

Calorimetric study on oxidation of alumina supported rhodium by dioxygen

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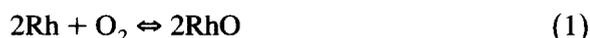
Abstract

Rhodium particles in nanometer size were prepared by impregnating alumina powders with aqueous solutions containing rhodium salts. The dispersion (D) of rhodium crystallites on the prepared samples was estimated by dioxygen adsorption measured at 300 K. Phenomena of oxidizing the supported crystallites with 2.5×10^4 Pa O_2 in a temperature range between 280 and 870 K were calorimetrically studied. Extent of oxidation may be distinguished into three stages, i.e., adsorption on surface ($T < 300$ K), progressive penetration into bulk, and formation of a stable bulk oxide ($T > 700$ K), on raising the oxidation temperature. Heat of dioxygen adsorption varies only slightly with the dispersion (D) of rhodium and has a value of 294 ± 6 kJ (mol O_2)⁻¹. Chemical stoichiometry of the bulk oxide formed, however, varies with the dispersion of rhodium crystallites. A dioxide (RhO₂) ($\Delta_f H = 225 \pm 3$ kJ (mol O_2)⁻¹) and a sesquioxide (Rh₂O₃) ($\Delta_f H = 273 \pm 3$ kJ (mol O_2)⁻¹) was formed at $D < 60\%$ and $D > 80\%$, respectively.

Keywords: Calorimetry; Heat of adsorption; Heat of oxidation; Oxidation Phenomena; Rhodium

1. Introduction

Alumina supported rhodium is a commercially-important catalyst that has been used in a variety of reactions [1], i.e., reduction of nitric oxide [2], oxidation of CO molecule and hydrocarbons [3], and redox reactions in catalytic converters of modern automobiles. In the oxidation reactions and the catalytic converters, following fundamental step of adsorption and desorption of oxygen on the surface of supported nanometer-rhodium particles plays an important role:



Accordingly, a detailed understanding on the chemistry of the step Eq. (1) is generally required.

Interaction of dioxygen with bulk rhodium has been extensively studied in literature [4–6]. Following oxygen species have been distinguished from the thermal desorption spectroscopy of the interacted samples:

(1) Molecularly adsorbed dioxygen (the α -state): this weakly adsorbed species was formed upon the interaction at low temperatures (~ 100 K) and was found to desorb from the bulk rhodium on raising the system temperature over 200 K.

(2) Atomically adsorbed oxygen (the β -state): this strongly adsorbed species was formed upon interactions at temperature higher than 200 K

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Table 1
Heat of dioxygen adsorption on rhodium reported in previous literature

Sample	Technique	$-Q_{ad}$ (kJ (mol O ₂) ⁻¹)	Ref.
Rh (111)	TPD	$\beta = 234$	[4]
Rh (100)	TPD	($\beta_3 = 360, \beta_2 = 260, \beta_1 = 210$)	[7]
Rh (poly)	TPD	$\beta_2 = 280, \beta_1 = 210-220$	[8]
Rh film	calorimetry	318	[9]

and was found to desorb from rhodium surface at temperature over 900 K.

(3) Bulk oxides: this species was caused by a penetration of atomically adsorbed oxygen anions into the lattice of rhodium crystals at temperatures higher than 400 K. The penetrated anions became unstable and started to desorb at $T > 1200$ K.

Heat of dioxygen adsorption (Q_{ad}) on surface of bulk rhodium have been reported in literature (Table 1) to vary from 320 to 210 kJ (mol O₂)⁻¹. The formation enthalpy ($\Delta_f H$) of powdered rhodium oxide, reported in literature (Table 2), also varies from 190 to 300 kJ (mol O₂)⁻¹.

In this paper, we employ a simultaneous TG-DSC technique to measure the Q_{ox} (heat of oxidation, including Q_{ad} and $\Delta_f H$) of nanometer-ranged rhodium crystallites supported on alumina over a wide temperature range (280–870 K). Particular emphasis is placed on the variation in the extent of dioxygen uptake (N_{O}/N_{Rh}) with oxidation temperature and the size effect of rhodium crystallites (d) on the Q_{ox} values.

