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Characterization of a Pt-Pd combustion catalyst on an alumina washcoat, with and without prior hydrothermal treatment of the washcoat

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Two Pt/Pd catalysts on cordierite monoliths were prepared by impregnating two differently treated alumina washcoats with 10 μmol [Pt+Pd] per gram catalyst in the atomic ratio Pt/Pd = 4.0. Both washcoats were first thermally treated, calcined, for 2 h at 550°C in air and one of them was additionally treated, hydrothermally, in 100% steam for 2 h at 814°C. The hydrothermally treated catalyst was more active for complete oxidation of xylene in air: its light-off temperature was 232°C, compared to 259°C for the sample calcined only. To explain this higher activity, both catalysts were characterized by BET surface area, pore-size distribution, hydrogen chemisorption, X-ray diffraction, TEM/STEM/EDS and low-energy ion scattering spectroscopy (LEIS). The catalyst with a hydrothermally treated washcoat had 30% lower surface area, larger alumina crystal size, higher degree of crystallization of alumina and larger average catalyst pore size (11 nm vs. 6 nm), than the one with the washcoat, treated only thermally. The LEIS results indicated a surface enrichment of Pd on both catalysts. The Pt signal in LEIS was higher for the hydrothermally treated sample.

Keywords: Pt-Pd/alumina; combustion catalyst; hydrothermal treatment; xylene oxidation; light-off temperature; TEM/STEM/EDS; LEIS

1. Introduction

Emissions of pollutants from industry and automotives can be considerably reduced by catalytic combustion. Organic solvent vapors can be eliminated over catalysts which have many features in common with catalytic converters for cars

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[1]. Such catalysts often consist of a ceramic or metallic monolith coated with a washcoat, in most cases of alumina, which provides a high surface area. On the surface of the washcoat, precious metals such as Pt, Pd and Rh are deposited as the active catalytic component [2]. Organic solvent molecules are often considerably larger than CO and NO_x, so that compared to catalytic converters for cars, catalytic oxidators may require washcoats having pore-size distributions shifted towards larger pores in order to reduce intra-particle diffusional resistance.

When washcoats of corpuscular boehmite, which has pore-size distributions with a considerable portion of the surface area in small pores, was subjected to hydrothermal treatment the pores smaller than 50 Å disappeared [3]. Hydrothermal treatment of the alumina washcoat also gives a better developed crystallinity than that obtained with thermal treatment at the same temperature [4].

In our previous investigation, the effects of hydrothermal treatment, compared with thermal treatment, of alumina as substrate were studied for Pd-Pt catalysts. Metals deposited on hydrothermally treated alumina yielded a higher activity for the complete oxidation of xylene than those (of same concentration) deposited on thermally treated alumina [5]. Bimetallic catalyst systems of this type often exhibit surface enrichment of one of the component metals. Surface enrichment in alloy catalyst systems has been extensively reviewed in the past by Overbury et al. [6], Somorjai [7], Ponec [8], Sachtler [9] and others. Such enrichment in supported-metal and metal-oxide type industrial catalysts has been reviewed by Menon and Prasada Rao [10]. Quiroz et al. [11] suggest a partial electron deficiency of Pd and an electron enrichment of Pt in bimetallic Pt-Pd/Al_2O_3 catalysts. In the light of such results, it is of interest to characterize our Pt-Pd/Al_2O_3 catalysts with several modern techniques to check if the observed higher catalytic activity (lower light-off temperature) can be accounted for by surface enrichment or any such related phenomenon.

2. Experimental

MATERIALS

Platinum(II)chloride and palladium(II)chloride were obtained from Johnson Matthey Chemicals (Royston, U.K.). Disperal Alumina, a dispersible powder of boehmite, was supplied by Condea Chemie (Brunsbuettel, Germany) and cordierite monolith structure containing 64 square channels per square centimetre by Corning Glass (Wiesbaden-Biebrich, Germany). Xylene GR (pro analysi) and hydrochloric acid (pro analysi) were obtained from Merck (Darmstadt, Germany). Gases used were obtained from AGA (Gothenburg, Sweden) and ALFAX (Gothenburg, Sweden).

