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Impact of structured catalysts in amine oxidation under mild conditions

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ABSTRACT

A structured graphene/graphite catalyst grown on a commercial austenitic stainless steel sheet providing a micromonolith was obtained by submitting the nude stainless steel structure to a carbon-rich atmosphere (first 300 mL/min of a reductive H_2/N_2 (1:1) flow, then to 180 mL/min of a CH_4/H_2 (1:5)) at high temperature (900 °C) for 2 h. The preparation procedure resulted in a homogenous surface coated with a carbon-rich film as observed by EDX and SEM images. Further characterizations by Raman spectroscopy revealed characteristic Raman lines of graphene and crystalline graphite disposed in a hierarchical organization. The disposal of the obtained surface layers was also confirmed by grazing incidence X-ray diffraction. Besides this, XRD indicated the overlapping diffraction lines of graphite, cementite and M_7C_3 carbides. The graphene nature of the outermost layer was also confirmed by XPS. The catalytic behavior of the structured graphene/graphite catalyst was evaluated in the selective oxidation of heptylamine. At 200 °C it afforded a total conversion with a combined selectivity in heptanonitrile and *N*-heptylideneheptylamine of 67% (10% heptanonitrile) that corresponds indeed to a very efficient system in the absence of any metal. Kinetic experiments with the scope to calculate the activation energies were also performed.

1. Introduction

Naturally, nitriles are present in a diverse set of plant and animal sources. However, they are difficult to be extracted from these sources and therefore the synthesis of nitriles has already a long history [1,2]. This is mainly connected to the large utilization of these compounds in various fields, either as products or as intermediates for the production of amines, amides, carboxylic acids, aldehydes, esters, heterocycles, etc. For example, there are different types of pharmaceuticals containing nitriles, especially those with antidiabetic and anticancer effects. Also, nitrile rubber is highly resistant to chemicals being used as a protective material.

Nowadays, nitriles are usually produced by ammoxidation (where a hydrocarbon is partially oxidised in the presence of ammonia) [3], hydrocyanation (from hydrogen cyanide and alkenes) [4], dehydration of amides and aldoximes [5], condensation of aldehydes [6], alcohols [7], esters [8], of carboxylic acids with NH_3 [9], etc. However, these routes show some disadvantages, like rather strong environmental issues: the harsh reaction conditions, the use of toxic agents, the generation of undesired toxic by-products, etc.

The selective oxidation may provide an alternative to these synthesis routes. The introduction of oxygen atoms in the substrate molecule is a reaction moderately exothermic with water as the sole by-product [10,11]. However, the exothermic effect should be maintained under a severe control.

Several attempts to synthesize nitriles via selective oxidation of primary amines (Reaction Eq. (1)) have been already reported. Chen et al. used trichloroisocyanuric acid (TCCA) in the presence of catalytic TEMPO [12], Reddy et al. [13] KI or I_2 in combination with TBHP, Shi et al. [14] NaClO and beta-cyclodextrin in presence of water, Veisi [15] TCCA as an oxidant and reagent in aqueous ammonia, Kim and Stahl [16] homogeneous (bpy) Cu/TEMPO for selective oxidation, Schröder and Griffith [17] potassium ruthenate ($K_2[RuO_4]$) in the presence of persulfate ion, and Bagherzade et al. [18] pentylpyridiniumtribromide in aqueous NH_4OAc. However, all these procedures have the disadvantage of stoichiometric reactions in which at least one of the reactants is consumed providing by-products that are hard to be separated.

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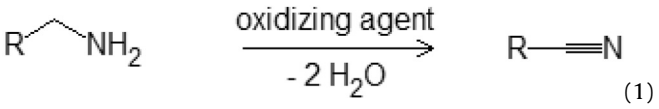
Tang et al. [19] suggested the use of ruthenium trichloride in tandem with dioxygen that offered a very high advantage due to an enhanced atom economy. However, the catalyst is not easily recyclable. To avoid this, it was proposed the replacement of homogeneous catalysts with heterogeneous ones. High catalytic activity of Ru/Al_2O_3 catalyst [20] was thus reported in the oxidation of both primary and secondary amines by molecular oxygen in liquid phase at atmospheric conditions. Cristian et al. [21] proposed the oxidation of both aliphatic and aromatic amines using a recyclable catalyst and dioxygen or air, as oxidants. The $Ru_2Cl_4(az\text{-}tpy)_2$ complex is highly effective in this reaction. Furthermore, the association of this catalyst with supported ionic liquids (SILP) enhanced the catalyst recyclability [22]. More recently, we demonstrated that such reactions can be carried out in carbocatalysts, where graphene oxide provided a very high activity and selectivity [23].



(1)

Except for the ammoxidation, all these reactions were carried out under batch conditions. Therefore, transferring it under a continuous flow reactor, will offer more advantages for the practical applications.

Based on it, the aim of this study was the investigation of the selective oxidation of primary amines under flow conditions using a structured graphene/graphite catalyst. The catalyst is generated by the in-situ growth of the graphene/graphite layer on a stainless steel micromonolith substrate, acting the unit as a microreactor. Accordingly, this study reports on the synthesis of a structured graphene/graphite catalyst that has been incorporated in a flow design, and on the results of the catalytic oxidation of heptylamine. Kinetic evaluation of these results is also considered.

