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An investigation on Pd/C industrial catalysts for the purification of terephthalic acid

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Abstract

Commercial 0.5% Pd/C catalysts for the production of purified terephthalic acid (PTA) have been investigated by several physical techniques (SEM-EDS, CO chemisorption, XRD) and by activity tests performed in conditions strictly similar to those of industrial operation. These catalysts show a strongly external Pd distribution, pointing to high Pd concentrations in the outer layers of the carrier. It was found that Pd sinters very easily and that a rough proportionality exists between catalytic activity and Pd surface area. Pd sintering was shown to be an important cause of deactivation for PTA catalysts. However, in some cases deactivation occurs by sulphur poisoning, with the formation of a Pd sulphide (Pd_4S).

Keywords: Palladium catalyst; Hydrogenation; Terephthalic acid purification; Deactivation

1. Introduction

Polyethylene terephthalate (PET) has recently become one of the most important and fastest growing plastic material. Its present production is ca. 20 million mt/year and its growth is estimated at a minimum of 7% annually to the year 2000. Until 1960, only dimethyl terephthalate (DMT) was used as raw material for PET production, but later the purified terephthalic acid (PTA) process, jointly developed by Scientific Design and Amoco, rapidly became the preferred one [1,2]. Briefly, by homogeneous-phase oxidation of *p*-xylene, crude terephthalic acid (CTA) is obtained, containing 4-carboxy-benzaldehyde (4-CBA) as the main impurity (2000–6000 ppm), besides several coloured polyaromatic compounds. In the Amoco process and the like (ICI, Inca-Dow, Mitsui), after dissolution of CTA in water at 270–280°C, all these impurities are hydrogenated over a granular 0.5% Pd/C catalyst in a trickle-bed reactor.

The worldwide consumption of PTA catalyst is expected to exceed 1000 mt/year around 2000, with a corresponding total business of ca. 30 million USD/year.

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Though it is clearly one of the most important petrochemical catalysts, scientific literature is almost completely lacking. Only some Chinese researchers published a few papers, mainly dealing with catalyst deactivation. They reported [3,4] that the main causes of deactivation in industrial plant are loss of Pd and decrease of Pd surface area. Deposits of metallic terephthalates were also found on the surface of exhausted catalyst [5].

Our group is making basic and applied research on PTA catalyst since a few years and certain preliminary results have been reported in recent congresses [6–8].

Here, we will report more detailed information about physical and catalytic properties of industrial PTA catalysts, discussing, in particular, problems connected with Pd dispersion and distribution as well as with catalyst deactivation.

2. Experimental

Commercial 0.5% Pd/C PTA catalysts including D-3065 from CHIMET, were used for this study.

A Cambridge scanning electron microscope, model S120, equipped with EDAX system for elemental analysis (PV 9800), was used to generate the maps of Pd distribution on carbon-granule cross sections. The electron gun acceleration voltage was 30 kV and the X-ray window was taken on the PdL_α line.

CO chemisorption measurements were performed at 25°C using a home-made pulse flow system. Prior to measurements, each sample was subjected to a pretreatment involving exposure to hydrogen at 25°C for 1 h, followed by helium purge at the same temperature for 2 h.

To obtain the Pd surface area a chemisorption stoichiometry Pd/CO equal to 2 and a surface Pd atomic density of 1.27×10^{19} atoms/m^2 were assumed.

X-ray powder diffraction patterns were collected using a Philips vertical goniometer connected to a highly stabilized generator. Nickel-filtered CuK_α radiation, a graphite monochromator and a proportional counter with pulse–height discrimination were used. A step-by-step technique was employed with steps of 0.05° in 2θ and accumulation counting time of 100 s per angular abscissa.

Activity measurements (4-CBA hydrogenation) were performed in a batch reactor under hydrogen (5 bar) at 277°C in 20% PTA–water mixture, i.e. in conditions strictly similar to the industrial ones. Analysis was performed by HPLC. Activity was expressed as rate constant derived from first-order plot of 4-CBA concentration vs. time. Preliminary experiments showed that the system works in a strictly kinetic regime.