CATALYST PREPARATION

Boehmite solutions from Disperal powder were made by slurrying the powder in dilute hydrochloric acid [12]. Monolith samples with a length of 15 mm and a cross section containing 69 channels were provided with a washcoat of boehmite by a dip-coating procedure [3]. The alumina, approximately 0.14 gram per gram of catalyst, was stabilized by calcining at 550°C for 2 h in air ("thermal treatment"). The "hydrothermally treated" samples were given an additional treatment in 100% steam at 814°C for 2 h [4] before the deposition of platinum and palladium salts. The noble metals, 10 μmol per gram catalyst, were applied by direct impregnation [13] by filling the monolith channels once with a solution of platinum and palladium chlorides. The concentration of the solution ($pH = 1.7$) was 9.5 μmol [Pt + Pd] per ml. The noble metals loading in the catalysts were 71 μmol [Pt + Pd] per gram alumina. After impregnation, the water in the catalysts was evaporated by keeping the sample for 1.5 h at 90°C and finally at 120°C for 30 min. Each catalyst was exposed to oxidizing conditions in an air flow of 500 cm^3 min^{-1} at 500°C for 30 min and to reducing conditions in a hydrogen flow of 200 cm^3 min^{-1} for 1 h at 450°C. To simulate aging, the catalysts were then kept in a stream ($SV = 144{,}000$ h^{-1}) of a mixture of 0.09 vol.% xylene in air at 600°C for 2 h.

CATALYST AND MATERIALS CHARACTERIZATION

Specific areas and pore size-distributions of catalysts were determined by nitrogen adsorption on a Digisorb 2600 from Micromeritics (Norcross, GA, U.S.A.).

The chemisorption of hydrogen on the particles of the noble metals was studied on a Chemisorb 2800 instrument from Micromeritics. The isotherms for the adsorption of hydrogen were made at 90°C in order to minimize absorption of hydrogen by samples containing palladium and chemisorbed ammounts of hydrogen were taken after back-extrapolation to zero pressure [14]. Surface areas, pore-size distributions and chemisorption of hydrogen were determined for catalyst samples *after* they were used in the catalytic oxidation experiments [5]. Coke formed during the reaction was first removed by calcining at 525°C in air for 2 h, which is milder than the conditions used during the experiments in the reactor.

X-ray diffraction (XRD) analyses were performed on powder samples of thermally and hydrothermally treated Disperal Alumina. The XRD-patterns were obtained on a Philips powder diffractometer using Ni-filtered, fine-focus CuKα radiation.

The platinum and palladium contents were determined by AAS (Perkin Elmer 370 Atomic Absorption Spectrophotometer) on used catalysts after crushing and dissolution in aqua regia.

PREPARATION OF TEM SPECIMENS

TEM specimens were prepared by conventional crushed powder technique described by e.g. Rice and Treacy [15]. Parts of the washcoat layer were abraded away and crushed with mortar and pestle. The powder was ultrasonically dispersed in methanol and transferred onto a holey carbon film, supported on a copper grid.

MICROSTRUCTURE CHARACTERIZATION

Transmission electron microscopy was performed using a JEOL 2000 FX TEM/STEM to determine the sizes of the noble metal particles and the alumina crystallites in the washcoat and a VG HB 501 D-STEM to estimate the composition of single noble metal particles. The microscopes were equipped with LINK X-ray energy dispersive spectrometers (EDS). Micrographs at high magnification ($\simeq 400{,}000\times$) were recorded from the samples used in this investigation. The composition of single particles were analysed using D-STEM and EDS.

Electron microscopy of catalysts is usually a quite straight forward technique to obtain information on the particle sizes in catalysts, but as mentioned earlier by e.g. Flynn et al. [16], care must be taken when interpreting particles of sizes $\leqslant 2$ nm. Below ≈ 1 nm, the particles are hardly visible at all. Diffraction contrast effects, arising from the alumina crystallites, also make the interpretation more difficult as also pointed out by Flynn et al. [16].

SURFACE CHARACTERIZATION BY LEIS

The surface of the samples were characterized by Low-Energy Ion Scattering spectroscopy (LEIS). Details of the LEIS equipment used in this investigation have been given in an earlier publication [17]. The targets were heated in 20 mbar of oxygen at about 300°C for 15 min to remove contamination by water and hydrocarbons. Other parameters were in principle the same for all measurements. The absolute intensities were somewhat different each time the instrument was started up, therefore absolute values of the two different sets of experiments (separated by 3 months) cannot be compared.