2. Materials and methods

2.1. Materials

All chemicals were used as purchased, without preliminary purification: *n*-heptylamine (Merck); 1,4-dioxane (Sigma-Aldrich) as solvent for preparing heptylamine feed solutions and oxygen (99.999%, Linde).

2.2. Preparation of the structured graphene/graphite catalyst

The catalyst was grown on a commercial austenitic stainless steel sheet (AISI 304, 50 μm thick, Goodfellow). Typically these Fe-based alloys contain 18 wt% Cr, 8 wt% Ni, percentages around 1 wt% of Si and Mn as well as minor amounts of other transition metals, carbon, nitrogen and sulphur. Micromonoliths were built on these sheets following a procedure described elsewhere [24,25]. The final micromonolith is a cylinder 3 cm height, 1.7 cm diameter with 540 cm^2 of total surface area and 320 cells/cm^2. A native oxide layer 1–3 nm thick grows naturally on air-stabilized stainless steel sheets [26].

Carbon-coated micromonoliths were obtained by submitting the nude stainless steel structure to a carbon-rich atmosphere at high temperature. First the temperature was ramped to 900 °C at 15 °C/min under 300 mL/min of a reductive H_2/N_2 (1:1) flow, then, the reductive atmosphere was switched to 180 mL/min of a CH_4/H_2 (1:5) mixture and the temperature kept for 2 h. Finally, a N_2 flow replaces the reactive flow and the system is allowed to cool down to room temperature.

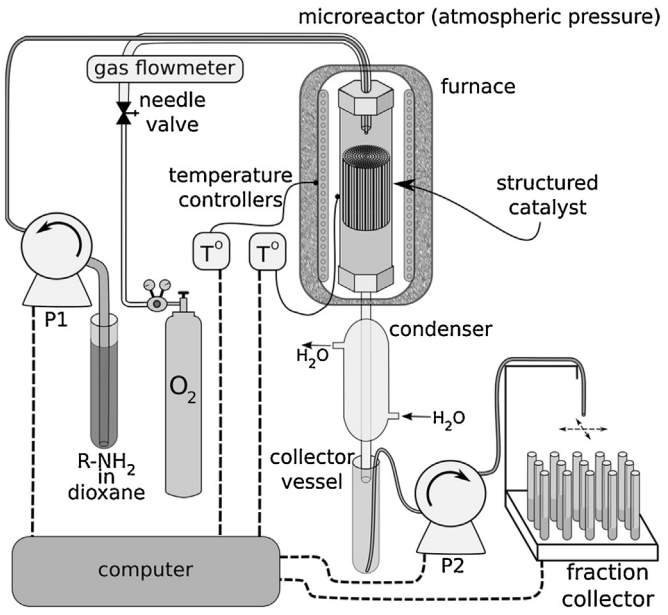


Fig. 1. Plug-flow reactor setup used to perform the catalytic tests on heptylamine oxidation (atmospheric pressure).

2.3. Plug-flow microreactor setup

The microreactor prepared as above was inserted in an *"in house"* built installation (Fig. 1). It was placed inside a ceramic resistance furnace where the temperature control was achieved with a Toho TTM-204 controller (K-type thermocouple at the middle-level of the ceramic jacket) and an Elko ELK-38 indicator (K-type thermocouple in contact with the microreactor body). Both instruments (calibrated against a high temperature glass thermometer) were computer interfaced through RS-232 to TTL level converters based on Maxim MAX-232 IC allowing bidirectional Modbus communication. The reactants were fed to the reactor through two concentric tubes: the inner one carried the solution of amine in dioxane and the oxygen gas flow through the outer thicker tube. The flow control was performed for the liquid phase by the pump P1 (Knauer K-501 HPLC pump, computer controlled by RS-232 serial interface) and for the gas phase by an ensemble of a micrometer-knob needle valve (HokeMilli-Mite) and a capillary gas flowmeter. The gas flow rate was checked before each experiment with a gas burette connected to the microreactor outlet. A condenser was attached by soldering directly on the distal microreactor tube. The liquid output from the reactor was collected into an open glass vessel. Samples were extracted every 10 min by fully depleting the content of the collector vessel with the peristaltic pump P2 (Heidolph PD 5001, computer controlled through a parallel port relay interface) and dispensed in individual glass tubes (covered with small funnels to reduce evaporation) by the help of a fraction collector (Teledyne ISCO Foxy Jr, computer connected by RS-232 serial link). The operational parameters of the installation (temperature, liquid flow rate, collection of samples) were controlled by a code developed in C-programming language running on GNU/Linux operating system (32-bit CentOS 6).

The structured catalyst was wrapped in Al foil and fitted at the middle of the microreactor body. All the inner surface of the microreactor (including the exposed metallic surface of the feeding tube) was covered with the Al foil so that the reagent mixture does not enter in contact with other heated metallic surface. The choice of Al over Pyrex glass was made from preliminary blank tests: Al is more effective than glass to avoid gas-phase free radicals [27] that