Table 2
Heat of formation reported in previous literature for various bulk rhodium oxide

Author	Method	$-\Delta_f H$ (kJ (mol O ₂) ⁻¹)	Ref.
Wohler and Jockum	calorimetry	190	[10]
Tagirov et al.	C–C equation ^a	220	[11]
Schmahl and Minzl	C–C equation ^a	222	[12]
Bayer and Wiedemann	C–C equation ^a	258	[13]
Merten and Bell	C–C equation ^a	279	[14]
Kleykamp	electrochemical	301 ± 11	[15]
CRC data		229	[16]

^a Calculated by Clausius–Clapeyron equation.

2. Experimental

Rhodium catalysts of various rhodium loadings were prepared via the incipient wetness technique by impregnating γ -Al₂O₃ powders (Merck, surface area = 108 m²/g) with an aqueous RhCl₃ · 3H₂O (designated hereafter as Rh(C) catalysts) or Rh(NO₃)₃ (designated as Rh(N)) solution. Obtained slurries were pre-treated sequentially with an overnight drying at 380 K and a 4 h calcination at 770 K in air, and were stored in vials as testing samples. The loading of rhodium on these testing samples was determined by the atomic-emission technique using a Perkin-Elmer, Sciex Elan 5000 ICP-MS.

The dispersion (D , percentage of atoms exposed to surface) of rhodium crystallites was estimated gravimetrically from adsorption of dioxygen (2.5 × 10⁴ Pa) at 300 K assuming a monolayer chemisorption of oxygen atom on rhodium surface. The amount of oxygen uptake was monitored in a Setaram TG/DSC 111 dual

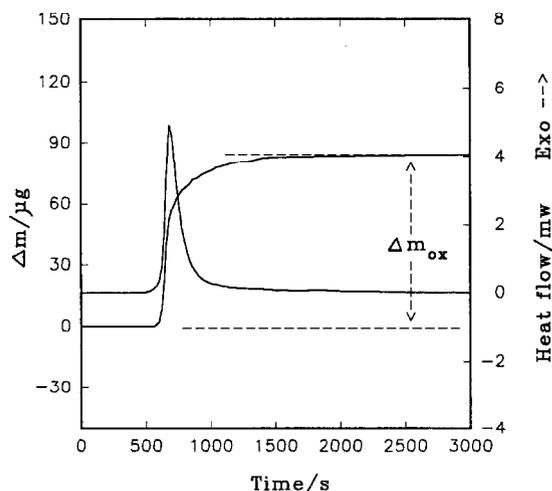


Fig. 1. The TG-DSC results of oxidation 31.3 mg 3.26%Rh(C)/Al₂O₃ sample with 2.5 × 10⁴ Pa dioxygen measured at 300 K. An oxygen uptake of 84.4 μg and a simultaneous evolved heat of 0.773 kJ was obtained after a 2 × 10³ s oxidation.

port calorimeter equipped with a sensitive ($\pm 0.25 \mu\text{g}$) balance. Before the adsorption measurement, each testing sample was pre-reduced in flowing dihydrogen gas at 670 K for 1 h and a subsequent evacuation for 1 h at 720 K. A detailed description of this system has been given in the previous reported [17].

Fig. 1 presents a TG-DSC time profile on oxidizing 31.3 mg of the 3.26%Rh(C)/Al₂O₃ with dioxygen at 300 K. The rate of adsorption was fast at the initial stage, but decreased with the reaction time. After 2×10^3 s of oxidation, a $\Delta m_{\text{ox}} = 84.4 \mu\text{g}$ and a $q_{\text{ox}} = -0.773$ J were obtained simultaneously from the TG and the DSC, respectively. The oxygen uptake in each adsorption, N_{O} , was determined according to the Δm_{ox} obtained after a 2×10^3 s of oxidation.

3. Results and discussion

3.1. Gravimetric measurement

TG-DSC measurements similar to Fig. 1 have been pursued for nine Rh/Al₂O₃ samples prepared. Previous literature [18–21] suggested that the oxidation of rhodium crystallites at 300 K was limited to surface chemisorption with a chemical stoichiometry of



where Rh^s denotes rhodium atoms exposed to the surface of supported rhodium crystallites. The second column of Table 3 lists the dispersion ($D = N_{\text{O}}^{\text{ad}}/N_{\text{Rh}}$, where N_{Rh} denotes number of rhodium atoms in each sample) measured for the samples prepared in this study. Calculated dispersions of rhodium crystallites were rather high for all the prepared samples with their average diameters ($d = 0.90/D$ [22], see column 3) in the range of 1.0–5.0 nm.

