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Identification of by-products issued from the catalytic oxidation of toluene by chemical and biological methods

Identification de sous-produits de l'oxydation catalytique du toluène par des méthodes chimiques et biologiques

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ABSTRACT

Benzene, toluene, ethylbenzene and xylenes (BTEX) are substances that are very commonly encountered in almost all sectors of the industry. Consequently, these molecules may be present in large amounts in industrial exhausts loaded with VOCs. An effective method for their elimination is catalytic oxidation, which is an economic and ecologic alternative to thermal oxidation. The aim of this work is to reveal the by-products issued from the total oxidation of toluene by palladium-based catalysts. The identification of these by-products was done using a chemical and toxicological approach. A toxicological validation of the developed catalysts was performed by coupling the catalytic system with an air–liquid interface (aLI) system, called Vitrocell®, to expose lung cells to catalytic exhausts.

Mots clés :
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RÉSUMÉ

Le benzène, le toluène, l'éthylbenzène et les xylènes (BTEX) sont des molécules très couramment rencontrées dans l'industrie, et ceci dans tous les secteurs d'activité. Ces molécules peuvent donc être présentes en quantités importantes dans les effluents industriels chargés en COV. Une méthode efficace pour l'élimination de ces COV est l'oxydation catalytique, qui est une alternative économique et écologique à l'oxydation thermique. L'objectif de ce travail est d'identifier les sous-produits issus de l'oxydation totale du toluène par des catalyseurs à base de palladium. L'identification de ces sous-produits a été faite en utilisant une approche chimique et toxicologique. Une validation toxicologique des catalyseurs développés a été réalisée en couplant le système catalytique à un système d'interface air–liquide (ALI), appelé Vitrocell®, afin d'exposer des cellules pulmonaires aux gaz issus du traitement catalytique.

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1. Introduction

Volatile organic compounds (VOCs) are known as one of the major contributors to atmospheric pollution. Their anthropic releases are particularly important and have some consequences in health, environment, and construction materials.

An important part of these VOCs are single-aromatic molecules, which are principally represented by the BTEX class (benzene, toluene, ethylbenzene and xylenes). Indeed, these compounds are widely used in all industrial sectors: fuel additives, solvents (paints, varnishes, lacquers, inks, adhesives and glues), cleaning or extracting agents, synthesis precursors (production of explosives, pesticides, drugs and polymers). In addition to their highly inflammable and explosive character, BTEX compounds are highly volatile and have a high mobility in air, soil and water. Being very irritating and highly toxic (disorders of the digestive, respiratory, nervous and neurological systems), they can quickly contaminate and poison an ecosystem.

Therefore, it is necessary to set up techniques for reducing BTEX emissions. Nowadays, catalytic oxidation represents an economical and environmental alternative to the thermal oxidation, the latter being the most common in the industry. Indeed, the use of catalysts allows a drastic reduction of the process temperature (200–500 °C), which prevents the formation of toxic by-products (NO_x, dioxins) and reduces the energetic cost of the process.

In order to treat gaseous effluents loaded in BTEX from industry, the catalytic total oxidation of toluene was here studied using several Pd-based materials. These materials have been selected by taking into account their cost, activity, stability (thermal, mechanical and chemical), and it can be easy to produce this material at a large scale. Concerning supports, titanium oxide and HY Faujasite show interesting performances in the catalytic oxidation reactions of BTEX [1–4]. Then, cerium oxide is known for the treatment of automobile exhausts, but this material also shows good performances as a support for BTEX oxidation [5,6]. Finally, aluminium oxides were the most common support in catalytic process, especially α-Al_2O_3 and γ-Al_2O_3. They present some interesting properties, like a high thermal stability for α-Al_2O_3 or a high specific surface area with acidic properties for γ-Al_2O_3, and also present good performances as a support for BTEX oxidation [7–10]. Palladium was chosen as the active phase seeing that it is the most suitable noble metal in an oxidizing environment. In fact, palladium is more resistant than platinum to sintering, vaporizing metal species and poisoning [11–13]. These properties can be partly explained by the reversible transition between the two phases of palladium, $Pd^0/Pd^{II}O$, which has been demonstrated by Cordi et al. [11]. Moreover, palladium and platinum show very close performances for VOCs catalytic oxidation [14,15]. Therefore, palladium is a good compromise between performance and cost. Thus, palladium was impregnated to 0.5 wt% on α-Al_2O_3, TiO_2, HY Faujasite and CeO_2. A commercial catalyst (0.5 wt% Pd/γ-Al_2O_3) was selected as a reference.

As all destructive techniques for treating VOCs emissions (thermal oxidation, plasma, biological treatment...), catalytic oxidation can generate some by-products that are intermediate compounds more difficult to oxidize than the substrate and can be potentially released into the atmosphere. Some studies have demonstrated the formation of its intermediaries, particularly for oxygenates [16–18] and aromatics [19–21] compounds. Some of these compounds are known to interact with cell macromolecules, like DNA. They can therefore exert their toxicity, and induce some pathologies [22]. Recent concern has centred on the effects of continuous exposure to low concentrations of VOCs, like toluene and benzene, both occupationally and environmentally. Some of them have for a long time been recognised as carcinogenic for humans. For example, benzene, the major by-product produced by toluene catalytic degradation, is known to induce acute myeloid leukaemia (AML). In a previous work, we showed that A549 cells were a good cell model for the determination of benzene and toluene effects on human lung cells. Mutation hotspots in the tumour suppressor gene *TP53*, which are the most common genetic alterations involved in human cancer, were the same in AML and in A549 *in vitro* exposed to benzene [23]. Consequently, several questions can be asked. Are all by-products removed when the conversion of the initial VOC is total? If not, is it possible to find a compromise between efficiency and economic viability? Finally, can they have toxicological or ecotoxicological impacts? So, an important part of this work concerns the oxidation of toluene, specially the identification of toluene by-products. In a first time, light-off curves were determined by microGC analysis, which are suitable for fast and sensitive analyses. A coupling with a quadrupole mass spectrum allowed for a more complete identification of by-products. In a second time, coupling the catalytic process with a cell exposure system permitted us to study the impact of the by-products on human lung cells by measuring the gene expression of xenobiotic metabolizing enzymes (XMEs) involved in the biotransformation of the organic compounds. Coupling an air–liquid interface (ALI) system, called Vitrocell®, to a catalyst test was performed for the first time during this study.

2. Materials and method

2.1. Preparation of supports

The ceria support was prepared by a precipitation way. A solution of $Ce(NO_3)_3{\cdot}6H_2O$ was added dropwise to a NaOH solution with a molar ratio of 5 under stirring during 3 h. The suspension was left under agitation during 2 h at ambient temperature. Then, the suspension was filtered and washed 6 times with 200 mL of hot deionized water (~ 60 °C). The solid was dried 24 h at 100 °C and calcined for 4 h at 500 °C (heating at 1 °C/min) under an air flow (2 L/h).

The titania support was prepared by a sol–gel way. A 15-wt% cetyltrimethylammonium bromide (CTMABr) micellar solution was added dropwise to a solution of sulfuric acid (pH = 2) under magnetic agitation during 3 h at 40 °C. Then, a solution of titanium (IV) tetraethoxide