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PS analysis of dispersed catalysts prepared via w/o microemulsion

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BSTRACT Rh/Al_2O_3 catalysts prepared by water in oil w/o microemulsion were studied by X-ray otoelectron spectroscopy. The effect of water content (R_w) on rhodium particle size formed in icroemulsion was investigated. Interest is focused on core level binding energy shifting for Rh $3d_{5/2}$ ak and its relationship with rhodium particle size. The Rh $3d_{5/2}$ peak was found to undergo changes in rms of shifting in binding energy, and the amount of such changes depends on the size of rhodium rticle. TEM (transmission electron spectroscopy) studied showed that rhodium particle size on $/Al_2O_3$ catalysts increase as water content in microemulsion increases (Average diameter for catalysts ith $R_w = 4$, 5.7 and 11.5 are 4nm, 8nm and form aggregate like). These results were correlated with XPS sults where Rh $3d_{5/2}$ binding energy increases for catalysts with lower water content or smaller particle e (binding energy for catalysts with $R_w = 4$, 5.7 and 11.5 are 311.3eV, 311.0eV and 310.0eV). The odium catalysts with smaller particle size were found to exhibit a higher catalytic activity for the ethane oxidation in rich oxygen than those catalysts with bigger particle size. For catalysts with smaller rticle size, surface to volume ratio of rhodium metal increases which will increase the active sites of $/Al_2O_3$ catalysts and led to higher catalytic activity performance.

atalysts, Microemulsion; XPS, Catalytic activity, Binding energy)

INTRODUCTION

heterogeneous catalysts, the formation of all metal particles in nanosized is very portant for catalytic reaction because the large rface area formed may increase the reactive e/mass ratio which will enhance the catalytic tivity. Hence, many researches have used rious methods to synthesize nanoparticles and ed these nanostructured materials as precursors r catalysts preparation. Nanoparticles is near onodispersed particles that are generally less an 10 nm (100Å) in diameter [1]. Recently, noparticles is a frontier research area and its eparation, characterization and application ve received high attention from many searches. The nanoparticles usually show normal properties from those of the bulk aterial because of their extremely small size d large specific surface areas [1-2]. They have any potential applications such as nomagnetic [2], semiconductor [3] and talysis [4-6]. According to Aiken III and Finke], nanoparticles are only kinetically stable and they must stabilize against aggregation. Nanoparticles can be stabilized through electrostatic stabilization and steric ('organic') stabilization. Electrostatic stabilization occurs when adsorption of ion onto metal surface occurs which create electrical double layer and results in a coulombic repulsion among particles itself. Steric stabilization is achieved when metal center is surrounded by layer of materials such as polymers [7], surfactants and solvents [8] which prevents close contact of the metal particle centers.

Here we report the synthesis of rhodium nanoparticles by water in oil microemulsion by reducing rhodium(III) nitrate with hydrazine using surfactant Brij 30. In addition, the application of these nanostructured materials as precursors for a new type of catalyst will be discussed mainly using technique X-ray photoelectron spectroscopy (XPS).

XPS is among the frequently used surface science techniques in catalysis [9]. It give information on the elemental composition, the oxidation state of the element as well as chemical interaction between metal particles and metal oxide substrates in which binding energy shift gives direct information about the metal and substrate electronic properties [10]. In XPS, the core level binding energy of the photoelectrons depend on the size of the metal particle studied. Generally, the binding energy of photoelectrons decreases with increasing particle size until the binding energy of bulk metal is reached [11-12]. Binding energy shift for small metal particles deposited on poorly conducting substrate can be attributed to initial state and/or final state effects [10, 13-14]. Mason [13] describes this small particle size effect as initial state effect: particles with 1-2 nm range show a different binding energy from the normal bulk atom. Final state effect arises when electrons relax to screen the hole which resulting in a photoemitted electron with a higher kinetic energy or lower binding energy [10, 14]. For small particles deposited on poorly conducting substrates, there is no rapid transfer of electrons to the nanoparticles as in bulk metal and the photoemission peaks will shift to higher binding energy.

EXPERIMENTAL

Preparation of nanoparticles and catalysts

The water in oil microemulsion was prepared by injecting an aqueous solution of rhodium(III) nitrate into a solution composed of a surfactant polyethylene(4) lauryl ether (commercial name, Brij 30 or $C_{12}H_4$) and organic solvent (n-hexane). Microemulsion system of water/surfactant mol ratio (R_w) were fixed to 4, 5.7 and 11.5 while the weight ratio of solvent/surfactant was fixed at 11/7. The rhodium-hydrazine nanoparticles were formed by adding directly hydrazine hydrate to the microemulsion solution. The amount of hydrazine was fixed at six times as much as that of rhodium(III) nitrate. Alumina as a support was added slowly to the microemulsion solution while stirring with pH in the range of 1-2. The catalysts prepared were dried in oven at 80°C for 4 hours and calcined at 400°C for 2 hours and 500°C for 1 hour with oxygen flow through it. All the catalysts prepared consist of rhodium content 1 % by weight.

