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X-ray photoelectron spectroscopy investigation over supported palladium catalysts prepared using water-in-oil microemulsion

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ABSTRACT Supported palladium catalysts have been prepared using water-in-oil microemulsions consisting of $Pd(NO_3)_2$ aq, *Brij 30* (surfactant) and n-hexane (oil). The binding energies of palladium from those catalysts were measured using x-ray photoelectron spectroscopy (XPS) and were compared with that of the catalysts prepared by conventional impregnation method. It was observed that the majority of the palladium is present at a binding energy shifted between 0.8 to 1.0eV higher than the impregnation catalysts observed for PdO. Such shift appeared to be associated with a metal-support interaction where the palladium was very small in size and highly dispersed. These findings were supported with a much higher activity in methane combustion under lean conditions. However, not only the size and dispersity of palladium that determined their catalytic performance, it was found that the active phase or state of the catalysts that existed during the reaction has great influence on the catalyst activity. The result showed PdO was the most active state for methane combustion but it did not rule out the possibilities of a mixed phase, Pd^0/PdO_x.

(Supported palladium catalyst, XPS, Small and dispersed Pd, Methane oxidation)

INTRODUCTION

Nanoparticles constitute a frontline area of research today. Nanoparticles represent new materials to the extent that their physical or chemical properties are different from those of the bulk materials. [1,2] Thus, they have various potential applications such electronic, optical, magnetic recording media, superconductors, high performance engineering materials, dyes, pigments, drug delivery and many more. [1,3-6] Among the various physical and chemical methods employed to synthesis nanoparticles, it has recently been shown that an interesting and promising one is based on the use of water-in-oil (w/o) microemulsions as reaction and solvent media. Water-in-oil microemulsion system, consisting of a surfactant phase, an oil phase and an aqueous phase, is a thermodynamically stable isotropic dispersion of the aqueous phase with surfactant molecules stabilized at the water-oil interface. These surfactant-covered water pools offer a unique microenvironment for the formation of nanoparticles. They not only act as microreactors for processing reactions but also inhibit the excess aggregation of particles because of the surfactants adsorbed on the particle surface.

Heterogeneous catalysis is an area where nanomaterials in the form of supported metal and compound particles have been utilized for a long time. Here, the catalytically active component is finely dispersed over a support to gain a high surface area of the usually expensive metal. Many have reported the fabrication of very small metal particles through numerous physical and chemical methods [7-9]. Systematic characterization using suitable tools such as electron microscopy [9-13], X-ray and electron diffraction [10,11], UV-Vis and FT-IR spectroscopy [7,14] and small angle x-ray scattering [15] has been employed. However, only a few studies were based on the measurement of core-level photoemission technique in relation to particle sizes and dispersions. Nevertheless, photoemission is an

especially useful probe of electronic structure and have been applied to supported metal clusters to understand better the basic physics involving in the transition from the discrete energy levels of free atoms to the continuous, k-dependent energy bands of bulk materials. [16-18] From chemistry point of view, x-ray photoemission (XPS) appears to be an ideal tool for analyzing near-surface layers of a solid. Every element, with exception of hydrogen, is susceptible to this technique [19]. As a result, chemical shifts of core levels measured by XPS are often used to characterize the chemical states of elements in different matrices.

In this study, we are looking into electronic properties, i.e. the binding energy, BE of palladium in Pd/Al_2O_3 of nano-sized particles, synthesized in controlled environment (water-in-oil microemulsion). Methane oxidation was performed over these catalysts to determine their catalytic activity. The relation between catalytic activity, particle size effects and the chemical states of palladium will be discussed.

EXPERIMENTAL

The palladium catalysts were prepared by two different methods via incipient wetness impregnation of the support (γ-alumina) with aqueous solution of $Pd(NO_3)_2$ and in water-in-oil microemulsion. The microemulsions were prepared by mixing specified volumes of surfactant, *Brij 30* ($C_{12}E_4$) with n-hexane with appropriate volume of palladium nitrate solution. The resulting microemulsion, which contained the metal ion dissolved within the water pools of reversed micelles, was equilibrate over 2 hours with continuous stirring. A reduction with hydrazine hydrate was added drop-wise with stirring. γ-Al_2O_3 was then added to the metal colloids and stirring continued for another 1 hour. Excess solution was removed by drying in an oven at 80°C overnight. All the supported catalysts were calcined under flowing oxygen in two stages; 400°C for 2 hr followed by 500°C for 1 hr. Catalysts were prepared for two different metal loadings. Concentrations of palladium salts and reducing agent used plus metal loading are given in Table 1. Catalyst DEP1C was synthesized in a microemulsion prepared from aqueous $Pd(NO_3)_2$ solution injected drop-wise to stable microemulsion while catalyst DEP1D was obtained by reduction in double microemulsions [20].