3. Results and discussion

EFFECT OF THERMAL AND HYDROTHERMAL TREATMENTS ON CATALYTIC PERFORMANCE

In our previous investigation [5], the effects of a) the total content of Pt + Pd, b) the atomic ratio of Pt to Pd, c) the oxygen concentration and d) hydrothermal

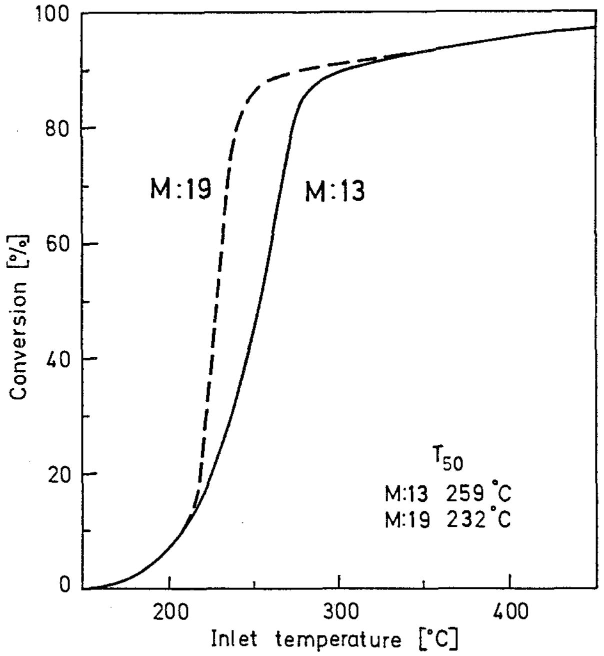

Fig. 1. Conversion vs. inlet temperature for the combustion of 220 ppm xylene in air ($SV = 144{,}000$ h^{-1}) over catalysts M:13 and M:19.

treatment of the washcoat on the light-off temperature, T_{50}, (defined as the temperature of inlet gas at which the conversion of the reactant was 50%) for the complete oxidation of xylene, propene and CO were studied. The conclusion from that work was that, at a Pt/Pd atomic ratio of 0.25, Pt promotes the complete oxidation of CO and xylene over Pd. For a fixed amount of total metals, the light-off temperature had a minimum at a Pt/Pd atomic ratio of 0.25. Relative to catalysts with only thermally treated washcoats, catalysts with hydrothermally treated washcoats have lower light-off temperatures (by up to 27°C) for the oxidation of xylene [5].

With increasing total metals content, T_{50} decreased for the oxidation of xylene and CO [5]. For the oxidation of CO, however, T_{50} was rather insensitive to the total metals concentration at a Pt/Pd atomic ratio of 0.25. The T_{50} values for the complete oxidation of xylene and CO decreased rapidly with increasing oxygen concentrations at oxygen concentrations below 5 vol.%, but level thereafter to an almost constant value at oxygen concentrations higher than 10% by volume [5].

Fig. 1. shows typical conversion data for the complete oxidation of 220 ppm xylene in air on the two catalysts described in this paper (10 μmol [Pt + Pd] per gram catalyst; Pt/Pd atomic ratio 4.0; calcined only, denoted henceforth as M:13, and further hydrothermally treated, denoted as M:19). The light-off

temperature for M: 13 was 259°C and for M: 19, 232°C. For the oxidation of CO, the light-off temperature for both the catalysts was the same: 219°C.

Recently, it has been shown from our laboratory [4] that the performance of Pt and Pt-Rh supported on alumina washcoats was also considerably improved, if the washcoats were hydrothermally treated, i.e. heated in 100% steam at temperatures in the range 700–900°C before the noble metals were deposited. Compared to Pt and Pt-Rh on thermally treated supports, i.e. calcined only at 550°C for 2 h, the light-off temperatures for the combustion of xylene over the same metals on hydrothermally treated alumina were lowered by about 15°C.