The uptake of dioxygen by each prepared Rh/Al₂O₃ sample generally increased with the oxidation temperature. Fig. 2 compares the temperature profiles of the $N_{\text{O}}/N_{\text{Rh}}$ uptake ratio observed after 2×10^3 s of oxidation on samples of 3.26% Rh(C)/Al₂O₃ and 2.86%Rh(N)/Al₂O₃. In this temperature study, a fresh sample was used in each data point. Both profiles can be distinguished into three stages on raising the oxidation temperature from 280 K to 870 K:

(a) The $N_{\text{O}}/N_{\text{Rh}}$ ratio remained at a constant plain value at $T < 300$ K.

(b) The ratio gradually increased from the plain value to a plateau value in the temperature range between 300 K and 700 K.

(c) The ratio remained at the plateau value in the temperature range between 700 K and 870 K.

The three stages are assigned as chemisorption of dioxygen on the surface of rhodium

Table 3
Heats of adsorption and heats of RhO_x formation for oxygen on Rh/Al₂O₃

Sample	Oxygen adsorption			Formation of rhodium oxide		
	$D (N_{\text{O}}^{\text{ad}}/N_{\text{Rh}})$	d (nm)	$-Q_{\text{ad}}$ (kJ (mol O ₂) ⁻¹)	$N_{\text{O}}^{\text{b}}/N_{\text{Rh}}$	$-\Delta_f H$ (kJ (mol O ₂) ⁻¹)	possible oxide
8.25%Rh(C)	0.25	3.6	289	1.93	222	RhO ₂
8.25%Rh(C) ^a	0.19	4.7	282	1.94	222	RhO ₂
4.00%Rh(C)	0.50	1.8	293	2.03	228	RhO ₂
3.26%Rh(C)	0.55	1.6	293	1.95	229	RhO ₂
3.26%Rh(C) ^a	0.52	1.7	290	2.02	231	RhO ₂
3.56%Rh(C)	0.67	1.4	298	1.85	250	Rh ₂ O ₃ and RhO ₂
2.33%Rh(C)	0.70	1.3	297	1.88	248	Rh ₂ O ₃ and RhO ₂
2.45%Rh(C)	0.80	1.1	299	1.54	270	Rh ₂ O ₃
2.86%Rh(N)	0.91	1.0	305	1.51	276	Rh ₂ O ₃

N_{O}^{ad} : Uptake of dioxygen atom at 300 K, N_{O}^{b} : Uptake of dioxygen atom at 770 K, d : Average diameter of rhodium crystallites calculated from $0.90/D$.

^a Reduction at 970 K for 1 h.

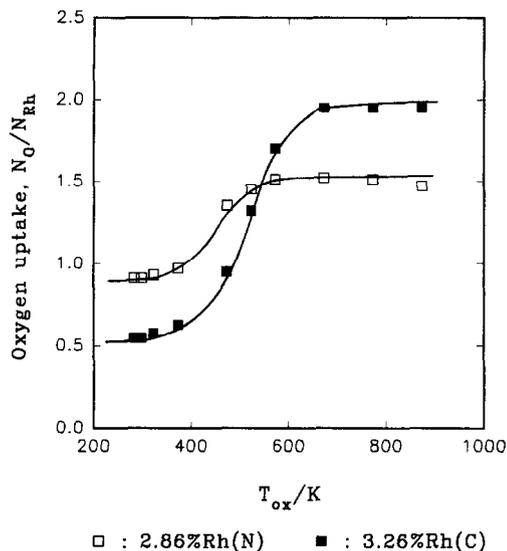


Fig. 2. Temperature profiles of dioxygen uptake from samples of (a): 2.86%Rh(N) (□) and (b): 3.26%Rh(C) (■).

crystallites, progressive penetration of adsorbed oxide ions into the bulk, and formation of a stable bulk oxide structure, respectively. The limitation to the surface adsorption at low temperatures (< 300 K) implies not only that the migration of adsorbed oxide ions into sublayers of rhodium has an energy barrier, but also that the thermal agitation at low temperature was insufficient to overcome the barrier. The expected migration process in our tiny rhodium crystallites ($d < 5.0$ nm) started at a $T > 300$ K which is somewhat lower than that (~ 400 K) required for samples of rhodium crystals [4,8]. The loose texture of nanometer crystallites in our samples likely had a lower energy barrier for the migration of oxygen anions than their well packed crystals.