Table 1: Details of the catalyst descriptions and preparations.

Catalyst	Metal Loading (Wt%)	Conc. $Pd(NO_3)_2$ (mol/L)	Conc. $N_2H_4.xH_2O$ (mol/L)	Method of preparation
IMP1	1	-	-	Impregnation
IMP2	3	-	-	Impregnation
DEP1A	1	1	1	Bulk microemulsion
DEP2A	3	3	3	Bulk microemulsion
DEP1B	1	1	3	Bulk microemulsion
DEP2B	3	1	1	Bulk microemulsion
DEP1C	1	1	1	Drop-wise microemulsion
DEP1D	1	1	1	Double microemulsions

The particle sizes were determined by TEM using a LEO Model 912AB operating at 120kV. The sample for TEM analysis was obtained by placing a drop of the dispersed solution onto a holey carbon film of 200 mesh of copper grid and evaporated in air at room temperature. XPS experiments were performed using XSAM-HS spectrometer from Kratos Analytical with MgKα as x-ray source. The residual pressure in the analysis chamber was $1x10^{-9}$ Torr. The samples were held to a metal by a double-sided tape and all conditions of sample preparations, recording of the spectra and data processing were identical for all samples. The core level binding energy for oxidized palladium was referenced to the support Al 2p line at 75.5eV. The Pd 3d spectra curve fits represent the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ spin orbit splitting and therefore the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energy separation and intensity ratio were fixed to empirically determined values of 5.25eV and 1.5, respectively. An average FWHM (full width at half maximum) of 2.0eV was achieved for the components of the peak fits. Only the binding energy value of the Pd $3d_{5/2}$ line is reported in this work.

Catalytic activities of the Pd catalysts for methane oxidation were investigated using a conventional flow reactor operated at atmospheric pressure. 0.1gm catalyst was held in the center of a stainless steel tube with glass wool and mounted centrally in a vertical tube furnace controlled by a temperature controller. A gaseous mixture consisting of 10% CH_4, 50% O_2 and 40% N_2, resulting in a total flow rate of 200ml/min was passed down through the catalyst bed. Reactants and products were analyzed using a Hewlett-Packard gas chromatograph filled with a GS-Gaspro column operating at 60°C and a thermal conductivity detector maintained at 230°C. Carbon monoxide formation was never detected throughout the reaction. Samples were reduced in-situ under H_2 flow at atmospheric pressure, 400°C for 1 hour. Then the samples were purged with N_2 and cooled to 200°C under N_2 flow before the introduction of the reactant mixture.

RESULTS AND DISCUSSION

The relation between the size and the electronic state of supported Pd was investigated by XPS experiments. Table 2 summarizes the XPS binding energies of Pd 3d from catalysts with 1.0 wt% loading after calcination at 500°C for I hour. Theirs respective particle size obtained under TEM observation are also given.

Table 2: Binding energy (BE) of Pd $3d_{5/2}$ XPS and average diameter of PdO particles.

Catalyst	IMP1	DEP1A	DEP1C	DEP1D
Pd $3d_{5/2}$ BE (eV)	336.8	337.3	337.8	337.0 338.5
Average Diameter (nm)	40-50	24.4	16.9	10.8

Calcination of catalyst IMP1 in O_2 at 500°C gave a single peak at Pd $3d_{5/2}$ binding energy of 336.8eV, indicating a complete oxidation of palladium to PdO. [21] However, a shift to a higher binding energy values were observed for PdO in all catalysts prepared using microemulsions. The positive shifts of the core electronic level of palladium agreed well with size reduction in PdO particles determined from TEM experiments. A shift of 0.5 – 1.7eV higher than for bulk PdO, gives an overall size reduction from 24nm to 11nm.

Similar observations were reported earlier by Widjaja *et al.* [22] whereby the particle-size-induced BE shift depended on the crystalline phase of the support. Others defined positive binding energy shifts to be attributed to an electron deficiency of the palladium atoms. [23,24] A much higher BE shifts to 338.5eV from computer peak-fit of Pd 3d core level spectra for catalyst DEP1D, shown in Fig.1, is close to a binding energy assigned to PdO_2.[25] However, it is known to be highly unstable and decomposes to PdO upon drying. Nevertheless, these facts suggested that PdO_2, if it exists in the ultra high vacuum environment of the spectrometer, was stabilized by an interaction with alumina support. Alternatively, the species could be attributed to a highly dispersed and deficiently coordinated (ionic) Pd^{2+} in intimate contact with the γ-alumina support. [25] In short, larger PdO, deduced from its BE (336.8eV), is found in catalyst IMP1 prepared by incipient wetness. Catalyst prepared from microemulsions consists of small crystallites

and dispersed palladium with a metal-support interaction indicated by its higher BE.

