Preparation of Pt–MO$_x$ Systems via Oxidation of Alloys

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Abstract—Supported platinum systems Pt–MO$_x$ (M = Mo or Ce) were prepared by oxidizing Pt–Mo or Pt–Ce alloys of various compositions. The phase composition and crystal structure of samples before and after oxidative treatment were characterized by powder X-ray diffraction (XRD). Morphology was studied using scanning electron microscopy (SEM). The oxidation of Pt–Mo alloys or Pt–Ce intermetallic compounds yields Pt-MO$_x$ systems in which nanosized platinum particles are homogeneously supported on metal oxide. This method can be used to synthesize Pt–MO$_x$ systems with other transition or rare-earth elements and with various component concentrations.

Pt–MO$_x$ systems are of great interest as catalysts for many industrial processes in petrochemistry and oil processing. Reactions of platinum with transition- and rare-earth metal oxides are known to change the physical-chemical and catalytic properties of platinum, increasing its efficiency in hydriding [1], hydrodesulfurization [2], afterburning of exhaust gases [3], and other processes. As a rule, the manufacture of such systems consists in the impregnation of metal oxides with solutions of platinum salts. However, this method of platinum application is not suitable for all oxides.

Here, we propose a method for preparing Pt–MO$_x$ systems via alloying of pure components and subsequent oxidation of alloys. The selective oxidation of the modifier metal in a platinum alloy generates a Pt–MO$_x$ system where platinum is homogeneously distributed over metal oxide (MO$_x$). The main advantage of this method over conventional ones is its ability to generate Pt–MO$_x$ systems with various types of metal oxides.

RESULTS AND DISCUSSION

Two sets of alloys (Pt–Mo and Pt–Ce) with various component ratios were prepared. Pt$_x$M$_y$ samples were alloyed from pure components in an arc furnace on a water-cooled copper electrode under the 50 kPa argon pressure. The indices x and y in sample notations correspond to the atomic ratios of the elements in alloys. Alloys were crushed in an agate mortar, and the 0.05–0.10 mm fraction was sieved out. The second stage of sample preparation involved oxidation at 550°C in flowing dry air for 10 h. X-ray powder diffraction (XRD) analysis was carried out on a Theta Bruker D-500 diffractometer (CuK_α radiation, 2θ = 20°–80°, Kevex Si(Li) solid-state detector). Particle sizes were calculated from the Scherrer equation. Morphology

was studied using scanning electron microscopy (SEM) on a 5900 LV Jeol instrument.

The phase composition and unit cell parameters of supported platinum systems are listed in the table. One can see from these data that platinum reacts completely differently with transition and rare-earth metals. As a result of a relatively small difference between the atomic sizes of molybdenum and platinum (1.45 against 1.39 Å, respectively), the system characteristically forms substitutional solid solutions over a considerable range of concentrations [2]. The X-ray diffraction pattern of a Pt$_{75}$Mo$_{25}$ sample only contains reflections from the face-centered cubic (fcc) lattice of metallic platinum. Alloys with higher molybdenum percentages consist of two phases. X-ray diffraction proves that the major components of the alloy Pt$_{30}$Mo$_{70}$ are the high-temperature phase of the intermetallic compound Mo$_3$Pt$_2$ (Mg$_3$Cd-type structure) and a solid solution of platinum in molybdenum whose structure and unit cell parameters are close to those of the body-centered cubic (bcc) lattice of metallic molybdenum [2] (table).

Rare-earth elements (in particular cerium), unlike molybdenum, are insignificantly soluble in platinum but readily form various intermetallic compounds with it. In the case of Pt$_{83}$Ce$_{17}$, a Pt$_5$Ce intermetallic phase (CaCu$_5$-type hexagonal structure) is formed; in the case of Pt$_{67}$Ce$_{33}$, the cubic lattice of the Pt$_2$Ce phase (MgCu$_2$-type structure) is formed.

Treatment in flowing air at 550°C changes the phase composition (table). Pt$_{75}$Mo$_{25}$ samples do not change considerably; lines due to metallic platinum are only observed in their X-ray diffraction pattern, as before treatment. MoO$_3$ formation becomes noticeable during the oxidation of high-molybdenum alloys. The X-ray diffraction pattern of an oxidized Pt$_{30}$Mo$_{70}$ sample (Fig. 1) contains reflections associated with metallic

Phase composition and unit cell parameters of the starting and oxidized platinum-containing samples as determined by XRD

