters. Highly dispersed bimetallic structures highly resistant to sintering under high-temperature oxidation-reduction conditions were evident. Increases in the amount of W initially bonded to Pt, increased resistance of the supported Pt to migration and aggregation on the support. The resistance to aggregation was ascribed to the oxophilic metal-noble metal interactions. The interaction of W cations with Pt decreased the chemisorption capacity of Pt clusters for H_2 and CO, and the catalytic activity for toluene hydrogenation.

In other paper, one interesting investigation related with different preparation method of Pt/Al_2O_3 was made by Ikeda, et al.[Ikeda et al., 2001]. They found that the catalyst prepared by microemulsion had a higher resistance to sintering than the catalysts prepared by the sol-gel and impregnation methods. The resistance to sintering in all the catalysts was improved by pressing. The pressed microemulsion catalyst was little deactivated in the NO-CO reaction by thermal treatment at 700 °C for 12 h, and had a high activity relative to that of the sol-gel and impregnation catalysts.

In other stabilization work, sintering behavior of $Pt/γ- Al_2O_3$, Pt/ZrO_2 and Pt/CeO_2 catalyst was studied using an originally developed 3D sintering simulator [Shinjoh,, et al.,2009]. While Pt on the γ-Al_2O_3 sintered significantly, Pt on CeO_2 presented the highest stability against sintering. On the other hand, grain growth of supports was significant in the order; $ZrO_2 > CeO_2 > γ- Al_2O_3$.

In other interesting work made by Romero et al., [Romero, et al., 2002] a series of Pt/Al_2O_3 catalysts were prepared using a sol-gel method. It was found that the BET surface area decreased with an increase in the platinum content. A surface area of 500 m^2/g was obtained following calcination at 773K. The structure of fresh samples corresponded to a pseudoboehmite structure. Samples prepared using a water/alkoxide ratio (H_2O/ammonium ter-butoxide (ATB)) of 9 showed a well-defined, uniform pore size distribution following calcination at 773K. Aging studies (calcination at 873K for 24h) performed on these catalysts, exhibited sintering behavior which were similar to Pt/Al_2O_3 catalysts prepared by other methods. The sample prepared using a H_2O/ATB ratio of 9 had the highest surface area and was more thermally resistant towards metal sintering. A bimodal metal particle size distribution was observed: some particles exhibited sintering while others of similar size showed a greater thermal stability to sintering. The sample having the largest surface area and the highest thermal stability following thermal treatment was a consequence of a more condensed structure and a higher pore roughness obtained after drying the gel.

The use of zeolite as catalysts with noble metals was proved by Kanazawa [Kanazawa, 2006] in automotive exhaust systems. These catalysts were subjected to sintering at extreme temperatures, leading to deterioration of catalytic activity. Zeolite with the zeolite MFI structure having mesoporosity (ZSM5) structure is examined as a support for Pt particulate catalysts. The MFI structure is composed of agglomerates of single-crystal zeolite with interstitial mesoporosity. Pt fixed within these mesopores is shown through high-temperature

aging tests in air to be highly resistant to sintering due to the mechanical constraints on particle size imparted by the mesoporous structure. The deterioration of catalytic activity after aging is significantly lower than that for comparable γ-alumina supported catalyst.

In other work, the stabilization of Pt particles was studied by Liotta et al.,[Liotta et al.2009]. The authors studied a structured 1wt%Pt/ceria-zirconia/alumina catalyst and the metal-free ceria-zirconia/alumina was prepared, by dip-coating, over a cordierite monolithic support. In the Pt supported catalysts ceria-zirconia were present as a $Ce_{0.6}Zr_{0.4}O_2$ homogeneous solid solution and that the deposition over the cordierite does not produce any structural modification. Moreover no Pt sintering occurs and TEM investigations of the redox cycled Pt/ceria-zirconia/alumina catalyst detected ceria-zirconia grains with diameter between 10 and 35 nm along with highly dispersed Pt particles (2-3 nm) strongly interacting with ceria. The effect of redox aging on the NO reduction by C_3H_6, in lean conditions, was investigated over the Pt/ceria-zirconia/alumina monolith. The catalyst shows at low temperature (290 °C) good NO removal activity and appreciable selectivity to N_2.

In another stabilization work, the addition of W^{6+} ions to Al_2O_3 has been found useful to the synthesis of Pt/Al_2O_3 catalysts. The simultaneous and sequential methods were used to study the effect of W^{6+} upon $Pt/γ-Al_2O_3$ reducibility, Pt dispersion, and benzene hydrogenation [Contreras et al.,1996]. The same authors studied the thermal stabilization of $γ-Al_2O_3$ using W^{+6} ions in the synthesis of Pt/Al_2O_3 catalysts applied to the n-heptane hydroconversion. The sequential impregnation method was used to study the effect of W^{6+} upon $Pt/γ-Al_2O_3$ reducibility and n-heptane hydroconversion. The authors found that the W^{6+} ions delayed reduction of a fraction of Pt^{+4} atoms beyond 773 K. At the same time, W^{6+} inhibited sintering of the metallic crystallites of Pt once they were formed on the surface. After reduction at 1073 K, Pt on $WOx/γ-Al_2O_3$ were more active and stable during n-heptane hydroconversion than monometallic $Pt/γ-Al_2O_3$ catalyst.

