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Preparation, characterization and deposition of Langmuir–Blodgett Co, Al organic films for the catalytic applications

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Abstract

VOC combustion is a demanding process for both reactor and catalyst design. As we have proved in recent papers the diffusional limitation of reaction rate that occur during combustion may be overcome by designing the metallic microstructures used as reactor internals. Their application on industrial scale depends on the development of an efficient method of catalyst layering on metallic supports and optimisation of a fine catalyst structure which would not change the elaborated microstructure geometry. In this study we propose the Langmuir–Blodgett (LB) film method to deposit various metals (Al, Co) in form of catalyst organic precursors. The film forming abilities of the precursors were checked by surface pressure measurements upon film compression, Brewster Angle Microscopy and by monolayers stability measurements. The amount of deposited materials was controlled by the LB parameters and verified by TG measurements. The catalyst obtained in this way were characterized at various stages of the preparation by SEM/XFS, XPS, AFM and RM methods and tested in *n*-hexane combustion. Oxidation of the Al washcoat precursor led to the formation of γ-Al_2O_3 improving the properties of the Al_2O_3 layer (α phase) developed on the precalcined CrAl carrier. Oxidation of cobalt stearate deposited on the CrAl gave dispersed Co_3O_4 spinel. The cobalt catalysts were active in combustion showing resistance to sintering, Compared to standard Pt supported catalyst they had twice as low activation energy (50 kJ/mol).

Keywords: Langmuir–Blodgett technique; Structured carrier; Wash-coat layer; Raman microscopy; XPS quantitative analysis

1. Introduction

An intrinsic problem connected with the utilization of metallic microstructural carriers used as reactor internals is finding a sufficient method of catalyst depositing on metallic surface. Not only should the deposited catalyst material (washcoat and catalyst) adhere to the surface, but also should leave an elaborate duct shape unchanged [1]. The problem lays in achieving a thin and uniform catalyst layer of a dimension comparable to a microstructure channel diameter, and preferably, of a controlled structure. Commonly used depositing methods (deposition from suspension, sol–gel) are not able to fulfil these requirements and especially to control the amount of the deposited material.

Microstructural reactor internals, recently surveyed as an efficient tool to intensify mass and heat transport during chemical processes, can also enhance catalytic combustion of volatile organic compounds (VOC) [2–4]. Indeed, the reduction of VOCs emission still poses a vital environmental problem and the existing technical solutions are still far from being optimal [5–7]. Catalytic combustion of VOCs, a promising solution among them, is in fact a demanding process for both reactor and catalyst design. The whole VOC combustion process is controlled by the mass transport and therefore its intensification can give rise to significant improvement of the converter efficiency. The problem is described more precisely in Refs. [1,2].

Two methods have been regarded as promising coating techniques: Langmuir–Blodgett deposition (abbreviated as LB) and chemisorption. Both techniques lead to the formation of ordered, uniform layer of a compound of interest on the solid surface. Chemisorption is a very easy to handle technique in comparison with the LB method, which requires a sophisticated equipment (Langmuir trough). However, the LB technique has the advantage over chemisorption, since it secures continuous control of the several physical parameters of layers transferred, such as molecular packing, lateral pressure, composition and quantity. This method thus allows modelling the surface by forming highly ordered, defectless layers of

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controlled thickness and architecture on the molecular level. The only limitation of the LB technique is that the compound to be deposited must have a proper chemical structure that enables the formation of a stable Langmuir monolayer. Typical molecules that form Langmuir films on water, having so-called "amphiphilic" or "amphiphatic" properties, should have a distinct polar group attached to an nonpolar part (usually a long hydrocarbon chain), such as *n*-octadecanoic acid (stearic acid) being the most common example. However, there have been a number of reports in the literature concerning film-forming abilities of "non-classical" compounds, such as organometallics [8] or purely hydrophobic molecules as fullerenes [9] or perfluorinated or partially fluorinated hydrocarbons [10,11].

These unique opportunities offered by the LB method have aroused our concern to apply it for catalyst material depositing on metallic surface both on flat steal sheets and on wire gauzes [1]. The method seems extremely useful at the stage of the optimisation of catalyst structure and composition. First attempts to engage the LB method in catalyst preparation to form both catalyst precursors and active catalysts were reported in 80's in Refs. [12,13] and recently in Refs. [14–17]. The latter papers report on the utilization of metal porphyrin complexes to obtain epoxidation and hydrogen evolving catalysts [14,15] and also of benzylideneacetone complexes for electroless metal plating [16,17].