Sample	Starting		Oxidized		
	phase composition	unit cell parameters, Å	phase composition	unit cell parameters, Å	Pt particle size, nm
$Pt_{75}Mo_{25}$	fcc Pt	$a = 3.912$	fcc Pt MoO_3^*	$a = 3.921$ –	35
$Pt_{30}Mo_{70}$	Mo 84.5% bcc Mo_3Pt_2 15.5% hex.	$a = 3.157$ $a = 5.560$ $c = 4.490$	fcc Pt MoO_3 orthorhomb.	$a = 3.919$ $a = 13.916$ $b = 3.694$ $c = 3.958$	23
Pt_2Mo_{98}	bcc Mo	$a = 3.144$	Pt 4.1% fcc MoO_3 95.9% orthorhomb.	$a = 3.917$ $a = 13.920$ $b = 3.700$ $c = 3.969$	19
$Pt_{83}Ce_{17}$	$CePt_5$ hex.	$a = 5.361$ $c = 4.384$	Pt 91% CeO_2 9%	$a = 3.915$ $a = 5.357$	10
$Pt_{67}Ce_{33}$	$CePt_2$ cub.	$a = 7.730$	Pt 53% CeO_2 47%	$a = 3.922$ $a = 5.415$	19

* Trace amounts.

platinum and orthorhombic MoO_3 phases. Oxidation leads to the destruction of the Mo_3Pt_2 intermetallic phase. The XRD spectrum of an oxidized Pt_2Mo_{98} sample was almost identical to that of orthorhombic MoO_3.

The oxidation of cerium-containing systems completely destroys intermetallic compounds, and reflections appear from metallic platinum and fcc CeO_2 phases (Fig. 2). The low intensity of CeO_2 lines observed in some cases can result from the high dispersivity of ceria (table). The particle size ascertained from XRD data was about 20–30 nm for the molybdenum systems and about 10–20 nm for the cerium ones (table).

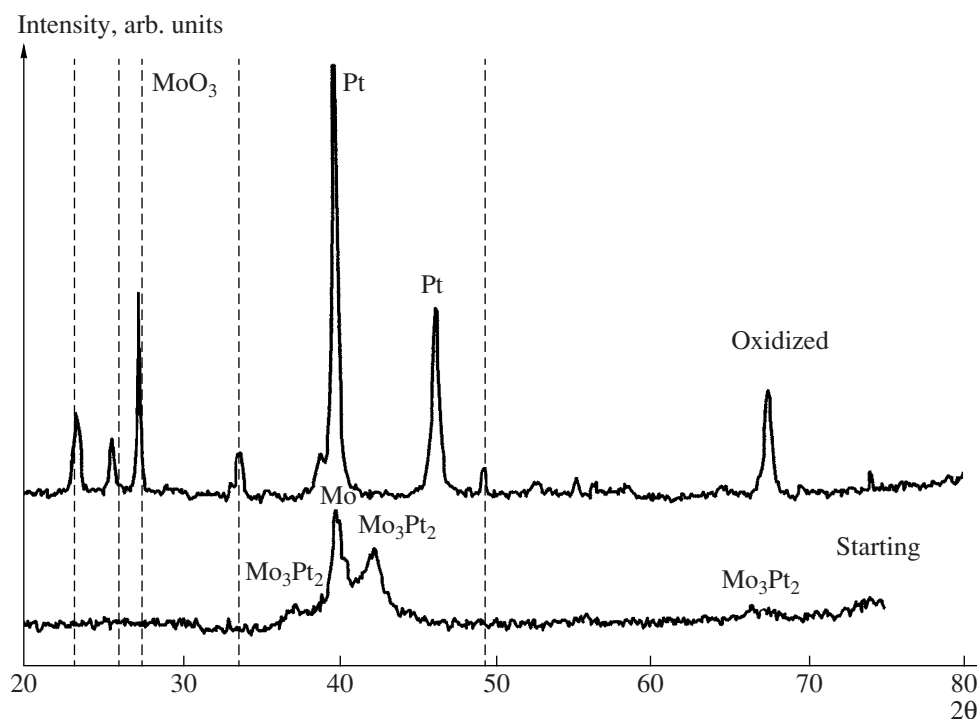Oxidation is accompanied by morphologic alterations. The specific volume of metallic molybdenum is

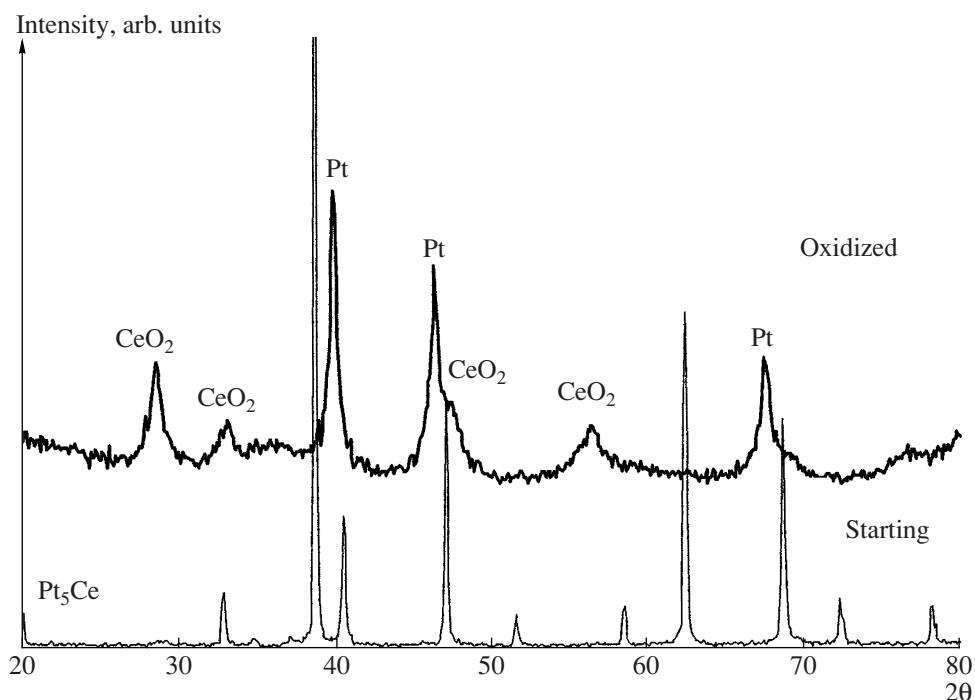**Fig. 1.** X-ray diffraction patterns for a $Pt_{30}Mo_{70}$ sample before and after oxidation.

