Structure and Morphology of Catalysts Produced via Oxidation of Mo–Pt Alloys

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Abstract—A novel approach has been proposed for producing platinum-containing catalysts via oxidation of molybdenum–platinum powders. The effect of alloy composition on the structure and morphology of the oxidation products has been studied by a variety of physicochemical methods, and heat-treatment conditions have been optimized to achieve a uniform distribution of platinum nanoparticles in the resulting molybdenum oxide. Selective oxidation has been shown to be a viable approach to producing platinum–transition metal oxide catalytic systems.

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INTRODUCTION

There is considerable scientific and technological interest in developing novel approaches for the preparation of modified Pt-containing catalysts offering enhanced stability to traditional catalyst poisons [1]. Selective oxidation of Pt-containing alloys makes it possible to produce catalysts with a small particle size of the active phase, stable to sintering [2]. The Pt–MoO₃ system, stable in the presence of sulfur-containing compounds, was chosen to study selective oxidation processes [3, 4].

The purpose of this work was to optimize procedures for the synthesis of modified catalysts and to study the relationship between their microstructure and physicochemical properties.

EXPERIMENTAL

Alloy preparation. Alloys for this investigation were prepared from platinum plates (99.99% purity) and carbothermal molybdenum (99.9%). Weighed samples (3 g) containing 2, 10, or 30 at % Pt were melted in an electric arc furnace using a nonconsumable tungsten electrode under a high purity argon atmosphere at a pressure of 1.1×10^5 Pa. The alloys were remelted four times for homogenization. The alloy compositions and melting losses were determined gravimetrically (Table 1).

Powder samples were prepared by an abrasive process. Particle size analyses were performed with a CILAS 1180 laser analyzer, which insured particle size determination in the range 40 nm to 2.5 mm. The immersion liquid was selected so that the powder to be analyzed was evenly dispersed without dissolution. Isopropanol was used as a surfactant to prevent particle aggregation. The samples were dispersed using an ultrasonic processor (discrete power levels from 20 to 50 W) and mechanical stirrer.

Heat treatment. The alloys were equilibrated by annealing at 900 \pm 5°C for 400 h in silica ampules which were pumped to ~10⁻² Pa and mounted in tubular resistance-heated furnaces.

Characterization techniques. The alloys were characterized by a variety of physicochemical methods.

X-ray diffraction (XRD) patterns were collected on a DRON-4 diffractometer (diffracted-beam graphite monochromator, EXPRESS software, CuK_{α} radiation, step-scan mode with a step of 0.1° and a counting time per data point of 3–5 s). The data were indexed and analyzed using RIETAN-94 [5] and STOE WinXPOW [6] (Table 2).

The crystallite size was evaluated from the width of diffraction line profiles using standard EXPRESS software and the Scherrer equation: $D = 0.94\alpha/(\beta \cos \theta)$ where D is the average crystallite size, α is the x-ray wavelength, β is the full width at half maximum of the XRD peak, and θ is the diffraction angle. The error of determination was within 10%.

Thermogravimetric analysis (TGA) was carried out with an SDT-Q600 system using powder samples (on the order of 0.5 g) prepared from the alloys. TGA data

 Table 1. Compositions of the synthesized molybdenumplatinum alloys

Mo, at %	Pt, at %	Mo, wt %	Pt, wt %
98	2	96	4
90	10	81.6	18.4
70	30	53.4	46.6



Fig. 1. Particle size distribution in the $Mo_{98}Pt_2$ powder.

were analyzed using the software package supplied with the instrument [7].

X-ray microanalysis was performed on a Leo Supra 50 VP scanning electron microscope equipped with an energy-dispersive x-ray spectrometer. The sampling volume was $0.1-0.3 \ \mu\text{m}^3$, the absolute local sensitivity 10^{-15} to 10^{-12} g, and the error of determination 2% [8]. Microstructures of the as-prepared and oxidized alloys were examined by scanning electron microscopy (SEM) in secondary electron mode at magnifications of 800x and 25000x. Powder specimens were cemented to a conductive carbon substrate. The average size and size distribution of platinum particles were determined by transmission electron microscopy (TEM) on a JEOL 3000F operated at an accelerating voltage of 300 kV.

RESULTS AND DISCUSSION

In studies of the oxidation of powder samples, information about the size and shape of the particles is of key importance. Figures 1–3 show the particle size distributions of the powders prepared from the Mo–Pt alloys, in the form of histograms (differential particle size distributions) and cumulative curves. The histograms present the volume fraction of each size range, equal to the weight fraction when all the particles have the same density, which is represented by the q3 parameter: the percentage of particles in a given size range. The cumulative curves present the percentage of particles whose diameter does not exceed the upper limit of a given size range, Q3.