The catalytic activities for methane oxidation over 1.0 wt% Pd/Al_2O_3 sample of IMP1 and series of DEP1'(s) are compared and given at increasing temperatures in Fig 2. Methane oxidation reaction starts as early at 310°C, 340°C and 380°C for reduced DEP1D, DEP1C and DEP1A respectively. On the other hand, catalyst IMP1 was 80°C higher. It can be seen that the activities of the four catalysts decrease in the following order: DEP1D > DEP1C > DEP1a > IMP1, given by its light-off temperature of 342°C, 355°C, 395°C and 405°C. When comparing the order of catalytic reaction with size of particles Pd from Table 2, the trend shows small grain size of Pd gave rise to high catalytic activity. Sample DEP1D with the smallest Pd particles displays the most active conversion where else IMP1 which one consist of large agglomerates of Pd over the support shows the least active among all the catalysts.

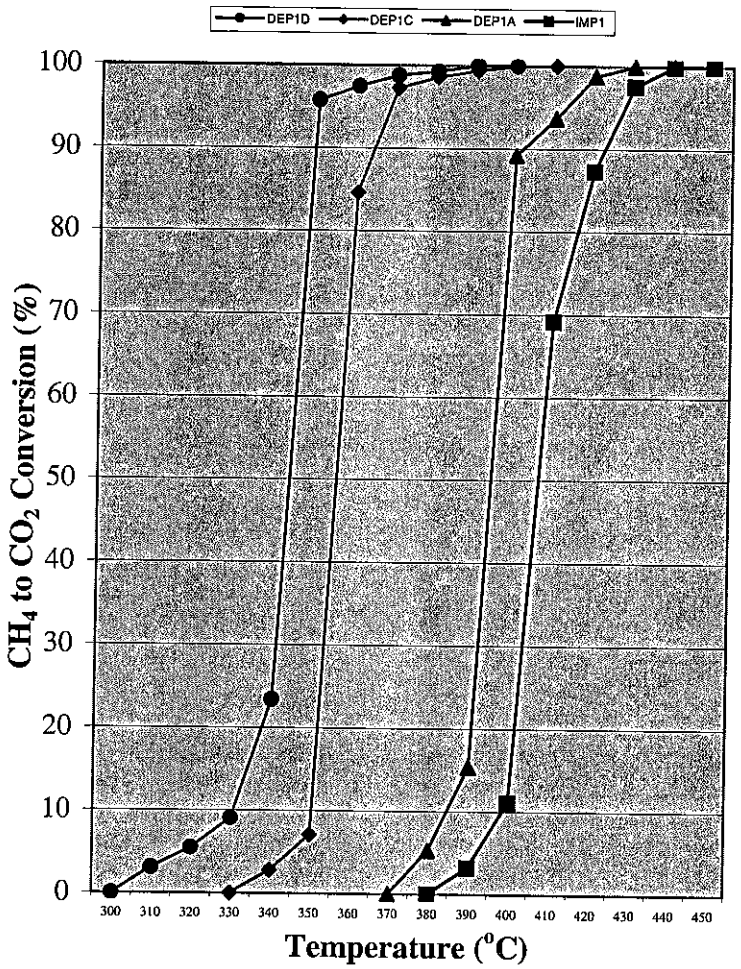

Figure 2. Activity for methane oxidation as a function of temperature over reduced 1.0 wt % Pd/Al_2O_3