STRUCTURE AND TEXTURE OF THE CATALYSTS

The effect of thermal and hydrothermal treatments on boehmite, applied as washcoat on ceramic monoliths, has also been elucidated in the above work of Löwendahl and Otterstedt [4]. The initial washcoat had a BET surface area of 195 m^2 per gram and a pore-size distribution (PSD) with a maximum at 6 nm. A dry calcination at 814°C for 2 h reduced the area to 135 m^2 per gram and shifted the PSD maximum to 8.5 nm. A hydrothermal treatment at 814°C for 2 h in 100% steam reduced the area to 120 m^2 per gram, but more significally shifted the PSD maximum to 11 nm. This was the reason for selecting the latter for the hydrothermal treatment used in this work to prepare catalyst M: 19.

The thermally treated catalyst, M: 13, chemisorbed 40×10^{-3} N cm^3 H_2 per gram catalyst and the hydrothermally treated one, M: 19, chemisorbed 30×10^{-3} N cm^3 H_2 per gram catalyst which corresponds to particle diameters of 2.8 nm resp. 3.9 nm according to Anderson and Pratt [14].

Hydrothermal treatment gave sharper and more well defined XRD-diffractograms, indicating a more well developed crystallinity than obtained with thermal treatment. This is in full agreement with our earlier results from XRD [4].

4. TEM / STEM

The main difference between the two samples as observed with TEM was, in general, the larger sizes of the alumina crystallites in the hydrothermally pretreated catalyst. The darkfield images of the washcoats, figs. 2A and B, show clearly the situation which is consistent with the XRD-analysis and earlier results from pore-size measurements [4], both of which indicated a higher degree of crystallization and larger pores in the hydrothermally treated alumina washcoat. However, the sizes of the visible noble metal particles does not seem to differ much between the two samples and were found to be in the range 1–4 nm (average ≈ 2 nm) in both. An area of the washcoat from the hydrothermally pretreated catalyst with some visible noble metal particles is shown in fig. 3. The presence and number of subnanometer particles is unknown in both cases and can perhaps account for the difference measured with hydrogen chemisorption.

The X-ray analysis in STEM of single noble metal particles indicated a variation in the Pt/Pd ratio from particle to particle. As expected, the majority of the particles analyzed were built up mainly by platinum, but in some cases more substantial amounts of palladium were present. The distribution of the two noble metals between individual particles is thus complex and so the interpretation of the results.

SURFACE CHARACTERIZATION BY LEIS

The quantification of LEIS results has been a subject of debate for many years. Recently it has been shown that, if correct experimental conditions are chosen, a quantitative analysis is even possible for highly dispersed catalysts. For a review on this subject, see ref. [18].

Four mass spectra were made in two series of measurements, separated by three months and on two sets of samples. The beam currents employed were 83 nA and 240 nA for the first series and 71 nA and 240 nA for the second. Apart