These data demonstrate that the average particle size of the powders increases with platinum content (Figs. 1–3, Table 3).

The SEM results for the powders (Figs. 4–6) are consistent with the above particle size distributions. Molybdenum and the Mo–Pt alloys studied here are characterized by high hardness and brittleness. The dis-



Fig. 2. Particle size distribution in the $Mo_{90}Pt_{10}$ powder.

persion procedure used in this study gives irregularly shaped particles of two types: plates and polyhedra.

Figures 7–10 present TGA results on the oxidation kinetics of the powdered alloys. The powders were found to oxidize much more rapidly compared to bulk samples [9]. For comparison, we also examined the oxidation of pure molybdenum powder prepared by the same procedure, including remelting.

The oxidation rate of $Mo_{90}Pt_{10}$ considerably exceeded that of the other alloys in all of the TGA runs. Note that, over the entire temperature range examined, the early-stage oxidation of the alloys proceeds faster than that of molybdenum, with the largest difference at a platinum content of 2 at %. At 500 and 550°C, the oxidation rate of the alloys decreases slightly with increasing platinum content (Figs. 8, 9). In addition to the reduced oxidation rate, a distinctive feature of the



Fig. 3. Particle size distribution in the $Mo_{70}Pt_{30}$ powder.

Alloy	Phase composition	<i>a</i> , nm	<i>c</i> , nm
Mo ₉₈ Pt ₂	(Mo) = 100	0.3143 ± 0.0001	_
$Mo_{90}Pt_{10}$	$(Mo): Mo_3Pt_2 = 84: 16$	$\begin{array}{c} 0.3133 \pm 0.0002 \\ 0.2793 \pm \ 0.0004 \end{array}$	- 0.4401 ± 0.0009
Mo ₇₀ Pt ₃₀	$(Mo): Mo_3Pt_2 = 43: 57*$	$\begin{array}{c} 0.31549 \pm 0.001 \\ 0.2780 \pm 0.0013 \end{array}$	- 0.448 ± 0.002

Table 2. Phase composition of the synthesized molybdenum–platinum alloys

Note: * Mo_3Pt_2 = high-temperature phase.

 450° C oxidation is that the above trend is broken down. In particular, $Mo_{90}Pt_{10}$ has the slowest oxidation rate.

Low-temperature nitrogen adsorption measurements showed that the specific surface area of the powders ranged from 2.0 to 2.5 m²/g. Thus, one can evaluate the oxidation rate constant for our powder samples. The plots of $\Delta m/S$ versus $\tau^{1/2}$ in Fig. 10 demonstrate that the early stage oxidation kinetics of the powders are well represented by a parabolic rate law.

Oxidation was run until full conversion of the molybdenum to oxides. Conversion was evaluated relative to the weight gain corresponding to the oxidation of all the molybdenum. The weight gain depended on the alloy composition and oxide stoichiometry:

	Mo ₇₀ Pt ₃₀	$Mo_{90}Pt_{10}$	$Mo_{98}Pt_2$	Mo
MoO ₃	26.7%	40.8%	48%	50%
MoO ₂	17.8%	27.2%	32%	33.3%

At 550°C, complete oxidation of the $Mo_{70}Pt_{30}$ and $Mo_{90}Pt_{10}$ powders took 100 min, and the weight gain was 24 and 41%, respectively (Fig. 9). At 500°C, these levels were reached in about 200 min. At 450°C, complete oxidation took a much longer time: even after 24 h of oxidation, the weight gain (~11%) in the alloy containing 2 at % platinum was below the theoretical level.

Table 3. Particle size distributions in the Mo–Pt powders (μm)

Alloy	Mo ₉₈ Pt ₂	Mo ₉₀ Pt ₁₀	Mo ₇₀ Pt ₃₀
<i>Q</i> 3 = 10%	13.4	21.6	25.2
<i>Q</i> 3 = 50%	41.0	50.8	62.6
<i>Q</i> 3 = 90%	77.9	95.2	138.5

The XRD data for the $Mo_{70}Pt_{30}$ alloy oxidized in air during steplike heating with 20-min isothermal holds at each temperature (Fig. 11) indicate that the formation of molybdenum oxides begins at 500°C. With increasing temperature, the process speeds up, leading to complete structural degradation of the alloy. Increasing the percentage of the active phase in the alloy or the oxidation temperature increases the intensity of the XRD peaks from metallic platinum (Fig. 12). The optimal selective oxidation temperature is 550°C. The upper limit of heat treatment is imposed by the significant MoO₃ volatility starting above 600°C.