The extent of the bulk oxidation depended strongly on the oxidation temperature and the particle size of rhodium samples. A stable $N_{\text{O}}/N_{\text{Rh}}$ plateau, however, was attained for each sample when the oxidation temperature was raised over 700 K. The fifth and seventh column of Table 3 list the $N_{\text{O}}/N_{\text{Rh}}$ ratio obtained at 770 K and the expected oxides formed, respectively. Interestingly, two different oxide species can be distinguished from the gravimet-

ric results. The plateau had a $N_{\text{O}}/N_{\text{Rh}} = 2.0$ (indicating a formation of rhodium dioxide, RhO_2) when the dispersion of rhodium was less than 60%, but decreased to 1.5 (indicating a formation of rhodium sesquioxide, Rh_2O_3) when the dispersion of rhodium increased over 80%.

Both the Rh_2O_3 (in either hexagonal corundum or orthorhombic structure) and the RhO_2 (rutile structure) crystallines have been prepared in literature [13,23] from decomposing $\text{Rh}(\text{NO}_3)_3$ or $\text{Rh}(\text{OH})_3$ under normal pressure at $T > 720$ K. Muller and Roy [24] established a phase diagram for the system of bulk rhodium oxide. The diagram suggested that a formation of Rh_2O_3 at $T > 950$ K and a formation of RhO_2 at $T < 950$ K under $p_{\text{O}_2} = 2.5 \times 10^4$ Pa. With IR spectroscopy, Prosychev et al. [25] could further distinguish the dioxide (550 cm^{-1}) from the sesquioxide (615 and 660 cm^{-1}) according to their vibration frequency. With TPR technique, Schunemann et al. [26] also proved a coexistence of both oxides in Rh/NaY catalysts according to the consumption of hydrogen at 300–320 K. In this study, we found that the stoichiometry of rhodium oxides formed upon a 770 K oxidation depended on the diameter of rhodium nanoparticles: formation of Rh_2O_3 or RhO_2 was preferred for $d < 1.5$ nm or $d > 1.5$ nm, respectively.

3.2. Calorimetric measurement

Fig. 3 presents the temperature profiles of heat ($-Q_{\text{ox}}$ in $\text{kJ} (\text{mol O}_2)^{-1}$) evolved upon oxidation of the 2.86%Rh(N) and the 3.26%Rh(C)/ Al_2O_3 catalysts. Observed heat varies with the rhodium dispersion and the oxidation temperature. However, the three oxidation stages described in the gravimetric measurement were also present in this Figure. Heats of oxidation displayed a plateau value at $T < 300$ K when the oxidation was limited to surface chemisorption for both samples. The heat of oxidation gradually decreased on the penetration stage to a plain value on the formation of a stable bulk oxide between 700 and 870 K. The

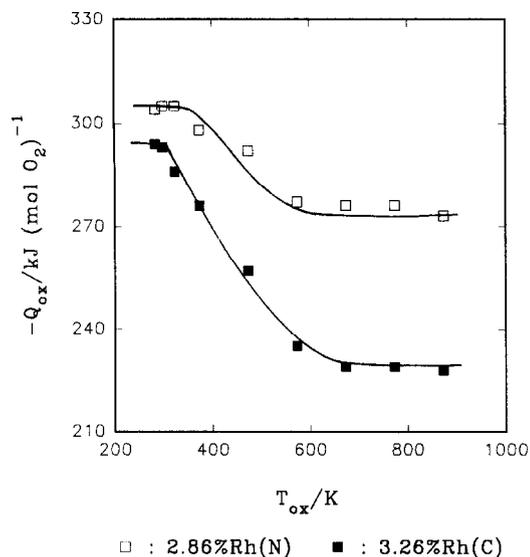


Fig. 3. Temperature profiles of heat of oxidation (Q_{ox}) from samples of (a): 2.86%Rh(N) (\square) and (b): 3.26%Rh(C) (\blacksquare).

plateau value is the heat of dioxygen adsorption ($-Q_{ad}$) while the plain value may be considered as the enthalpy of rhodium oxide formation ($-\Delta_f H$). The heat evolved in each sample generally decreased with an increase in the extent of oxidation.

