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NOTES

Tribophysical Preparation of Al_2O_3–Pt–Pd Catalyst

The surface of a plate of platinum was mechanically polished with a colloidal suspension of γ-Al_2O_3[1] *(1)* which served as an abrasive here. During this rubbing process the alumina suspension became a grey paste, since the fine particles of platinum were dispersed uniformly in it. The platinum content of the paste produced could be prescribed by controlling the rubbing duration with a given quantity of the abrasive.

The sludge, containing about 20 wt% platinum, was examined in terms of electron diffraction. The interference pattern observed is reproduced in Fig. 1. From the half-width value of the reflections in this figure the mean size of the particles composing the sludge is estimated to be about 50 Å. This particle size is suitable for contact catalysis.

The result of the analysis of Fig. 1 is given in Table 1. It is noted here that the interplanar spacings measured at the reflections coincide with one another between γ-Al_2O_3 and Pt. This is because the crystal lattices are nearly equal between these two substances. This seems to give rise to a uniform dispersion of the Pt particles in the Al_2O_3 *(2)*.

The Al_2O_3–Pt sludge corresponding to Fig. 1 was examined in catalytic activity. The thin fibers of natural asbestos were smeared with this sludgy paste. These fibers were immersed in an atmosphere with gaseous hydrocarbons, as is illustrated in Fig. 2. After the surface of the catalyst was once ignited, there took place a slow combustion here without interruption at about 400°C. Benzine, the boiling points of which lie between 30 and 150°C, was employed as fuel. The life span of this catalyst was long. Its activity still remained intact after it was used without rest for 4 months.

The experiment was performed in order to study quantitatively the catalytic performance of the Al_2O_3–Pt sludge produced. Two coiled elements of platinum wire resistor (diameter of the wire: 0.03 mm) were prepared, each of which had 12 turns (see Fig. 3). These elements covered with the Al_2O_3–Pt paste were utilized as the two resistors in a Wheatstone bridge, which were maintained at a temperature of about 400°C by applying electric current (see Fig. 4). After an electrical cancellation was obtained on the millivoltmeter (M) in the bridge, *one* of the resistance elements concerned was supplied with the air containing 0.6 wt% isobutane $CH(CH_3)_3$. Since a slow combustion of isobutane then took place on the catalyst surface, and consequently the resistance of the element in question changed, a potential difference was recorded on the millivoltmeter (M).

A reference experiment was carried out with the conventional type of Al_2O_3–Pt catalyst that was produced by decomposing thermochemically potassium chloroplatinate in alumina. The result of this experiment is compared with that of the sludge catalyst in question in Fig. 5. The potential differences measured on M in Fig. 4 against

[1] Product of Baikowski, France.

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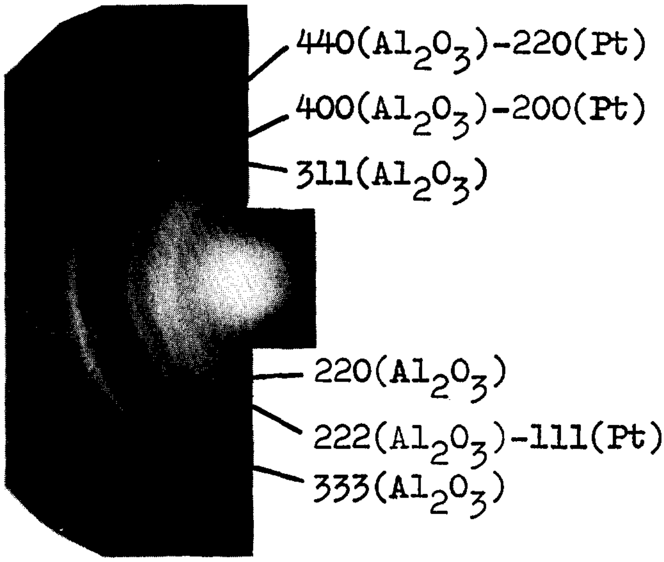

FIG. 1. Electron diffraction pattern of the Al_2O_3–Pt catalyst produced by the tribophysical procedure. Mean size of the particles composing the catalyst is estimated to be about 50 Å from the half-width of the reflections. Wavelength of the electrons applied: 0.0312 Å. Distance between the object and the photographic plate: 50 cm. Positive enlarged 2.3 times.

time lapse were plotted for the two types of catalyst in Fig. 5. It follows from this figure that the catalyst produced by the tribophysical procedure is more active longer than the conventional one, apart from the initial stage of reaction. The former catalyst was free from any catalytic poison, since it was produced by a physical way with pure Pt, Al_2O_3, and H_2O. On the contrary, the latter could be contaminated with reaction products, e.g., with alkali metal and chlorine. Furthermore, in the latter catalyst the constituent particles became granular, since sintering took place between them during the thermochemical process.

It is known that palladium often behaves more active as a catalyst than platinum.

TABLE 1
Results of the Analysis of Fig. 1[a]

d (Å)	Al_2O_3	Pt
4.56	111	—
2.80	220	—
2.38	311	—
2.28	222	111
1.97	400	200
1.52	333	—
1.40	440	220

[a] The interplanar spacings d (angstroms) measured in Fig. 1 coincide with one another between gamma-Al_2O_3 and Pt the cell edges of which are 7.90 and 7.84 (=3.92 × 2) Å, respectively.

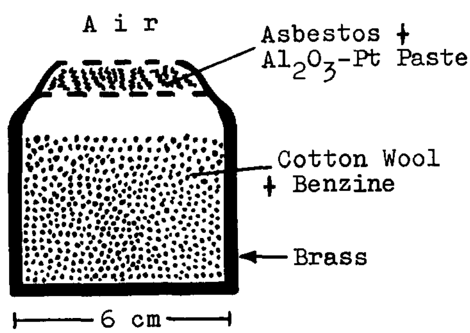

FIG. 2. Device for testing activity of the catalyst. The catalyst is composed of thin fibers of asbestos smeared with the Al_2O_3–Pt sludge. Boiling point of benzine: 30–150°C. Thickness of the benzine container: 10 mm.

