Eur. Phys. J. D **43**, 209–211 (2007)
DOI: 10.1140/epjd/e2007-00124-7

THE EUROPEAN PHYSICAL JOURNAL D

Differences in catalytic properties between mesoporous and nanoparticulate platinum

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Received 10 October 2006 / Received in final form 2nd November 2006

Abstract. Conventional Pt/Al_2O_3 catalysts prepared by wet-impregnation are composed of Pt nanoparticles exposing convex and facetted surfaces deposited on high-surface area γ-Al_2O_3 supports. A hexagonal phase mesoporous Pt material (denoted H_1-Pt) prepared by chemical reduction in the aqueous domains of a lyotropic liquid crystalline template exposes however mainly a concave surface with expected different catalytic properties. A series of Pt/Al_2O_3 catalysts were prepared using H_1-Pt, Pt-black or wet-impregnated Pt, and the samples were characterized by SEM-EDX and TEM, and finally evaluated for CO oxidation. The H_1-Pt/Al_2O_3 catalyst showed an ignition profile for CO oxidation at lower temperatures and thus appeared less sensitive to CO poisoning than the two other types of samples. This difference may be related to the differences in surface curvature.

PACS. 81.07.-b Nanoscale materials and structures: fabrication and characterization – 81.16.-c Methods of nanofabrication and processing – 82.33.Ln Reactions in sol gels, aerogels, porous media

1 Introduction

Oxidation catalysts typically consist of nanoparticles of Pt deposited on a high-surface area support such as γ-Al_2O_3. These deposited particles expose convex and facetted surfaces. In contrast, Pt can be prepared in the form of an ordered mesoporous structure using liquid crystalline templates [1]. In such materials the surfaces inside the pores are concave [2]. For structure sensitive reactions the activity and/or selectivity vary with the surface structure of the active phase [3]. It is thus of interest to compare the catalytic performance of mesoporous hexagonal platinum (H_1-Pt) to that of more conventionally prepared Pt nanoparticles. An interesting reaction for such an evaluation is the important CO oxidation reaction, which is known to be self-inhibited by CO at low temperatures before ignition. Different surface structures of platinum are expected to exhibit different sensitivity towards CO poisoning.

2 Experimental

Ordered mesoporous hexagonal platinum (H_1-Pt) was prepared by mixing an aqueous solution of hydrogen hexachloroplatinate hydrate (Aldrich) and the nonionic surfactant Brij76 (Aldrich) forming a lyotropic liquid crystal. The liquid crystalline phase was spread onto a steel sheet upon which the precursor of the mesoporous platinum was reduced following the method by Attard et al. [1]. The product was washed with water, ethanol and finally acetone before drying at 90 °C for 12 h producing the H_1-Pt powder. The desired amount of H_1-Pt powder was mixed with 5.0 g alumina washcoat slurry and was subsequently ultrasonicated for 10 min. The alumina washcoat slurry was taken from a batch containing 8.0 g γ-Al_2O_3 powder (Puralox SBa 200, Sasol Germany GmbH), 2.0 g boehmite powder (Disperal S, Sasol Germany GmbH), 0.3 wt-% of the solid content polyacryl acid (Dolapix PC21), 67.5 g distilled water and 22.5 g ethanol (+99.5%, Kemetyl). The H_1-Pt/Al_2O_3 slurry thus formed was deposited, using an air brush, on a stainless steel alloy sheet substrate (shaped as circular discs with a thickness of 0.03 mm and a diameter of 7 mm) suitable for use in a high-throughput screening reactor as previously described [4,5]. The discs used for catalyst preparation had been treated with acetone and subsequently calcined in air at 1000 °C for one day prior to catalyst deposition. This ensured formation of an oxide surface enabling good adhesion for the washcoat.

For comparison a commercial poly-agglomerated polydisperse platinum powder (Pt-black) (Johnson Matthey) was treated using same procedure for preparation of a Pt-black/Al_2O_3 catalyst. A third Pt/Al_2O_3 catalyst was

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Table 1. Elemental composition of the Pt/Al_2O_3 catalysts studied as determined by SEM-EDX.

Catalyst	Washcoat (mg)	Pt / Al / O (wt-%)	Pt-loading (mg)	Pt surface area (m^2/g)
H_1-Pt	1.81	28 / 30 / 42	0.50	34.9
Pt-black	1.78	22 / 34 / 44	0.39	34.2
Wet-imp.	2.25	20 / 37 / 43	0.46	-

Table 2. Turn-over frequency (TOF) of the Pt/Al_2O_3 catalysts.