The phenomena of $-Q_{ad} > -Q_{ox}$ found in Fig. 3 becomes somewhat logical when considering that little or negligible energy is required for breaking metal-metal bonds in the chemisorption stage. In contrast, the so called 'place-exchange' mechanism [27] of sublayer oxidation involves a serious breakdown of the original metal lattice. The discrepancy between Q_{ad} and Q_{ox} may therefore be attributed to the extent of metal bond breakage. A high extent of oxidation implied a small $-Q_{ox}$.

Fig. 4 correlates the $-Q_{ad}$ measured from the TG-DSC with the average diameter of rhodium crystallites determined from the dioxygen chemisorption. Apparently, the heat evolved upon adsorption of dioxygen on rhodium crystallites varies insignificantly with the diameter. The evolved heat of adsorption increased only from 282 to 305 kJ (mol O₂)⁻¹ as the size of rhodium crystallites was decreased from 5.0 nm to 1.0 nm. The obtained Q_{ad} value agrees de-

cently with literature values of 280 kJ (mol O₂)⁻¹ ($d \sim 7.0$ nm) and 260 kJ (mol O₂)⁻¹ ($d \sim 13$ nm) reported for nanometer-rhodium particles supported on active carbon [28]. However, this variation is quite minor on comparing to the big variation in Q_{ad} (from 250 to 360 kJ for Pd/Al₂O₃ [17] and from 230 to 330 kJ for Pt/Al₂O₃ [29]) with particle size (also in the nanometer range) found in our laboratory for adsorption of dioxygen on other noble metals.

The sixth column of Table 3 lists the $-\Delta_f H$ of bulk rhodium oxides formed on oxidation of Rh/Al₂O₃ samples at 770 K. The $-\Delta_f H$ value obtained in this study apparently varied with the species of rhodium oxides formed. A value of $-\Delta_f H = 225 \pm 3$ kJ (mol O₂)⁻¹ or 273 ± 3 kJ (mol O₂)⁻¹ was found for the formation of dioxide or sesquioxide, respectively. These $\Delta_f H$ values are falling into the range reported in the previous literature [10–16] for various samples of rhodium oxides (Table 2). We believe that the lower values (~ 220 kJ (mol O₂)⁻¹) in the literature may be the dioxide and the higher value (~ 280 kJ (mol O₂)⁻¹) may be the sesquioxide. The highest value (~ 300 kJ (mol O₂)⁻¹) that obtained from the electrochemical method [15] may be involved a chemisorption of oxygen on the surface of rhodium with the plate of cathode.

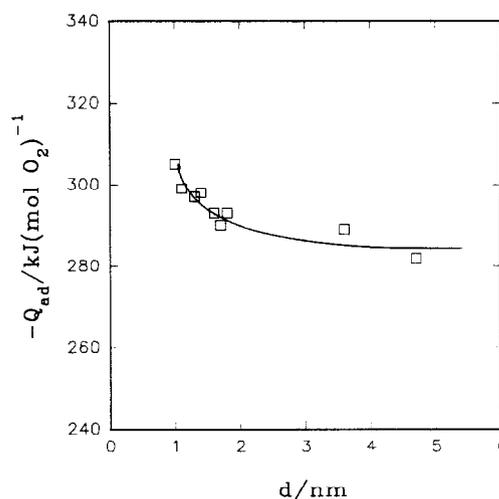


Fig. 4. Variation of Q_{ad} of dioxygen adsorption with the average diameter of rhodium crystallites.

4. Conclusions

Phenomena of oxidation of nanometer-rhodium crystallites supported on alumina with dioxygen were studied with a commercial TG-DSC simultaneous system. Based on obtained results, we conclude:

(1) The oxidation proceeds in three consecutive stages, i.e., surface adsorption ($T < 300$ K), progressive penetration of adsorbed oxide ions into bulk (300–700 K), and formation of a stable bulk oxide structure ($T > 700$ K), on increasing the oxidation temperature.

(2) Heat of dioxygen adsorption on rhodium surface varies only slightly with the dispersion of rhodium and has a value of 294 ± 6 kJ (mol O_2)⁻¹.

(3) The particle size of supported rhodium, however, has a profound effect on the bulk oxide formed. A dioxide (RhO_2) ($-\Delta_f H = 225 \pm 3$ kJ (mol O_2)⁻¹) or a sesquioxide (Rh_2O_3) ($-\Delta_f H = 273 \pm 3$ kJ (mol O_2)⁻¹) was formed as the diameter was larger or less than 1.5 nm, respectively.

Acknowledgements

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