In this paper our focus is on the applicability of various compounds containing Al, Co and Cu for the LB transfer onto metallic carrier surface. These compounds are regarded by us as precursors of catalytic material (washcoat and catalyst) for the combustion of volatile organic compounds.

2. Experimental

2.1. Materials

Stainless chromium–aluminium steel leaves (steel *00H20J5* — 0.3 mm thick, *Baildon*, Poland); denoted here as CrAl, were used as the deposited material carrier. The steel is similar to kanthal alloy and it contains: Cr—20.37%, Al—5.17% (and also Mn—0.25%, Ni—0.16%, Cu—0.034%, Co—0.021%). For some experiments a reference carrier made of pure Co was used (Co foil, +99.99%, 0.1 mm, *Aldrich*).

The catalyst preparation consisted of the following steps:

- Carrier pre-treatment: calcination of an initial CrAl steel samples in air at 1000 °C for 24 h.
- Material deposition: layering Al, Co and Cu compounds on precalcined samples by LB technique.
- Catalyst activation: oxidation of the deposited samples in air at 800 °C for 2 h.

All the materials used for monolayer preparation are listed in Table 1. These are various compounds of aluminium, cobalt or copper, equipped with organic molecules with different numbers of C atoms, in which metals are bound with metal–oxygen bonds. To modify surface properties of copper Cu2 sample, the solution of arachidic acid and additives of isopropanol and *n*-pentanol were used.

2.2. Monolayer preparation

The monolayers of the compounds listed in Table 1 were studied in order to check their stability on the water surface and to set up optimal transfer conditions. The monolayers of Al and Cu containing compounds were spread from the solvents (Table 1) on a single-barrier Langmuir trough (*NIMA*, Coventry, UK), equipped with a dipping device. Each time, the spreading volume from the stock solution was precisely measured with a gas-tight syringe (*Hamilton*™). After dropping the solution onto water surface, 10-min period was allowed for solvent evaporation. Then the compression was initiated with the speed of 40 cm^2/min. Bi-distilled water was used as a subphase. Exclusively for Co depositing, the monolayer of cobalt stearate was prepared in situ in a chamber of Langmuir trough from $Co(NO_3)_2$ diluted in bi-distilled water and stearic acid dissolved in chloroform. To secure cobalt stearate precipitation and to stabilize the monolayer, pH of a substrate solution was adjusted by adding an appropriate amount of HNO_3. Thus prepared solution was poured into a trough chamber. Next, a known volume of chloroform solution of stearic acid was spread on the $Co(NO_3)_2$ solution, and after chloroform evaporation (5 min), the compression began (40 cm^2/min).

The feasibility of monolayers was monitored by Brewster Angle Microscopy using a Mini Bam (*NFT*, Göttingen, Germany) and the monolayer stability measurements.

The LB transfer was possible only for Al1 and Co1 compounds which were layered onto CrAl carrier with the dipping speed of 4 mm/min. After each layer deposition a 5-min time was allowed. The number of monolayers deposited on the CrAl carrier surface is given in Table 2. The samples were then dried in air at room temperature for 24 h in a desiccator filled with silica gel and were subjected for further analysis.

Table 1
Compounds and solutions preselected for the Langmuir–Blodgett method

Symbol	Compound name	Solvent	Sollution concentration, mg/cm^3
Al1	Aluminum III 9-octadecenylacetoacetate *di*isopropoxide (90% Linegal Chemicals)	9-toluene	0.28
Al2	Aluminium III 2,2,6,6-tetramethyl-3,5-heptadionate (99% Linegal Chemicals)	Tetrahydrofurane	0.24
Co1	0.001 M $Co(NO_3)_2$ aqueous solution (99.999, Aldrich), stearic acid, SA (99+, Aldrich)	Chloroform (for SA)	0.47
Cu1	Copper II benzoylacetonate (99% Linegal Chemicals)	Toluene	0.27
Cu2-0	Copper II 2,9,16,23-tetra-*tert*-butyl-29H,31-phthalocyanine (97%, Aldrich)	Toluene	0.33
Cu2-1	As above	Toluene+arachidic acid (1 : 1)	0.37
Cu2-2	As above	As above+isopropanol (2%)	0.31