Characterization

XPS technique was used to characterize the effect of particle size on the core level binding energy of Rh $3d_{5/2}$. The XPS measurement was carried out in the a commercial system (Kratos, model XSAM HS) at a base pressure of 1×10^{-9} Torr (1Torr= 133.3 Pa) in analyzer chamber. The photoelectrons were excited by monochromatized Mg K_α (1253.6 eV) radiation. The binding energy of Rh $3d_{5/2}$ for Rh/Al_2O_3 due to charging effect was corrected refer to C_{1S} peak (284.5 eV). The particle size and size polydispersity of the resultant nanoparticles have been characterized by transmission electron microscopy (TEM) using a Hitachi model H-7100 operation in the transmission mode at 75 KV.

Catalytic activities

All the catalysts were reduced under hydrogen flow at 400°C for 1 hour before the reaction. The catalytic activity was conducted in a fixed-bed reactor. Gas ratio for O2: N_2: CH_4 were fixed at 100: 80: 20 and total flow gas was 200 ml/min.

RESULTS AND DISCUSSION

Transmission electron microscopy (TEM)

The size of rhodium particles formed is depended on the size of microemulsion droplets. As has been reported, the size of microemulsion droplets was dependent on water content in microemulsion [15-16]. Generally, the larger the water content, the bigger the particle size. Table 1 shows the rhodium particles size on alumina characterized using TEM technique. The TEM results show that rhodium particle size increases as the total volume of water increases. This phenomenon can be explained as follows: The interfacial area of microemulsion for a fixed amount of surfactant that can be stabilized by the surfactant is fixed. So, when extra water was added to the microemulsion system (R_w increase), new water droplets cannot be formed and the total volume of water droplets increased led to larger microemulsion droplets [15, 17] giving bigger rhodium particles produce as water content in microemulsion increase.

Table 1: Particle size of 1% Rh/Al_2O_3 catalysts by TEM technique

Catalyst samples	Water content, R_w	Particle size by TEM (nm)
R4	4	<5
R5.7	5.7	8
R11.5	11.5	Aggregate

e influence of water content (R_w) on rhodium rticle size in w/o microemulsion can be timated using mathematic calculation as ported by Barnickel et.al. [16]. If R_w is denoted e water/surfactant molar ratio for a given icroemulsion with N droplets per liter, the total lume of water corresponds to

$$N4\pi r^3 / 3 = [H_2O]\ \nu_{water} \text{------------}(1)$$

here ν_{water} denotes the molar volume of water d r denotes the radius of microemulsion oplets. As microemulsion droplets are rrounded by surfactant molecules and if σ = ea of one surfactant molecule at the interface; e total droplet surface is given by

$$N4\pi r^2 = [C_{12}H_4]\ N_A\sigma \text{------------}(2)$$

$$N_A = \text{Avogadro's constant}$$

aking the ratio of equation (1) and (2) and using e definition of R_w, one obtains

$$r = 3\ R_w\ \nu_{water} / \{\ N_A\sigma\} \text{---------}(3)$$

om the equation (3), we can see that the core dius of microemulsion droplet, r, increases oportionally to the water/surfactant molar ratio, $_w$. Hence, in our study, rhodium particle size creases, as total volume of water in icroemulsion increases is reasonable.

-ray photoelectron spectroscopy (XPS)

s we have described in previous section, the re level binding energy decreases with creasing metal particle size. We have used EM technique to characterize the rhodium rticle size on alumina. In this section, we will y to correlate XPS Rh $3d_{5/2}$ binding energy shift ith TEM results. Table 2 shows the binding ergy of Rh $3d_{5/2}$ and TEM diameter for odium(III) nitrate and catalysts prepared by /o microemulsion method with different water ntents. For $Rh(NO_3)_3.2H_2O$ metal salt, two peaks of Rh $3d_{5/2}$ at 30.9.5 eV and 311.2 eV are referred to Rh_2O_3 [18] and $Rh(NO_3)_3$ itself [19] as shown in Figure 1. There is only one peak of Rh $3d_{5/2}$ in rhodium-alumina supported catalyst which refers to Rh_2O_3 doublets and no evidence of Rh^0 (Rh $3d_{5/2}$ at 307.2 eV) present.