Fig. 2. X-ray diffraction patterns for a Pt$_{67}$Ce$_{33}$ sample before and after oxidation.
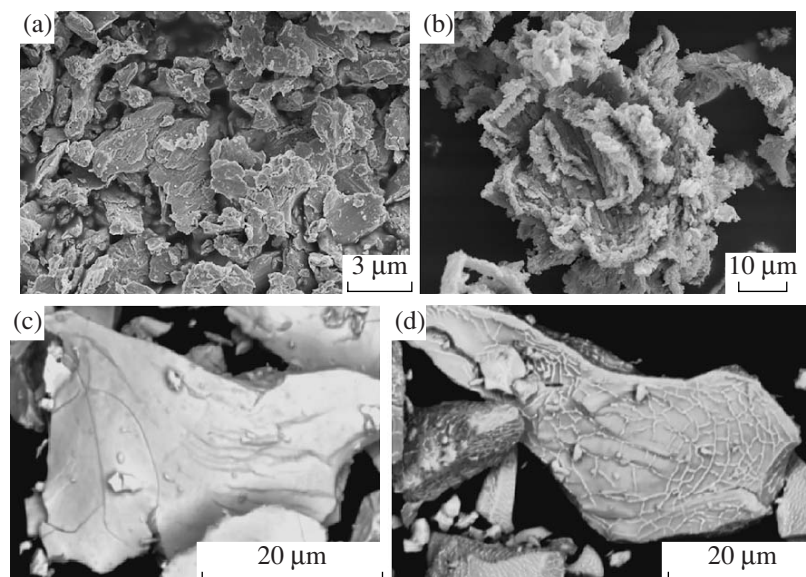
Fig. 3. SEM micrographs of Pt$_{30}$Mo$_{70}$ samples (a) before and (b) after oxidation and of Pt$_{67}$Ce$_{33}$ samples (c) before and (d) after oxidation.

less than one-third that of molybdena [3]; therefore, grains in the sample are cracked during the oxidation of Pt–Mo systems. Cracking is especially noticeable in high-molybdenum systems (Figs. 3a, 3b).

Grains are not destroyed during the oxidation of Pt–Ce samples. However, tracks 50–100 nm wide are observed on their surfaces. Energy-dispersive analysis shows these tracks to contain mainly platinum and regions in between are mainly ceria. An increase in the cerium percentage also induces grain cracking, which is, however, less significant than in molybdenum alloys.

In summary, alloying platinum with molybdenum generates Pt–Mo solid solutions. In platinum–cerium systems, intermetallic phases of various compositions

are formed. The oxidation of Pt–Mo alloys and Pt–Ce intermetallic compounds in flowing air at 550°C is accompanied by the destruction of the starting phases and the formation of nanosized particles of metallic platinum and molybdena or ceria. The proposed method for oxidizing platinum alloys can be used to prepare other Pt–MO_x systems containing highly disperse platinum distributed over the oxide component.

REFERENCES

1. Pinzon, M.H., Centeno, A., and Giraldo, S.A., *Appl. Cat. A: Gen.*, 2006, vol. 32, p. 118.

2. Paal, Z., Koltai, T., Matusek, K., Manoli, J.-M., Potvin, C., Muhler, M., Wild, U., and Tetenyi, P., *Phys. Chem. Chem. Phys.*, 2001, vol. 3, p. 1535.

3. Rogemond, E., Essayem, N., Frety, R., Perrichon, V., Prime, M., and Mathis, F., *J. Catal.*, 1997, vol. 166, p. 229.

4. Villars, P., Cenzual, K., and Daams, J.L.C., Hulliger F., Massalski T.B., Okamoto H., Osaki K, *Pauling File, Inorganic Materials Database and Design System A*, 2002.

5. *Fizicheskie velichiny. Spravochnik* (Physical Quantities: A Handbook), Moscow, 1991.