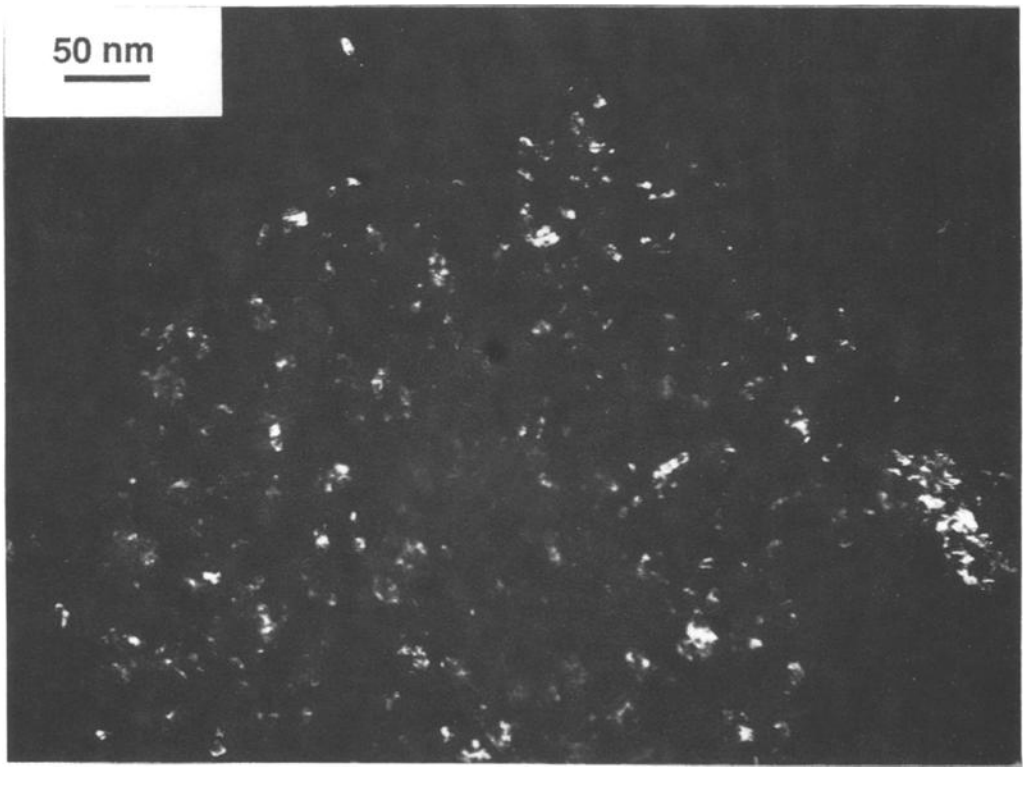

Fig. 2. TEM dark-field image of alumina crystallites in the thermally treated catalyst M:13 (A) and in the hydrothermally treated catalyst M:19 (B), showing, in general, larger alumina crystallites in the latter. Magnification 130,000×.

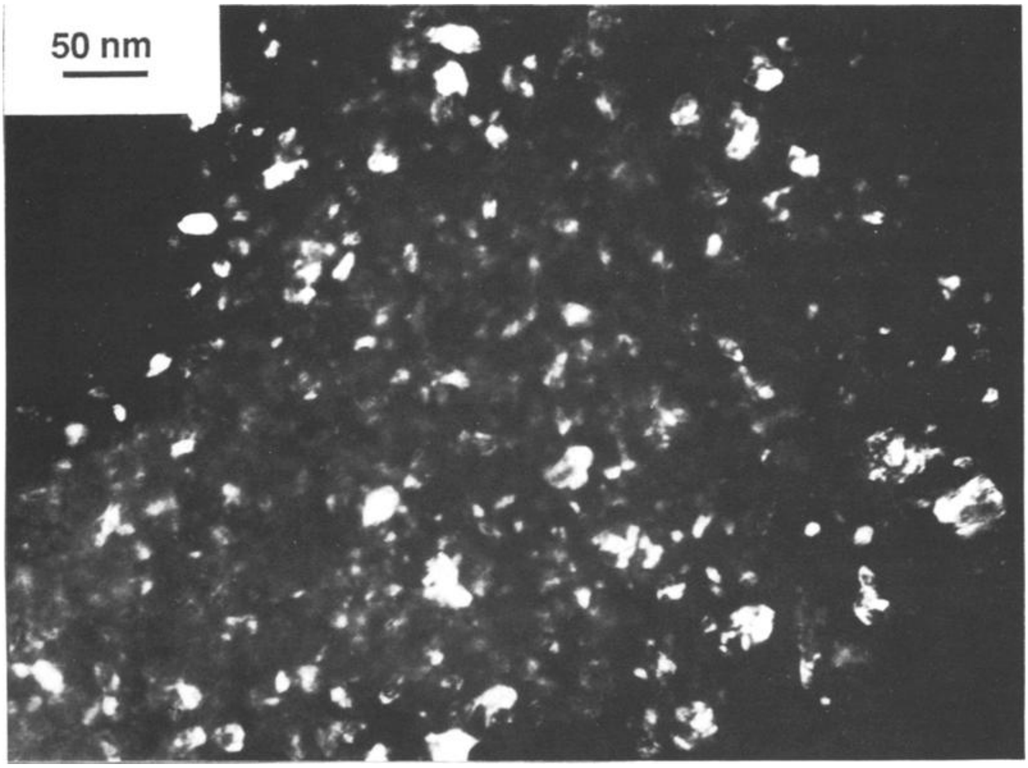

Fig. 2. (continued).

from Al, O and F (normal contaminant) the signals of Pt and Pd were clearly observed. Small quantities of other elements such as Fe were also seen. Typical LEIS spectra at 83 nA and 240 nA are shown in figs. 4 and 5, respectively.