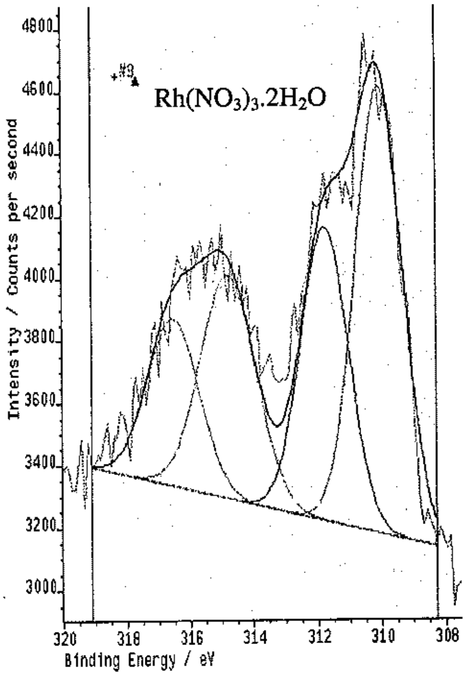

Figure 1. Narrow scan of XPS spectra shows two doublets Rh $3d_{5/2}$ for $Rh(NO_3)_3.2H_2O$

The Rh $3d_{5/2}$ peak shifts to higher binding energy as the rhodium particle size decreases is consistent with TEM results. For example, the Rh $3d_{5/2}$ peak shift by +0.5 eV from the $Rh(NO_3)_3.2H_2O$ for R11.5 catalyst prepared by w/o microemulsion because smaller particle rhodium produced for metal supported catalyst compared to bulk metal itself. Furthermore, the Rh $3d_{5/2}$ peak shift by +1.0 eV and +1.3 eV from Rh/Al_2O_3 catalyst with the highest water content (R_w = 11.5, average diameter= <5 nm) for catalysts with water content of R_w = 5.7 (average diameter= 8 nm) and R_w = 11.5 (average diameter = agglomerate). Hence, the core level binding energy increases reflects the decrease in rhodium particle size as water content in w/o microemulsion decreases for Rh/Al_2O_3 catalysts prepared using surfactant technique.

Table 2: Core level binding energy shift for catalyst prepared via impregnation and microemulsion method studied by XPS technique

Sample	Water content, R_w	TEM diameter, (nm)	(± 0.1 eV)	
			Rh $3d_{5/2}$, 1	Rh $3d_{5/2}$, 2
$Rh(NO_3)_3.2H_2O$	-	-	309.5	311.2
R4	4	<5	311.3	-
R5.7	5.7	8	311.0	-
R11.5	11.5	agglomerate	310.0	-

Catalytic activities

The catalytic performance of methane conversion in rich oxygen over Rh/Al_2O_3 catalysts is shown in Figure 2. The activity of the catalyst prepared by microemulsion method at lower water content or smaller rhodium particle size increases faster than those prepared with higher water content. For example, catalyst R4 convert 96% methane at 350 °C, but for the same temperature, catalysts R5.7 and R11.5 convert methane at 13% and 7.9% only. Methane start to be converted over R4 catalyst at 290 °C, and completely converted to CO_2 at 440 °C. On the other hand, R11.5 catalyst only starts methane conversion at 300 °C and converts 63% methane to CO_2 at 500 °C. The methane oxidation activity of Rh/Al_2O_3 supported catalysts in the presence of excess O_2 decreases in the order of R4>R5.7>R11.5. These results can be explained as follows: the Rh/Al_2O_3 catalysts prepared with lower water content were found to form smaller particles at nano scale, so the surface to volume ratio of rhodium metal increases which will increase the active site of catalyst and will enhance the catalytic activities.

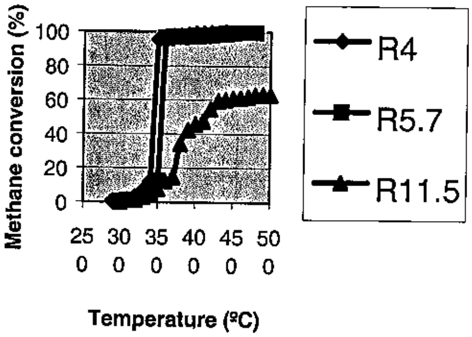

Figure 2. Methane oxidation in oxygen rich over various Rh/Al_2O_3 catalysts

CONCLUSION

The average rhodium particle size prepared by reduction of rhodium(III) nitrate dissolved in the water pools of w/o microemulsion increases with increasing average diameter of w/o microemulsion. The average diameter of w/o microemulsion increases the increase of the water content due to the decrease of the total surface of the aggregate. TEM studies showed that rhodium particle size on Rh/Al_2O_3 catalysts increases as water content in microemulsion increases, these results were correlated with XPS results where Rh $3d_{5/2}$ binding energy increases for catalysts with lower water content or smaller particle size. The methane conversion in rich oxygen catalytic activity increases as rhodium particle size on alumina decreases. Catalyst R4 shows the highest catalytic activity among the supported catalysts, because smallest rhodium particles were formed during w/o microemulsion preparation process. This is because for catalysts with smaller particle, surface to volume ratio of rhodium metal increases which will increase the active site of Rh/Al_2O_3 catalysts and led to higher catalytic activity performance.

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