In other study, the stabilization of Pt was obtained when the authors supported Pt on carbon black but their Pt nanoparticles were covered with microporous silica layers using successive hydrolysis of 3-aminopropyl-triethoxysilane and methyltriethoxysilane [Nakagawa, et al., 2010]. The Pt/carbon nanoparticles covered with microporous silica layers showed high sintering resistance of Pt metal particles to thermal treatment at 973 K in a H_2 atmosphere as compared with Pt/carbon. Furthermore, this catalyst showed higher catalytic activity for cyclohexane decomposition than Pt/carbon after thermal treatment.

An interesting paper made by Suzuki et al. [Suzuki, et al. 2010] studied multi-scale theoretical methods for predicting sintering behavior of Pt on various catalyst supports. In this regard, the capability of theoretical durability studies to offer an efficient alternative methodology for predicting the potential performance of catalysts has improved in recent years and various types of Pt diffusions depending on support were confirmed by the micro-scale ultra-accelerated quantum chemical molecular dynamics method. With this purpose, macro-scale sintering behavior of Pt/Al_2O_3, Pt/ZrO_2 and Pt/CeO_2 catalysts were studied using a developed 3D sintering simulator. Experimental results were well reproduced. While Pt on Al_2O_3 sintered significantly, Pt on ZrO_2 sintered slightly and Pt on CeO_2 demonstrated the highest stability against sintering.

A new procedure to stabilize Pt particles was developed by Lee et al., [Lee,et al., 2011]. The authors encapsulated supported Pt nanoparticles in heterogeneous catalysts to prevent their sintering. Model catalysts were first prepared by dispersing ~3-nm Pt nanoparticles on ~120-nm silica beads. These were then covered with a fresh layer of mesoporous silica, a few tens of nanometers thick, and etched to re-expose the metal surface to the reaction mixtures.. The resulting encapsulated platinum nanoparticles were shown to resist sintering during calcination at temperatures as high as 1075 K, whereas the unprotected catalysts were seen to sinter by 875 K.

In a recent investigation Li et al., [Li et al., 2011] prepared a support, composed by CeO_2-ZrO_2-La_2O_3-Al_2O_3(CZLA) with different contents of CeO_2, ZrO_2 and La_2O_3 by the peptizing method and characterized by XRD and N_2 adsorption-desorption. The low Pt-Rh content catalysts were prepared using $Ce_{0.4}Zr_{0.4}Y_{0.1} La_{0.1}O_{1.9}$ and CZLA samples as the support, and the catalytic performance showed that both La, Ce and Zr can inhibit the Al_2O_3 sintering and then suppress Al_2O_3 transition to α-phase. The CZLA sample with 2%La_2O_3 maintained a highest specific surface area (97 m^2/g) after aged at 1100°C for 5 h. The catalyst with CZLA and 2%La_2O_3 had an excellent catalytic performance. Its light-off temperature was 249°C, and full conversion temperature was 286°C for C_3H_8. Both results show that Ce-Zr-La co-modified alumina has great potential as support.

The stabilization of Pt nanoparticles supported on Al_2O_3 with conventional and perovskite based materials was reported by Dacquin et al.[Dacquin, et al.,2011]. Successive thermal treatments under reductive and oxidative atmospheres induced bulk and surface reconstructions. These modifications considerably alter the catalytic behavior of Pt in interaction with $LaFeO_3$ or γ- Al_2O_3 in terms of activity and selectivity toward the selective transformation of NOx. It has been found that oxidic Pt^{4+} species initially stabilized on $LaFeO_3$ lead after subsequent H_2 reduction to the formation of metallic nano-Pt particles in stronger interaction than on γ-Al_2O_3 support and then become more resistant to sintering during thermal aging in 1000 ppm NO, 1000 ppm N_2O, 3 vol % O_2, 0.5 vol % H_2O, and 0.5 vol % H_2 at 500 °C.

10. Conclusion

Based on the data reviewed from the literature, it is possible to draw some general conclusions about the factors that influence sintering of supported metal catalysts. Temperature and the characteristics of the atmosphere are the most important factors, although the nature of the support and type of structural promoters play an important role, too. Bimetallic catalysts have shown good catalytic stability for several industrial applications. Sintering can be slowed down by the use of additives to the support together with alternate preparation methods. These new procedures, particularly in the case of Pt nanoparticles, have shown to be effective in attaining more stability, and hence activity and selectivity, in several commercial reactions.

11. Aknowledgements

12. References

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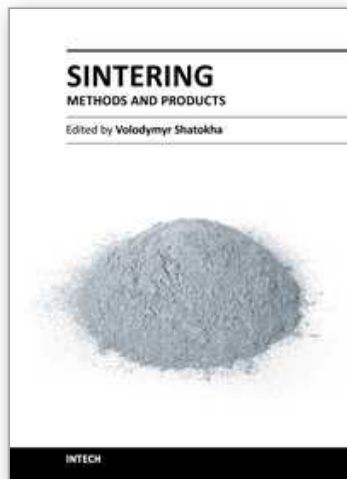
Sintering - Methods and Products

Edited by Dr. Volodymyr Shatokha

This book is addressed to a large and multidisciplinary audience of researchers and students dealing with or interested in sintering. Though commonly known as a method for production of objects from fines or powders, sintering is a very complex physicochemical phenomenon. It is complex because it involves a number of phenomena exhibiting themselves in various heterogeneous material systems, in a wide temperature range, and in different physical states. It is multidisciplinary research area because understanding of sintering requires a broad knowledge - from solid state physics and fluid dynamics to thermodynamics and kinetics of chemical reactions. Finally, sintering is not only a phenomenon. As a material processing method, sintering embraces the wide group of technologies used to obtain such different products as for example iron ore agglomerate and luminescent powders. As a matter of fact, this publication is a rare opportunity to connect the researchers involved in different domains of sintering in a single book.

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