Calibration: The peak height of pure Pt was 1.2 times that of pure Pd. The measurements were made on two occasions and on different samples. The results from the measurements on the different occasions agreed well which suggests that the homogeneity of the samples was good.

In all cases the Pt signal was clearly higher for the hydrothermally treated sample M:19 than for the thermally treated sample M:13. Taking into account the atomic ratio Pt/Pd = 4.0 of the catalysts and the slightly higher sensitivity of Pt, the surfaces are significantly enriched in Pd. The increase in Pt signal on the hydrothermally treated sample may be due to chemically induced segregation. Although this has not been specifically studied, the rather constant signals, as a function of time and beam current, suggest that increased dispersion is (on the basis of the LEIS results) perhaps even more likely.

In the first study, the M:13 and M:19 samples were examined after treatment at a calcination temperature of 200°C. In view of the present reproducibility for 300°C treatment it is very likely that the different composition found for higher temperature, was not due to any inhomogeneity of the sample.

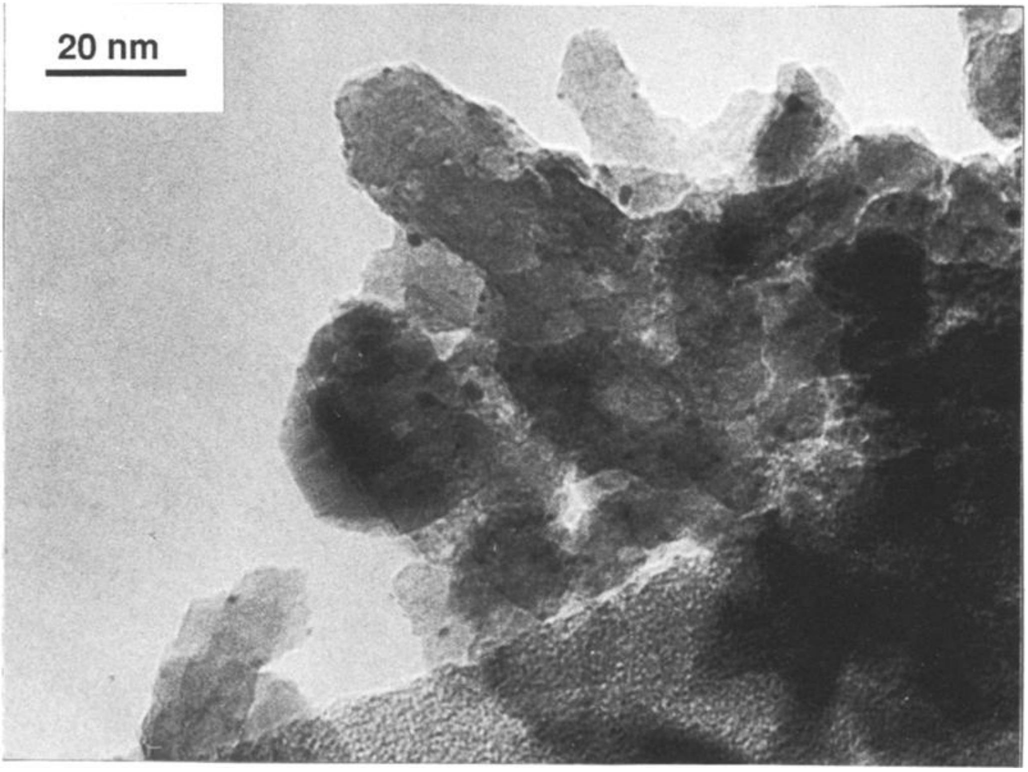

Fig. 3. TEM bright-field image of the hydrothermally treated catalyst M:19 showing the alumina support with noble metal particles. Magnification 410,000×.