SEM results demonstrate that oxidation at 550°C is accompanied by significant morphological changes (Fig. 5). At low Mo contents (\leq 70%), the alloy particles do not fully break down, and oxidation leads to the formation of needlelike MoO₃ crystals up to 40 µm in length on the particle surface (Fig. 6). At Mo contents above 90%, oxidation causes complete structural degradation due to the increase in sample volume upon MoO₃ formation.

According to XRD results, the oxidized powders consisted of two phases: orthorhombic MoO_3 and metallic platinum. None of the other molybdenum oxides described in the literature [10] were detected in this study. It seems likely that they only appear in intermediate stages of oxidation. The XRD patterns in Fig. 12 illustrate the effect of platinum content on the phase composition of the oxidized powders. The lattice parameters of platinum and molybdenum trioxide in our samples agree well with those reported in the literature (Table 4).

The average sizes of the platinum particles (coherently scattering domains) evaluated from the XRD data for the oxidized powders using the Scherrer equation indicate that the metal-oxide matrix composites produced in this study contain nanoparticles less than 50 nm in size (Table 5). The present results lead us to



Fig. 4. Microstructure of the as-prepared $Mo_{70}Pt_{30}$ powder.

Fig. 5. Microstructure of the $Mo_{70}Pt_{30}$ powder oxidized at $550^{\circ}C$.



Fig. 6. Microstructure of the oxide scale on the $Mo_{70}Pt_{30}$ powder oxidized at 550°C.



Fig. 7. Oxidation kinetic curves for the Mo–Pt powders at 450° C in air.

Table 4. Lattice parameters of the phases present in the alloys oxidized at 550° C

Alloy	Mo ₆₀ Pt ₄₀	Mo ₇₀ Pt ₃₀	Mo ₉₀ Pt ₁₀	Mo ₉₈ Pt ₂
Pt a, Å	3.9204(14)	3.9133(3)	3.9196(10)	3.917(6)
$MoO_3 a, Å$	13.918(8)	13.916(7)	13.921(3)	13.920(2)
b, Å	3.699(5)	3.694(2)	3.701(5)	3.700(4)
<i>c</i> , Å	3.961(3)	3.960(2)	3.958(8)	3.968(5)

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Table 5. Effect of oxidation temperature on the crystallite size of Pt in the oxidized powders

<i>t</i> _{oxidation} , °C	Particle size, nm			
	Mo ₆₀ Pt ₄₀	Mo ₇₀ Pt ₃₀	Mo ₉₀ Pt ₁₀	Mo ₉₈ Pt ₂
400	12	16	16	18
450	19	18	22	14
500	24	23	28	27
550	_	37	31	_



Fig. 8. Oxidation kinetic curves for the Mo–Pt powders at 500°C in air.



Fig. 9. Oxidation kinetic curves for the Mo–Pt powders at 550° C in air.

conclude that the size of the Pt particles in the alloys is a weak function of Pt content but strongly depends on oxidation conditions. For example, reducing the oxidation temperature from 550 to 450°C markedly reduces the average size of the Pt particles in oxidized $Mo_{70}Pt_{30}$ and $Mo_{90}Pt_{10}$. The likely reason for this is the high-temperature particle migration over the surface of molybdenum trioxide and cluster growth.

TEM results (Figs. 13, 14) correlate with the platinum particle sizes inferred from XRD data. As seen in Fig. 13, platinum particles are present not only on the surface but also in the interior of molybdenum trioxide crystals. One possible reason for this is that the alloy



Fig. 10. Parabolic plots for the oxidation of the Mo–Pt powders at (a) 450, (b) 500 and (c) 550°C in air.

particles differed in shape, which might lead to selective oxidation by different mechanisms.

The present results demonstrate that selective oxidation of molybdenum–platinum powders is a viable approach to producing fine-particle platinum-containing oxide catalysts. Optimizing oxidation conditions, one can produce Pt-containing catalytic systems with a uniform distribution of the active phase, stable to sintering.

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Fig. 11. In situ XRD data for the $Mo_{70}Pt_{30}$ alloy oxidized in air during steplike heating.



Fig. 12. XRD patterns of the (1) $Mo_{98}Pt_2$, (2) $Mo_{90}Pt_{10}$, and (3) $Mo_{70}Pt_{30}$ powders oxidized at 550°C.

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Fig. 13. Platinum distribution in the $Mo_{70}Pt_{30}$ alloy oxidized at 550°C.



Fig. 14. Individual platinum particle in oxidized Mo₇₀Pt₃₀.

CONCLUSIONS

We studied selective oxidation of molybdenumplatinum alloys as a novel approach to producing Pt-MoO₃ catalysts.

The structural and morphological features of the distribution of fine platinum particles in the resultant oxide matrix were investigated by TGA, XRD, and SEM.

The results indicate that the optimal oxidation temperature lies in the range 500–550°C.

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