3. Results and discussion

3.1. Palladium distribution in PTA catalysts

It is well known that, in supported catalysts prepared by wet impregnation, the metal is not always distributed homogeneously throughout the whole volume of the carrier particles, but very frequently is confined to a peripheral layer of the carrier. This external, otherwise called egg-shell, metal distribution is often intentional, as it makes the active phase more accessible to the reactants, which is very important not only for activity and selectivity reasons, but also to minimize the metal content in the case of precious metal catalysts. Clearly, this effect can be highly relevant for granules or pellets of several millimeters size, not so much for powdered catalysts. The PTA catalysts are supported on irregular, active carbon granules of size in the 2–4 mm range. For the measurement of Pd penetration depth, we have used SEM-EDS, as optical microscopy, commonly used for Pd-Al_2O_3 catalysts, is obviously useless in this case. The SEM-EDS pattern of a typical commercial catalyst (CHIMET D-3065) is shown in Fig. 1. The average Pd penetration depth is ca. 15 μm. A value of the same order of magnitude was obtained through a completely different method, namely by determining the Pd content of catalyst fractions with different particle sizes [9]. Assuming an average particle size of 3 mm and a cubic particle shape, it can be easily calculated that the average Pd content in the Pd-containing external catalyst layer is ca. 17%, from a nominal content of 0.5% in the whole catalyst. In such conditions, a very high metal dispersion should not be expected in spite of the high apparent surface area of the carrier (>1000 m^2/g) and of the low total metal content.

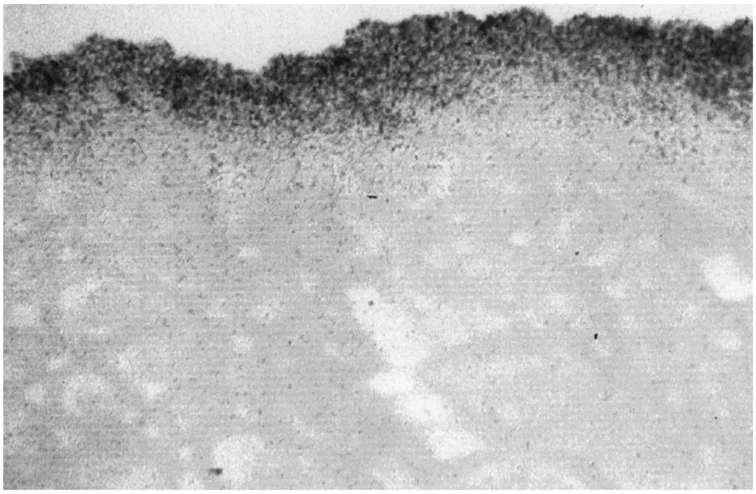

Fig. 1. Typical SEM-EDS pattern of 0.5% Pd/C CHIMET D-3065 PTA catalyst (Pd and C images).

Sometimes PTA catalysts can be found showing an even more external Pd distribution. In such cases, the Pd dispersion is lower and the risk of Pd losses by abrasion, causing a fast deactivation, much higher.

3.2. Palladium dispersion in fresh and aged PTA catalysts

It was deemed interesting to measure the Pd dispersion of various commercial PTA catalysts and check whether any correlation exists between Pd dispersion and catalytic activity in 4-CBA hydrogenation. XRD offers an easy way for the evaluation of Pd crystallite size, from which Pd dispersion can be easily derived. The XRD patterns of four different commercial catalysts are reported in Fig. 2. The Pd (111) peak at $2\theta=40^\circ$ is the one relevant for our purpose, while the wide band centred at $2\theta=43.5^\circ$ pertains to active carbon. In the absence of a preferred orientation, the area of the Pd (111) peak is proportional to the amount of Pd detectable by X-rays, namely that having a crystallite size larger than ≈15 A.

As it was found that the peak width does not change too much, in practice there is a roughly inverse proportionality between Pd dispersion and peak area. It can be seen that there are large differences of Pd dispersion in fresh PTA commercial catalysts. From Fig. 3, it can also be seen

