ARTICLE IN PRESS

C. R. Chimie xxx (2017) 1–12

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

ELSEVIER

Full paper/Mémoire

Influence of the formulation of catalysts deposited on cordierite monoliths for acetic acid oxidation

Influence de la composition des catalyseurs déposés sur des monolithes en cordiérite pour l'oxydation de l'acide acétique

Henri-Joël Sedjame [a], Rachid Brahmi [b], Gwendoline Lafaye [a], Jacques Barbier Jr. [a], Céline Fontaine [a, *]

[a] *Université de Poitiers, CNRS UMR 7285 IC2MP, 4, rue Michel-Brunet, 86073 Poitiers cedex, France*
[b] *UCD, Laboratoire de catalyse et de corrosion des matériaux, Faculté des sciences, 24000 El Jadida, Morocco*

ARTICLE INFO

Article history:
Received 8 March 2017
Accepted 24 August 2017
Available online xxxx

Keywords:
Heterogeneous catalysis
Acetic acid
Catalytic oxidation
Monoliths
Platinum
Basicity
Redox chemistry

ABSTRACT

Monolithic catalysts are prepared by washcoating cordierite monoliths with different sols (Pt/Al_2O_3, Pt/CeO_2, Pt/ZrO_2, $Pt/Al_2O_3–CeO_2$, $Pt/Al_2O_3–ZrO_2$, and $Pt/CeO_2–ZrO_2$). These sols are prepared by a sol–gel process and characterized by specific surface area (S_{BET}), inductively coupled plasma, hydrogen chemisorption, high-resolution transmission electron microscopy, field emission scanning electron microscopy, oxygen storage capacity, X-ray diffraction, temperature-programmed reduction, CO_2 chemisorption, and the model reaction of 3,3-dimethylbutene isomerization. The catalytic performances of the monolithic catalysts are then evaluated for the acetic acid oxidation. The nature of catalyst coating has been found to influence the adherence with the cordierite monolith and the presence of cerium in the catalyst appears to increase the adherence of the latter. Pt/CeO_2, $Pt/Al_2O_3–CeO_2$, and $Pt/CeO_2–ZrO_2$ are found to be the most reducible catalysts (oxygen storage capacity and temperature-programmed reduction) and to have the lowest acidities (3,3-dimethylbutene isomerization). CO_2 chemisorption shows that these catalysts possess a good basicity. From the relation established between the catalytic activity and the redox and acid–base properties it has been concluded that the reducibility is the key factor for a good catalytic activity although the basicity has a significant influence on the catalytic performance.

RÉSUMÉ

Mots clés:
Catalyse hétérogène
Acide acétique
Oxydation catalytique
Monolithes

L'oxydation catalytique de l'acide acétique a été étudiée sur des catalyseurs monolithiques enduits de divers matériaux à base de platine. Les matériaux utilisés sont Pt/Al_2O_3, Pt/CeO_2, Pt/ZrO_2, $Pt/Al_2O_3–CeO_2$, $Pt/Al_2O_3–ZrO_2$ et $Pt/CeO_2–ZrO_2$. Les solutions d'enduction ont été préparées par la méthode sol–gel et les matériaux ont, dans un premier temps, été caractérisés par mesure de surface spécifique (S_{BET}), analyse

---

* Corresponding author.
E-mail address: celine.fontaine@univ-poitiers.fr (C. Fontaine).

http://dx.doi.org/10.1016/j.crci.2017.08.004

Please cite this article in press as: H.-J. Sedjame, et al., Influence of the formulation of catalysts deposited on cordierite monoliths for acetic acid oxidation, Comptes Rendus Chimie (2017), http://dx.doi.org/10.1016/j.crci.2017.08.004

Platine
Basicité
Oxydo-réduction

élémentaire (ICP), chimisorptions d'hydrogène et de CO_2, microscopie (HRTEM et FESEM), mesure des capacités de stockage de l'oxygène (OSC), diffraction des rayons X (XRD), réduction en température programmée (TPR) et la réaction modèle d'isomérisation du 3,3-diméthylbutène. Les performances catalytiques des solides ont ensuite été évaluées pour la réaction d'oxydation de l'acide acétique. Il semble que la nature de la solution d'enduction influence l'adhérence aux parois du monolithe. Ainsi la cérine apparait comme le support qui adhère le mieux au monolithe et la zircone celui qui adhère la moins bien. Les caractérisations semblent montrer que Pt/CeO_2, $Pt/Al_2O_3-CeO_2$ et Pt/CeO_2-ZrO_2 sont les matériaux les plus réductibles (OSC et TPR), ainsi que la plus faible acidité (isomérisation du 3,3-diméthylbutène). La chimisorption de CO_2 indique que ces solides présentent une basicité intéressante. À partir de la relation entre l'activité catalytique et les propriétés redox et acido-basiques, il semble que la réductibilité des matériaux soit le paramètre clé afin d'obtenir une bonne activité catalytique, bien que la basicité ait également une influence significative sur les performances des matériaux.