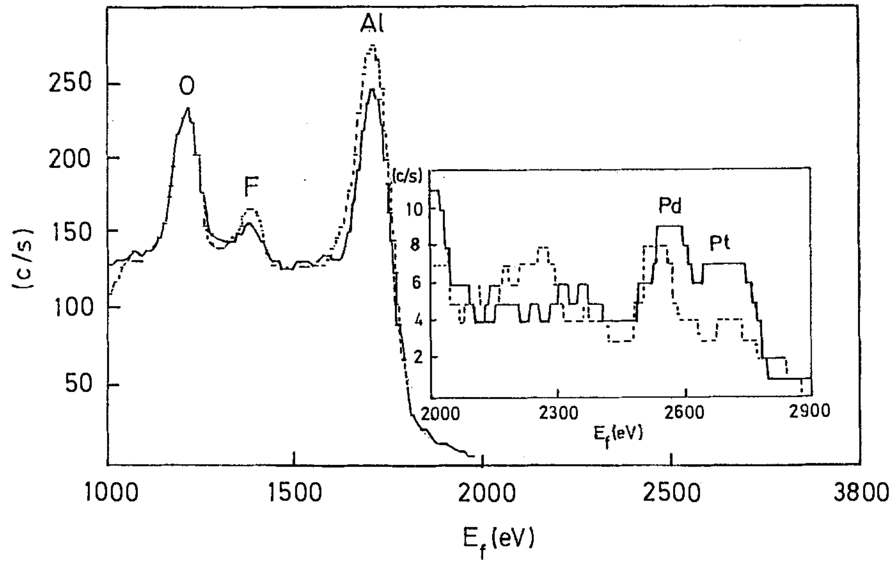

Fig. 4. Comparison of LEIS spectra for the catalyst samples with M:19 (———) and without M:13 (- - - - - -) hydrothermal treatment of the washcoat. LEIS conditions: He4, 3000 eV, 83 nA, 25°C.

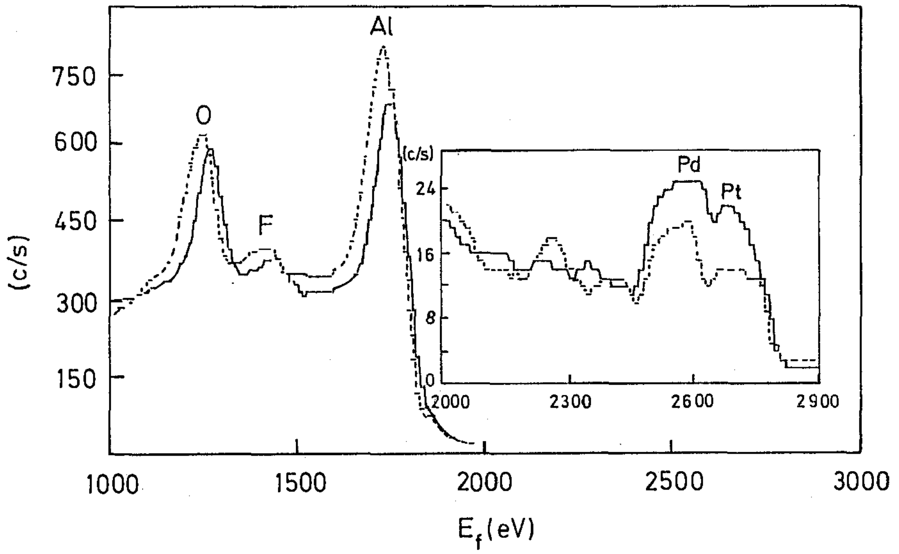

Fig. 5. Comparison of LEIS spectra for the M:19 (———) and M:13 (- - - - -) samples at 240 nA. Other conditions same as for fig. 4.

5. Conclusions

Compared with the thermally treated catalyst, the hydrothermally treated catalyst showed a substantially lower light-off temperature for the complete oxidation of xylene. The BET-surface area was lowered by 30% and the average pore size was shifted from 6 nm to 11 nm while a great deal of the pores smaller than 5 nm were eliminated. XRD-measurements and TEM/STEM-analysis showed larger and more well defined alumina crystallites when the catalyst was hydrothermally treated.

Both TEM/STEM-analysis and hydrogen chemisorption measurements suggest noble metal particle diameters in the range 1–4 nm for the thermally and the hydrothermally treated catalyst. Particles smaller than 1 nm might also be present, but they cannot be observed with the resolutions of the TEM/STEM used in this work. LEIS-analysis indicates that both the thermally and hydrothermally treated alumina surfaces are significantly enriched in Pd. Furthermore, the hydrothermal treatment gave higher Pt signals compared to the thermal treatment.

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