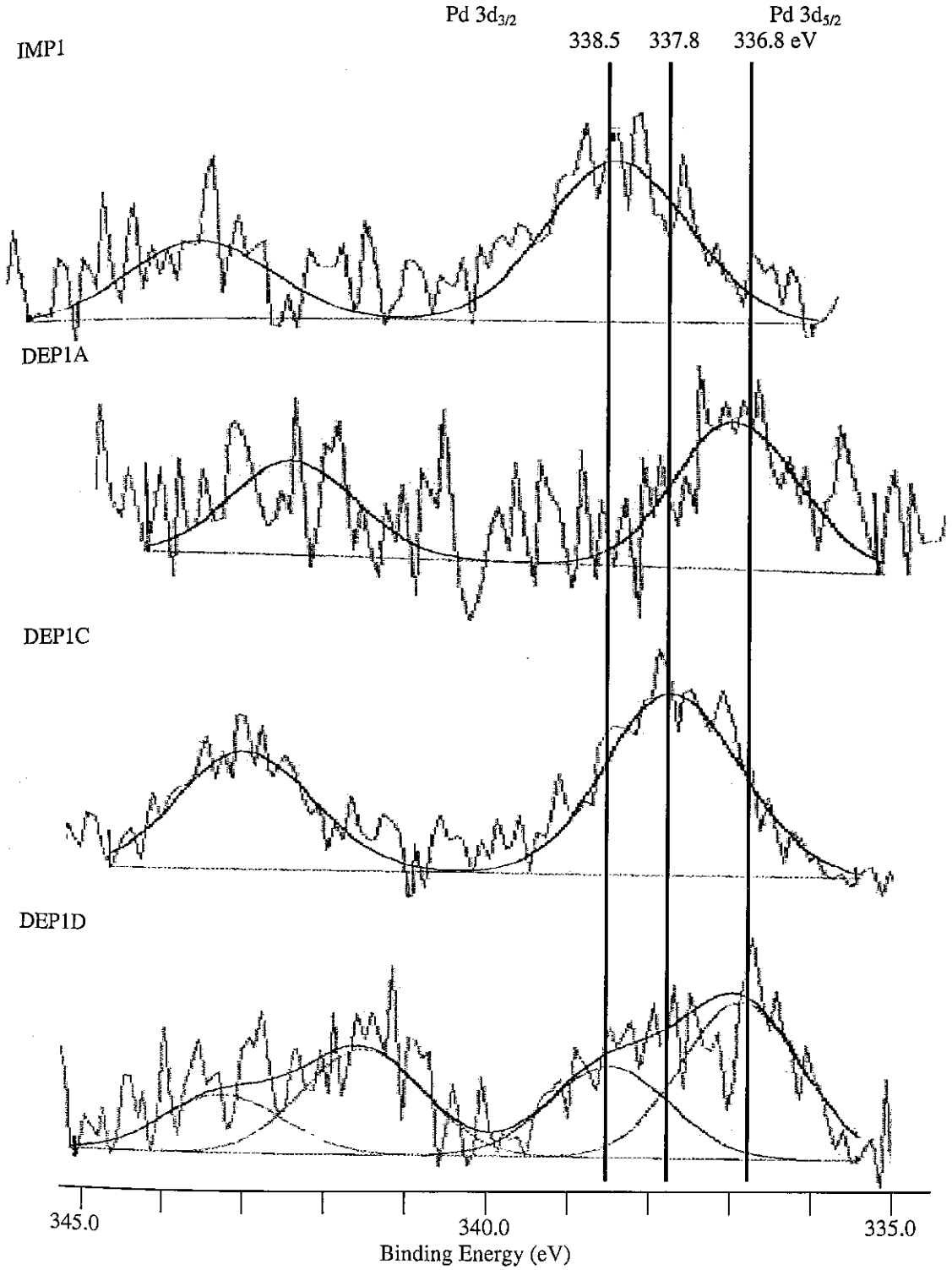

Figure 1. Computer peak-fit of Pd 3d core level XPS spectra after sample oxidation at 500°C for 1hour.

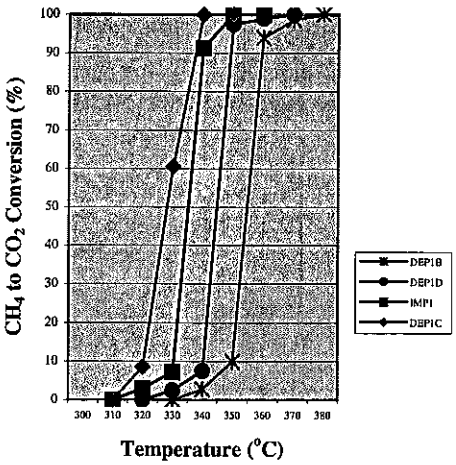

Figure 3. Activity for methane oxidation as a function of temperature for 1.0 wt% Pd/Al_2O_3 calcined in O_2 at 400°C for 2 hr followed by an hour at 500°C.

A complete result of XPS analysis of Pd/Al_2O_3 samples in 2 different metal loading; 1.0 and 3.0 wt% Pd are tabled in Table 3. As given by the variations in the activity order (Fig. 3) and the chemical states of the active phase (presented in Table 3), it can be seen that palladium in the form of an oxidized state initiated a more active conversion. We have found that samples DEP1B and DEP2A exist from three different forms of Pd. Two chemically different forms of oxidized palladium and a metallic phase are differentiated by their electron binding energies.