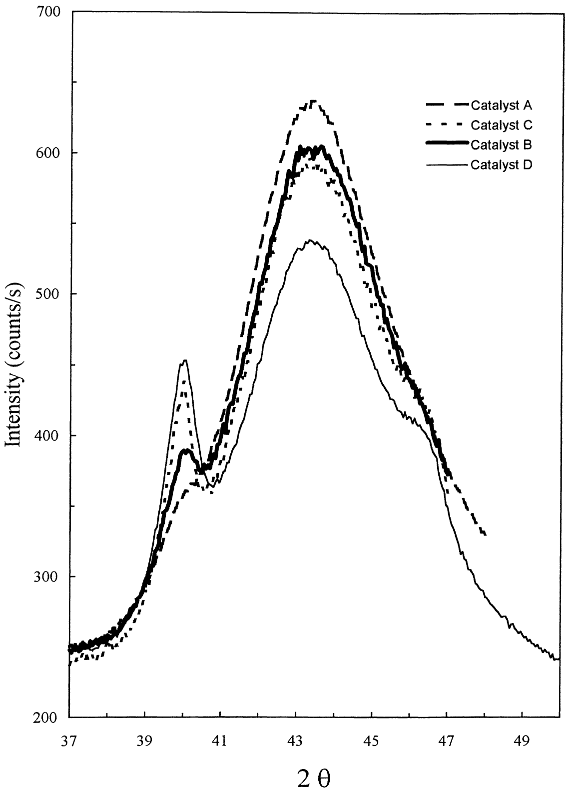

Fig. 2. XRD patterns of several commercial 0.5% Pd/C PTA catalysts.

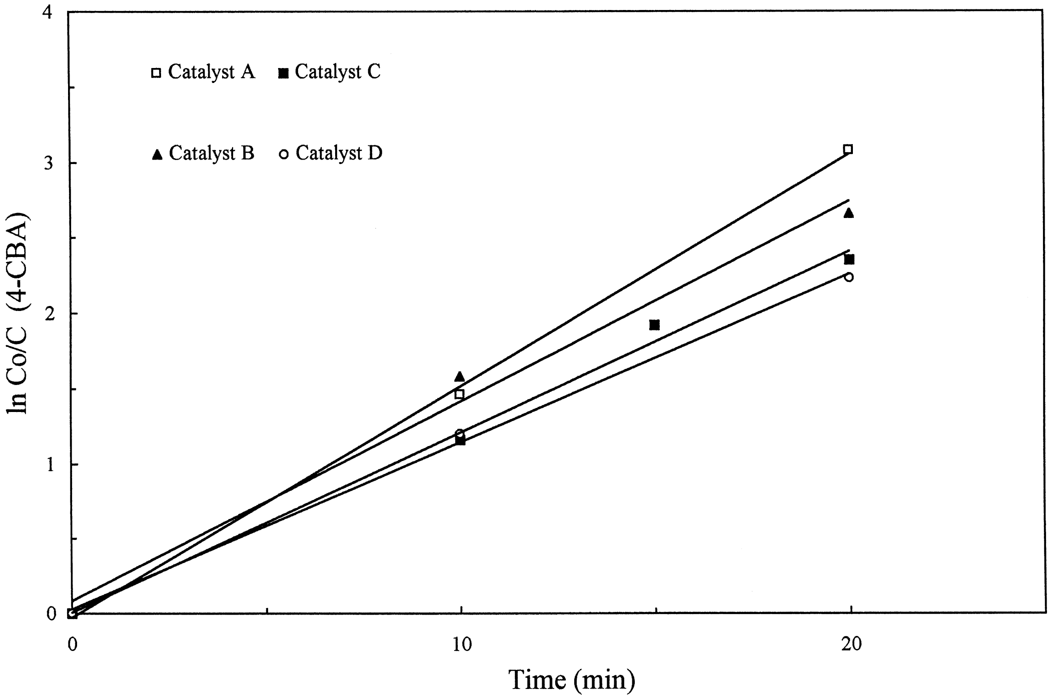

Fig. 3. Activity pattern of several commercial 0.5% Pd/C PTA catalysts.

that such dispersion differences are connected with similar differences in catalytic activity. In fact, the four catalysts examined rank in the same order as Pd dispersion and catalytic activity. Though the relationship is not strictly quantitative, it can be concluded that the Pd dispersion in fresh commercial PTA catalysts is an important parameter for their evaluation, even if other factors are certainly relevant to catalytic activity.

It was found that fresh PTA catalysts undergo a fast Pd sintering as soon as they are brought to the reaction temperature of ca. 280°C (Fig. 4). This is due to the high Pd content in the Pd-containing external layer and to the low metal-support interaction typical of active carbon, both coupled with the fact that, very likely, these catalysts were never treated at such high temperatures during manufacture. It should be remarked that this sintering also occurs for the fresh catalysts having lower Pd dispersion (Fig. 2(C and D)), otherwise no corresponding activity difference should have been found (Fig. 3).