	H_1-Pt		Pt-black	
Temperature (°C)	TOF [mmole/(s m^2 Pt)]	CO conversion (%)	TOF [mmole/(s m^2 Pt)]	CO conversion (%)
140	0.155	10	0.014	0.70%
141	0.233	15	0.018	0.90%
143	0.310	20	0.030	1.50%
146	0.388	25	0.035	1.70%

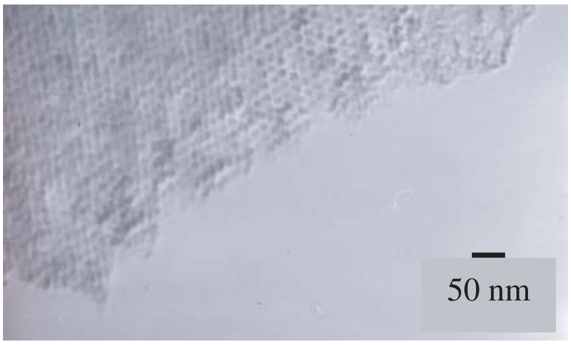

Fig. 1. TEM image of the ordered mesoporous H_1-platinum phase used in the catalytic reactor study.

prepared by wet-impregnating an Al_2O_3 washcoated substrate disc with a Pt salt solution. In this case ca. 2 mg Al_2O_3 washcoat was deposited on the disc using an air brush, after which the disc was calcined in air at 600 °C for 1 h. Then, a 0.01 M platinum nitrate water solution was used to "wet"-impregnate the washcoated substrate using a micropipette. This procedure was performed on a magnetic heater and the disc was kept at around 200 °C. In all cases used, the air brush nozzle pressure was approximately 2 bars and the temperature of the heater was set to 200 °C. All catalyst samples were finally calcined in air at 250 °C for 30 min.

The catalytic conversion of CO to CO_2 was studied within the temperature range of 50−250 °C. The total gas flow used in the reactor was 20 ml/min. and the feed was composed by 2000 vol-ppm CO and 20 vol-% O_2,balanced with argon. The temperature was linearly increased at a rate of 8 °C/min.

3 Results and discussion

Figure 1 shows a TEM micrograph of the platinum sample prepared using the liquid crystal template route. The sample exhibits a hexagonally ordered arrangement of mesopores in accordance with the H_1-Pt phase previously reported by Attard et al. [1]. The total amount of deposited washcoat and the concentration of platinum in the different catalysts prepared as determined by SEM-EDX are given in Table 1 and were used to obtain the overall platinum loading for each of the catalysts.

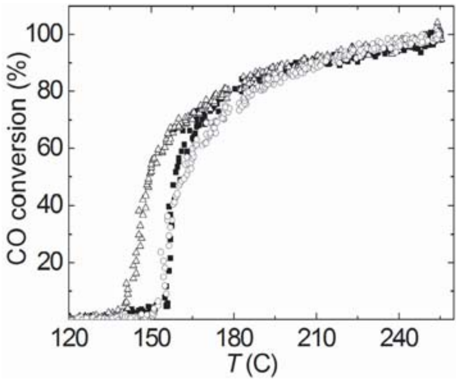

Fig. 2. The catalytic conversion of CO to CO_2 as a function of temperature comparing the H_1-Pt/Al_2O_3 (Δ) with wet-impregnated Pt/Al_2O_3 (■) and Pt-black/Al_2O_3 (○). The heating rate was 8 °C/min. The feed consisted of 20 vol-% O_2 and 2000 vol-ppm CO balanced with Ar.

The platinum loading was 45 mg Pt ±13% in the samples compared, as given in Table 1.

In Figure 2 the conversion profiles for CO oxidation to CO_2 over the three different catalysts show that ignition occurs at lowest temperature for the H_1-Pt sample.

In order to compare the catalytic activity of the samples prepared, the turn-over frequencies (TOF) expressed as conversion rates for CO oxidation normalized per Pt surface area were calculated for the H_1-Pt and Pt-black samples and the results are presented in Table 2 for the early part of the ignition profiles. Due to the different preparation route it was not possible to calculate the corresponding TOF for the wet-impregnated Pt/Al_2O_3 catalyst sample.

At low conversions the reaction rate is determined by the kinetics of the surface reaction. The reaction rate normalized with the platinum surface area shows that the CO oxidation proceeds considerably faster for the H_1-Pt sample than for the Pt-black sample during these conditions. This finding indicates that H_1-Pt is less sensitive towards CO poisoning during the ignition phase.

This work has been performed within the Competence Centre for Catalysis, which is financially supported by The Swedish Energy Agency, AB Volvo, Volvo Car Corporation, Scania CV AB, GM Powertrain Sweden AB, Haldor Topsøe A/S, Perstorp Specialty Chemicals AB, and The Swedish Space Agency. AECP thanks the Swedish Research Council for a senior researcher grant.

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