Table 3: Results of XPS analysis of Pd/Al_2O_3 Samples

Sample	Metal loading wt%	BE (eV) Pd $3d_{5/2}$	Assignment	% PdO	% Pd
IMP1	1	336.8	PdO	100	-
DEP1A	1	337.3	PdO[a]	100	-
DEP1B	1	334.7	Pd[b]	-	32
		336.7	PdO	43	-
		338.5	PdO[c]	25	-
DEP1C	1	337.8	PdO[a]	100	-
DEP1D	1	337.0	PdO	63	-
		338.5	PdO[c]	37	-
IMP2	3	336.2	PdO	100	-
DEP2A	3	334.5	Pd[b]	-	26
		336.5	PdO	47	-
		338.7	PdO[c]	27	-
DEP2B	3	336.8	PdO	74	-
		338.5	PdO[c]	26	-

[a] small particulate PdO indicated by shifted BE
[b] ref [26]
[c] highly dispersed PdO

Clearly the existence of a mixed phase Pd^0/PdO_x ($1 \leq x \leq 2$) led to the loss in the activity. Thus, the activation of methane is most favourable on an oxidized form of palladium. This piece of information adds to the findings and supported the groups [27-29], that the oxidized state of palladium is more active and consider the metal phase to be less active.

It is also worth noting that the presence of a mixed phase, Pd^0/PdO_x although gives lower activities in a series of calcined samples, this form of combined oxidation state has lower light-off temperature and is more active than its reduced counterpart sample (Fig. 4 and Fig. 5). These results imply that the mixed phase may be more be active for methane oxidation, depending on the condition of pretreatment.

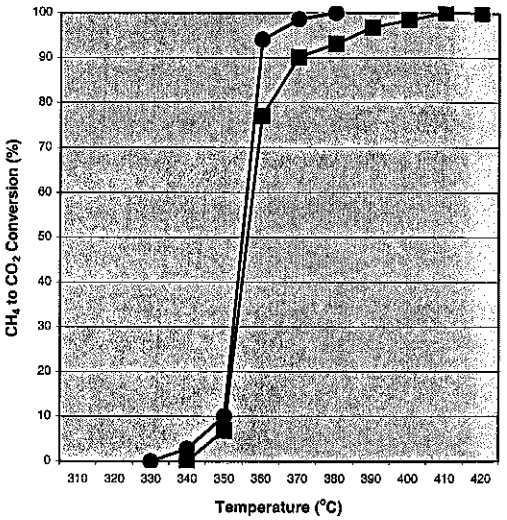

Figure 4. Activity for methane oxidation of sample DEP1B pretreated under different conditions: calcined in O_2 at 500°C [●] and reduced with H_2 at 400°C [■].

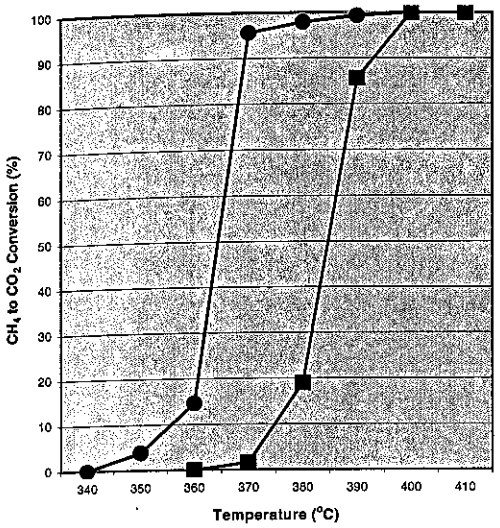

Figure 5. Activity for methane oxidation of sample DEP2A pretreated under different conditions: calcined in O_2 for 3 hr [●] and reduced with H_2 for 1 hr [■]

CONCLUSION

The use of XPS has been demonstrated in correlation with particle sizes of oxidized palladium on γ-alumina prepared via water-in-oil microemulsion. Most of the oxidized Pd/γ-alumina is chemically different from large agglomerates palladium, obtained through wet impregnation method, and is described by a binding energy difference from that of bulk PdO. It is argued that the energy shift reflects small and dispersed crystallites (10-20nm) with an interaction with the alumina support.

These catalysts under various pretreatment conditions showed various order of catalytic activity when investigated for catalytic combustion. Comparison with the reaction results allows us to deduce that the catalytic activity in the methane oxidation of the supported palladium catalysts depends not only on the size of the active phase but also the on the oxidation states of the palladium and latter is controlled by the pretreatment condition of the catalyst.

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