Thus, it can be concluded that the availability of fresh PTA catalysts having high Pd dispersion is very important from an industrial point of view.

3.3. *Catalyst deactivation by Pd sintering*

Metal sintering is one of the most frequent causes of deactivation of industrial supported metal catalysts. We have, therefore, investigated PTA catalysts from this point of view as well. To this purpose, we have submitted a commercial PTA catalyst (CHIMET D-3065) to thermal treatment at different temperatures up to 800°C under inert atmosphere, and both Pd surface area, proportional to Pd dispersion, as well as catalytic activity were measured. It was found that the Pd surface area strongly decreases when the treatment temperature increases (Fig. 5). This confirms that Pd easily sinters in this catalyst. A sufficiently good linear relationship was found between catalytic activity and Pd surface area in this set of samples (Fig. 6), thus confirming that Pd sintering is an important cause of deactivation for PTA catalysts.

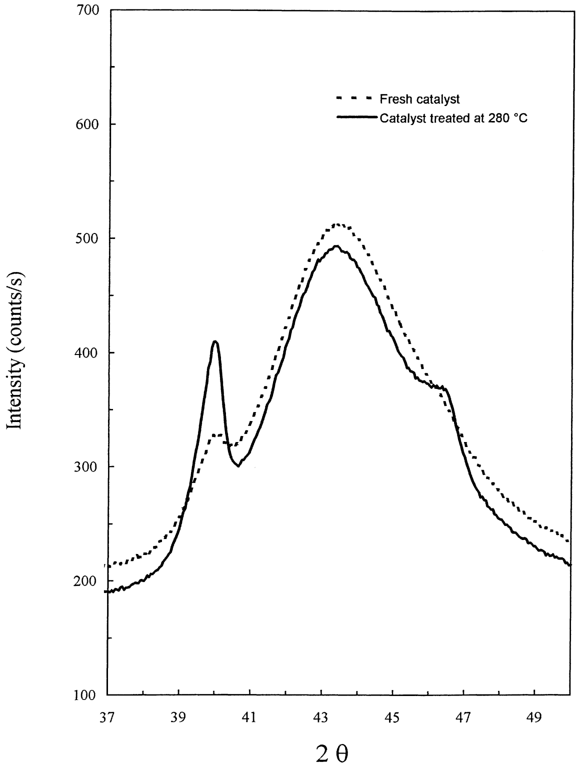

Fig. 4. XRD patterns of 0.5% Pd/C PTA catalyst before, and after, exposure to reaction conditions.

3.4. *Catalyst deactivation in industrial plants*

In order to obtain more information about possible deactivation mechanisms of PTA catalysts, several samples of exhausted industrial catalysts discharged from different plants have been examined by XRD. Some of them show very intense Pd (111) peaks (Fig. 7), which is indicative of strong Pd sintering, without extra peaks due to other phases.

Other samples show only the peaks of the sulphide (Pd_4S) (Fig. 8), which is indicative of rapid poisoning by sulphur compounds before Pd sintering could have taken place. A few samples were also found, where both phenomena coexist (Fig. 9).

The degree of deactivation of the exhausted catalysts can be easily evaluated by our activity test (Fig. 10). However, from the data collected until now, no conclusion can be drawn about the relative importance of the two above-described causes of deactivation.

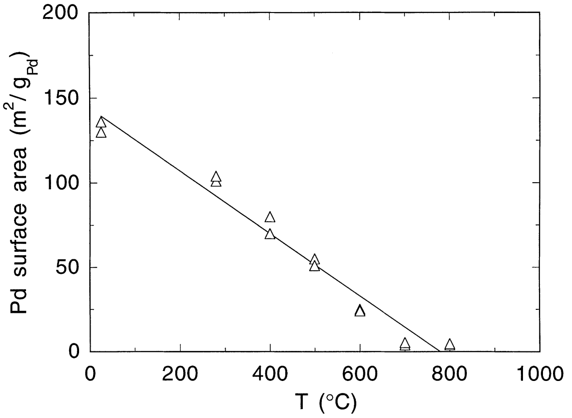

Fig. 5. Relationship between Pd surface area and treatment temperature for 0.5% Pd/C PTA catalyst.