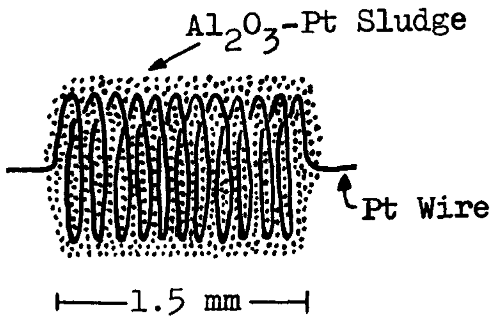

FIG. 3. Platinum wire resistor covered with the Al_2O_3–Pt sludge, which is disposed in a Wheatstone bridge. Resistance of this coil: 2 ohms at 25°C.

The former, however, is susceptible to oxidation, and so it becomes volatile. Hence, it may be proposed to utilize an alloy of Pd–Pt system as catalyst. But it is, as a rule, difficult to produce alloy catalyst. The present tribophysical method permitted me to surmount this difficulty.

A cast alloy composed of Pt and Pd (10% by wt) was employed as a starting material for producing the catalyst. The electron diffraction pattern from this alloy is shown in Fig. 6 that corresponds to the intermetallic compound Pt_5Pd with the long lattice period 86.5 Å. The surface of

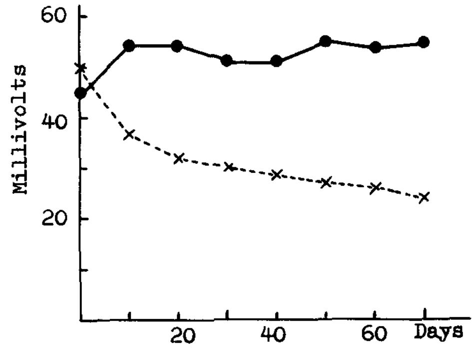

FIG. 5. The results of the tests of the two types of Al_2O_3–Pt catalyst. Potential changes measured on M in Fig. 4 are plotted against time lapse. Solid line: the catalyst produced tribophysically. Broken line: the catalyst produced thermochemically.

this cast was polished mechanically with the alumina suspension in order to obtain a rubbing sludge containing about 20 wt% of the alloy. The pasty matter prepared gave the electron diffraction pattern of Fig. 7. The features of this pattern are similar to those of Fig. 1. This means that the fine alloy particles are so evenly scattered in the alumina as in the case of the Al_2O_3–Pt catalyst. Catalytic life of this

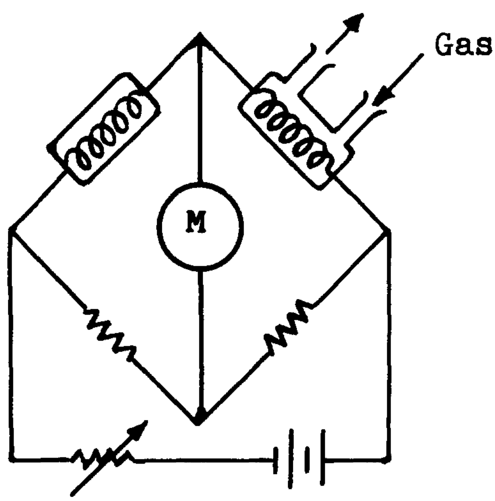

FIG. 4. Wheatstone bridge in which the two resistors as illustrated in Fig. 3 are disposed. One of them maintained at a temperature of about 400°C is exposed to a stream of fuel gas. Voltage of the battery applied: 3 V.

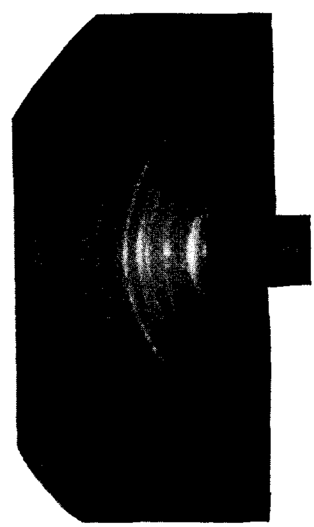

FIG. 6. Electron diffraction pattern of Pt–Pd alloy, which corresponds to the intermetallic compound Pt_5Pd as characterized by a long lattice period of 86.5 Å.

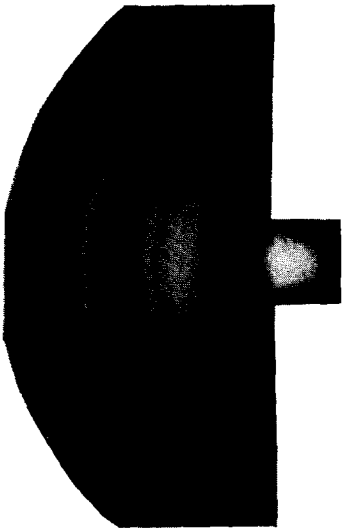

FIG. 7. Electron diffraction pattern of the rubbing sludge obtained by polishing mechanically the Pt–Pd ingot surface with the alumina suspension. This figure is similar to Fig. 1. This alloy–alumina sludge performs well in the petrochemical catalysis.

alloy catalyst proved longer than that of Al_2O_3–Pd. Specifics of the former should be studied further.

It is of interest that a colloidal suspension of γ-Al_2O_3 plays two roles at the same time, i.e., it is the support as well as the abrasive for platinum.

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