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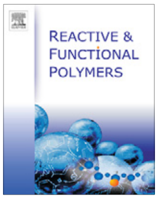

Metal catalysis with nanostructured metals supported on strongly acidic cross-linked polymer frameworks. Part I. The behaviour of M^{2+} ions (M = Ni, Pd, Pt, Cu) supported on Rohm & Haas's resin A70 and Du Pont's SAC-13, towards H_2 in the solid state and $NaBH_4$ in aqueous medium

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ABSTRACT

The macroreticular Rohm & Haas resin A70 and the DuPont silica/nafion microcomposite SAC-13 undergo facile metalation with Ni^{II}, Pd^{II}, Pt^{II}, Cu^{II} cationic species to give materials that do react with both molecular hydrogen in the "dry" state and sodium borohydride in the aqueous phase. The distribution of the reduced species in the body of the support particles is sensitive to the reduction protocol.

1. Introduction

Cross-linked functional polymers (CFPs) [1] are functional materials currently utilized as ion-exchangers [2] of strategic industrial relevance and as technologically important strongly acidic catalysts [2]. After a seminal discovery by the german technologists Wöllner and Neier in 1968 [3] strongly acidic CFPs, Ⓟ-SO_3H, started to appear promising active supports in the synthesis of M^0/Ⓟ-SO_3H catalysts for which a poly-functional character was requested. In fact, in their quite innovative new process for the synthesis of methyl isobutyl ketone from acetone and molecular hydrogen, the "function" Ⓟ-SO_3H was deputed to promote the condensation of two acetone molecules to give an intermediate functional olefin (mesityl oxide) and the "function" Pd^0 was deputed to promote its hydrogenation to give the desired ketone.

As a matter of fact, catalyst Pd^0/Ⓟ-SO_3H (Ⓟ-SO_3H = VP (OC 1038) met a great success and it is currently utilized by Deutsche Texaco (now RWE-DEA) for the synthesis of such important industrial solvent in their 10,000 ton/year facility in Cologne [4]. In 1974 Gates and associates [5] did show the ability of a catalyst Pt^0/Ⓟ-SO_3H (Ⓟ-SO_3H = Amberlyst 15 (Rohm & Haas) in the synthesis of acetone from propene and water, followed by the metal-promoted dehydrogenation of 2-propanol to give acetone. Recently Hölderich and associates [6] in 2002 (direct hydroxylation of benzene with dioxygen) and in 2007 [7] (one-pot direct synthesis of a complex potential analgesic molecule) and Baiker and associates [8] in 2008 (selective one-pot formation of 2-ethylhexanal from crotonaldehyde) did confirm the very promising prospects of these kind of bifunctional catalysts in fairly demanding organic syntheses.

We have been active in these laboratories since 1995 [9] in the synthesis of a variety of M^0/CFP catalysts, in which the organic support was by choice utilized either as a neutral macroligand or as a polyanion neutralized with Na^+. This circumstance follows our original aims that were focused on the issue of setting the quantitative bases of the evaluation of the nanostructure and molecular accessibility in given solvents, of gel-type resins bearing M^0 nanoclusters, with particular regard to their size control [10]; to this end, we decided that the acidity of the matrix might be a potential unnecessary complication.

On the contrary, we have recently decided to include in our interests also M^0/Ⓟ-SO_3H catalysts with the goal of preparing useful catalytic promoters of reactions involving both a condensation and a hydrogenation step such as e.g. of the hydrogenolysis of glycerol in water under possibly milder conditions [11,12].

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We report in this paper on our first contribution to the synthesis of new bifunctional M^0/S(F) catalysts, where M = Ni, Pd, Pt, Cu, and S(F) is the macroreticular Rohm & Haas (now Dow Chemical Company) strongly acidic, particularly thermally stable resin, named Amberlyst 70 (hereafter referred to as A70) and the DuPont silica–nafion microcomposite SAC-13. The choice of Pd and Pt rests on their well known general relevance to industrial catalysis and the choice of Ni and Cu rests on the expectation that $Ni^0/S(H^+)$ and $Cu^0/S(H^+)$ catalysts might be useful in demanding and challenging reactions such as the hydrogenolysis of glycerol [11], i.e. a process just mentioned above, that is going to become a strategic one in the emerging industrial chemistry of biodiesel. In the practical development of this project we utilized for sake of useful comparison, molecular hydrogen as reducing agent in the dry state suitable to produce M^0/Ⓟ-SO_3H catalysts [6–8] and $NaBH_4$ in water suitable to produce M^0/Ⓟ-SO_3Na ones [9].

2. Experimental

2.1. Materials and instruments

$Pd(NH_3)_4(NO_3)_2$ and $Pt(NH_3)_4Cl_2\cdot H_2O$ were commercial products of Chemicals Alpha Aesar. $NiSO_4\cdot 7H_2O$ was from Carlo Erba chemical and anhydrous $CuSO_4$ was from Aldrich, A70 is a Dow Chemicals (former Rohm & Haas) macroreticular sulfonic resin in beaded form, with an ion-exchange capacity of 2.55 meq/g (web site R&H) and a specific surface area equal to 36 m^2/g (web site R&H). SAC-13 is a DuPont silica–nafion microcomposite in the form of extrudates 5 mm long with a specific surface area equal to ca. 200 m^2/g (web site Aldrich) and exchange capacity equal to 0.15 meq/g (web site Aldrich). SAC-13 was used as received. A70 was washed inside a suitable glass column with 2 l of deionized water per 100 g of resin, filtered on a Gooch filter and finally dried at 55 °C in a ventilated oven for 24 h. Treated samples of both A70 and SAC-13 were stored under nitrogen.