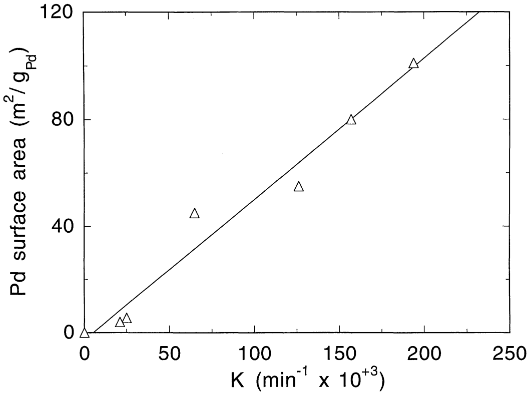

Fig. 6. Relationship between Pd surface area and catalytic activity for 0.5% Pd/C PTA catalyst.

As the life of PTA catalysts in industrial plants is relatively short (6–18 months, depending on plant operation and catalyst properties), it is highly desirable to carry out further research to improve it. This requires the availability of laboratory tests measuring the tendency of the catalyst to deactivation. It has been shown [10] that a previous identification of the possible deactivation mechanisms and of the pertinent accelerating factors is required. Thus, an accelerated life test for each deactivation mechanism can be developed by suitably tuning the accelerating factors. Work along such directions is being performed in CHIMET laboratories for the improvement of PTA catalysts and will be reported later on.

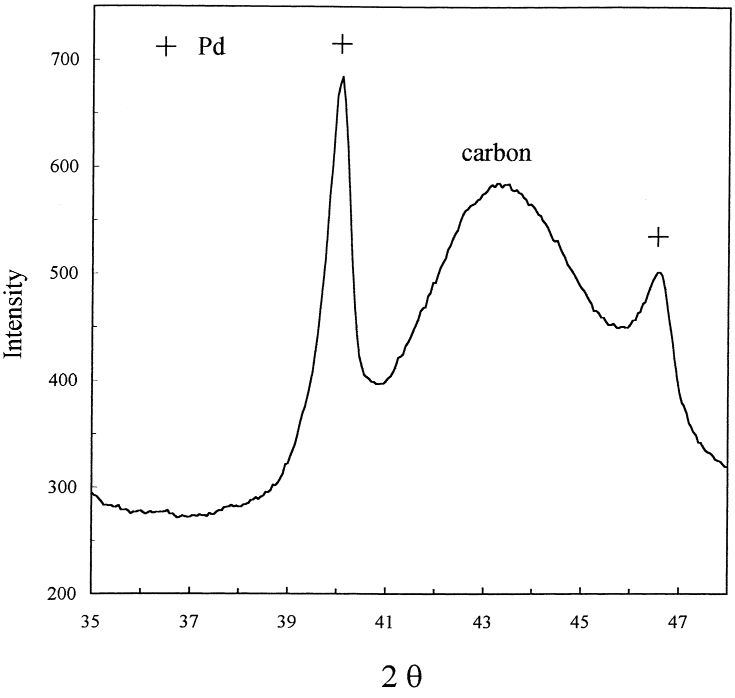

Fig. 7. XRD pattern of strongly sintered 0.5% Pd/C industrial PTA exhausted catalyst.

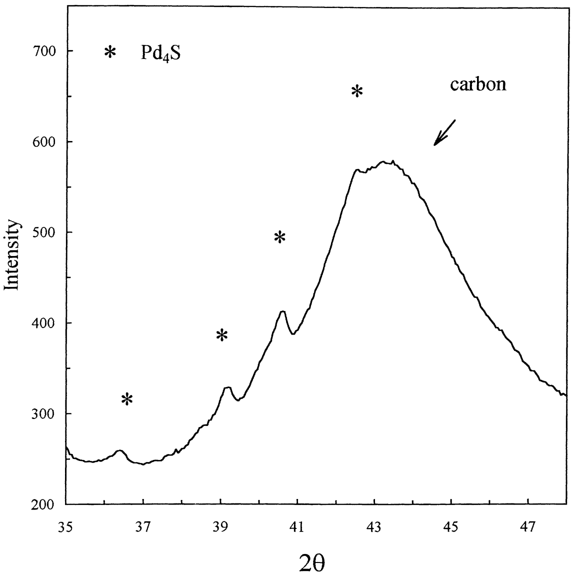

Fig. 8. XRD pattern of sulphur-poisoned 0.5% Pd/C industrial PTA exhausted catalyst

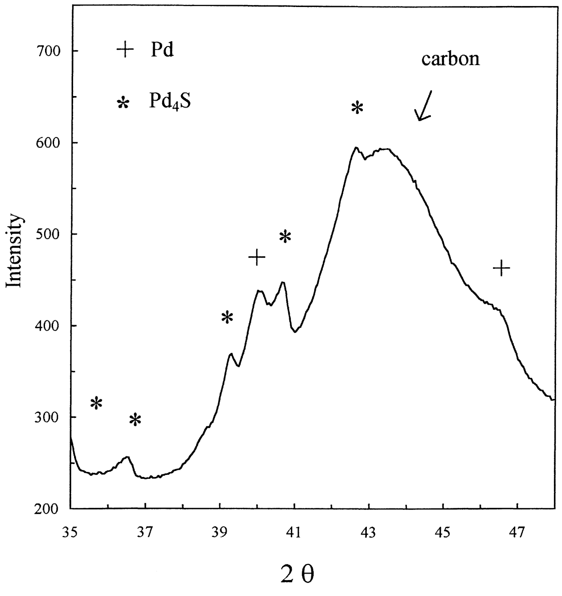

Fig. 9. XRD pattern of both sintered and sulphur-poisoned 0.5% Pd/C industrial PTA exhausted catalyst.

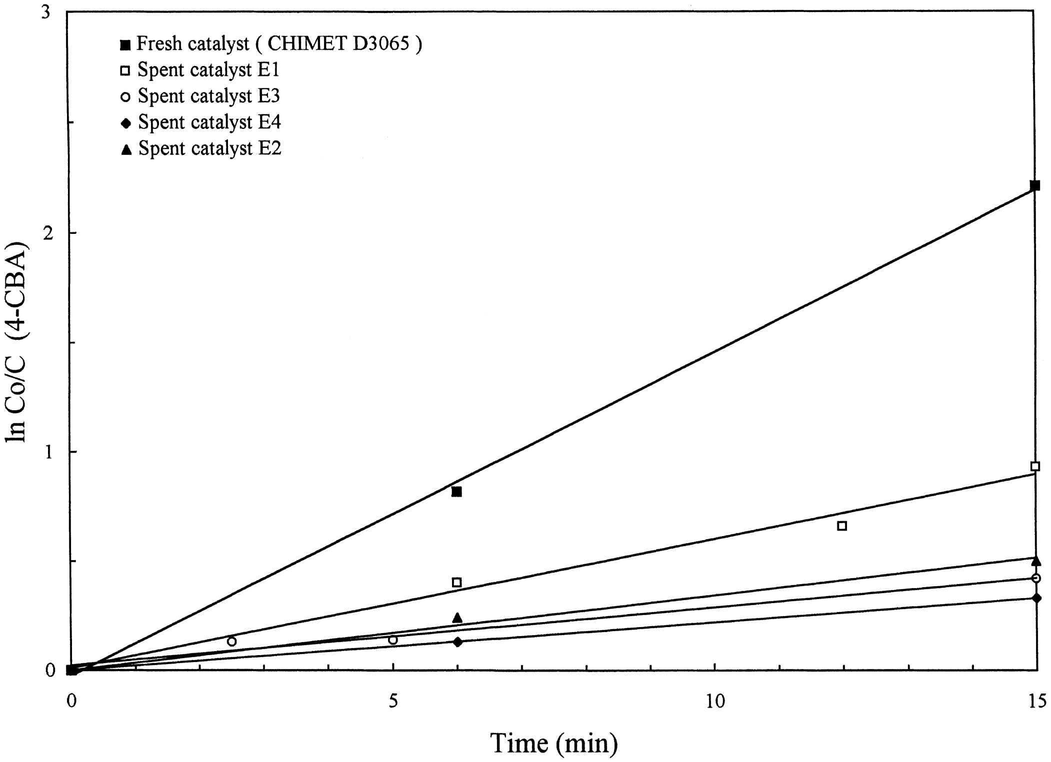

Fig. 10. Activity pattern of several 0.5% Pd/C industrial PTA exhausted catalysts compared with a fresh one.

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