A CamScan MX2500 scanning electron microscope has been used for microanalysis and X-ray Mapping, equipped with a tungsten cathode and a four quadrant solid state BSE detector, operating at 20 kV accelerating voltage, ~150 μA filament emission, ~35 mm working distance. Technical specifications on XRMA are available as supplementary material. TEM analysis was carried out with JEM 3010 (JEOL) electron microscope operating at 300 kV, point to point resolution at Scherzer defocus of 0.17 nm. Specimens for conventional transmission electron microscopy (CTEM) analysis were sonicated in iso-propanol and then transferred as a suspension to a copper grid covered with a lacey carbon film. ISEC, "Inverse Steric Exclusion Chromatography" analysis, [13] was kindly provided by Dr. Karel Jerabek, Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Suchdol–Prague. TGA analysis was carried out under nitrogen with an SDT 2960 (TA Instruments) thermobalance.

Details of the preparation of the samples to be examined with XRMA, are given below. An ordinary glass slide (24×76×1.2 mm) was used as support for each sample. One side was previously ground with silicon carbide (800 grit) to obtain a rough surface, which was subsequently cleaned with an ultrasonic bath and oven-dried.

A drop of epoxy resin (Araldite 2020, Huntsman) was placed on the surface of the slide and several beads of the sample to be examined were dipped into the fluid resin. Other four drops of epoxy resin were then placed at the corners of the slide.

The sample was left in an oven at 40 °C for 24 h to obtain a perfect hardening of the epoxy resin. After hardening, the drop enclosing the spheres was ground by means of a vertical diamond wheel (Petrothin, Buehler) in order to obtain a rough flat surface exposing the spheres cut at different height. A micrometer allows the appropriate thickness to be reached depending on the mean diameter of the spheres of each sample.

The sample was gently cleaned with ethanol and then smoothed by means of an automatized polisher (Planopol, V-Struers). The first polishing was achieved using a 6 μm size diamond suspension (Dp-suspension, Struers) on a silk cloth for 60 s at 300 RPM; after a gentle cleaning by ethanol, the final result was obtained with a 1 μm size suspension under the same conditions.

A description of the employed autoclave for the dry state reduction of metalated resins, a picture at the optical microscope of Pd^0/SAC-13 reacted with H_2 and XRMA pictures of sections of SAC-13/Pd^{II} and SAC-13/Pt^{II} reacted with H_2 are available as Supplementary material.

2.2. Metalation of A70 and of SAC-13

2.2.1. Metalation of A70 and of SAC-13 with Pd^{II} and Pt^{II} (1 wt.%)

The reaction was carried out in 40 ml water at room temperature under moderate shaking for 20 h. Typically 2.50 g of A70 were let to react with 74 mg of $Pd(NH_3)_4(NO_3)_2$ and 2.55 g of resin with 46.00 mg of $Pt(NH_3)_4Cl_2\cdot H_2O$ (to give 1% of metal). Typically 2.50 g of SAC-13 were let to react with 63.10 mg of $Pd(NH_3)_4Cl_2$ and 2.50 g of SAC-13 with 55.70 mg of $Pt(NH_3)_4Cl_2\cdot H_2O$ (to give 1% of metal). After 20 h the metalated materials were recovered upon filtration with a Gooch filter, washed with 3 × 30 ml water and dried at 55 °C under vacuum for 10 h. ICP analysis revealed a practically quantitative incorporation of the metal, i.e. more than 99 wt.%.

2.2.2. Metalation of A70 with Ni^{II} and Cu^{II} (5 wt.%)

The conditions were quite similar to those described above for Pd^{II} and Pt^{II} but we chose a theoretical metalation degree equal to 5 wt.%. Again the incorporation in 3.05 g of A70 was quantitative for 389 mg of $CuSO_4$ and the same was observed in 3.01 g of resin for 750 mg of $NiSO_4\cdot 7H_2O$.

2.3. Action of H_2 on A70/Pd^{II}, A70/ Pt^{II}, SAC-13/Pd^{II}, SAC-13/Pt^{II}, (1 wt.%)

2 g of A70/Pd^{II} or 2 g of SAC-13/Pt^{II} precursors were introduced into a 200 ml glass located into a stainless steel autoclave. After pressurization with H_2 at 40 bar for Pd^{II} and 45 bar for Pt^{II}, the autoclave was immersed into an oil bad at 100 °C for Pd^{II} and for Pt^{II} and the metalated beads were subjected to a gentle stirring by means of a 1.5 cm long Teflon-coated magnetic bar, for 4 h (Pd^{II}) and 6 h for Pt^{II}. The protocol leads to homogeneously black beads (control with the optical microscope) ready for catalytic testing. A quite similar protocol was employed for acting on Pd^{II} and Pt^{II} dispersed in SAC-13. The materials turn out to be homogeneously black in the case of palladium and homogeneously dark gray in the case of platinum. Blank experiments carried out in the absence of H_2 (replaced by N_2) revealed that the metalated resins are stable *per se* at 100 °C for at least 4 (Pd^{II}) and 6 (Pt^{II}) hours.

2.4. Action of H_2 on A70/$Ni^{II}$and on A70/Cu^{II} (5 wt.%)

2.5 g of A70/Ni^{II} and 2.5 g of A70/Cu^{II} were treated exactly as described above for Pd^{II} and Pt^{II}, but no visual evidence of reaction was gathered. A promising evidence (visual estimate) of reduction was obtained upon treating with H_2 the beads of A70/Ni^{II} and of A70/Cu^{II} precursors after pre-swelling the organic support with the least amount (1.5 g/g) of 99% formic acid.