1. Introduction

Volatile organic compounds (VOCs) are defined as any organic compound whose vapor pressure is at least 10 Pa at 20 °C or having a corresponding volatility under the particular conditions of use. Emissions of these compounds from natural-gas-fed engines, wastewater treatment plants, food processing plants, landfills, composting of different solid wastes, and animal feeding operations [1–5] are known to be a problem because many of these compounds are malodorous and dangerous for human health and nature [6–10]. It is the case of some organic acids such as formic and acetic acids, which are known to be important constituents of the “natural” atmosphere both in gas phase and hydrometeors [11,12]. These acids play a major role in the rainwater acidity observed in some parts of the world [11,13].

To reduce these emissions several techniques have been developed such as incineration, irradiation, biotreatment, adsorption, absorption, condensation, and membrane techniques [14]. Among these techniques, catalytic oxidation appears to be the most effective for the removal of low concentrations of VOCs [15]. In fact, catalytic oxidation decreases the oxidation temperature compared to thermal methods. The energy consumed is thus lowered.

Organic acids are also obtained as byproducts for VOC oxidation [16]. Ali et al. have shown that among several organic acids, acetic acid is the most difficult to oxidize [2]. In fact, this refractory aspect to oxidize acetic acid is widely mentioned in the literature even if most of the studies deal with its degradation in water [16,17]. Oliviero et al. [16] have noted that acetic acid obtained as a byproduct in phenol catalytic wet air oxidation is one of the most refractory molecules. Acetic acid oxidation is, therefore, regarded as a rate-determining step in the oxidation reaction of various organic compounds. However, the elimination of acetic acid in the gas phase is only barely studied, even if its volatility is relatively high (saturation vapor pressure = 1.5 kPa at 20 °C). As a consequence, only a few studies can be found in the literature [2]. To our knowledge, only Ali et al. reported a catalytic oxidation of acetic acid over copper supported on alumina catalysts. On the contrary, numerous catalytic systems such as zeolites [18–21], mixed oxide catalysts [22–26], or noble metacatalysts [27–32] are proposed to be efficient for the removal of other VOC classes. In gas phase catalytic reactions, these catalysts are often used in a powder form in a fixed bed reactor for laboratory research. Therefore, for almost all industrial applications, the catalysts used are structural shaped materials. Different forms of carriers have been studied such as monoliths, foams, pellets, and spheres [33–39].

Among the shaped carriers developed and used as catacomb monoliths are the most successful because of their advantages compared to extrudates or pellets (used in packed bed reactor) [14,40]. In fact, monoliths are unibody structures composed of interconnected repeating cells or channels, which lead to a large open frontal area resulting in very little resistance to flow and hence low pressure drop. Moreover, monolithic supports allow a better thermal shock, attrition resistance, uniform flow distribution and mass/heat transfer conditions, and shorter diffusion length [14,40]. Although in the past catalytic converters are commonly used in the vehicle exhausts systems, nowadays the monolith is the favorite support for almost all environmental applications where high flow rates and low pressure are required. This is why it seems to be very interesting to study monolithic-shaped catalysts in our experimental conditions to compare the results with the powder catalysts. Because the cordierite monolith possesses a low surface area (0.5–0.7 $m^2\ g^{-1}$), another catalytically active and high-surface area material is applied on the monolith walls by a washcoating procedure [39,41,42]. Although a few years ago γ alumina was practically the only support used for the washcoating of monoliths, today several sol–gel procedures that allow the deposition of other supports, which present interesting properties for oxidation (acid–base, redox, high oxygen storage, mobility, and so forth), are being developed.

This article is focused on the catalytic oxidation of acetic acid using monolithic catalysts. The cordierite monoliths have been coated with different platinum-supported

Please cite this article in press as: H.-J. Sedjame, et al., Influence of the formulation of catalysts deposited on cordierite monoliths for acetic acid oxidation, Comptes Rendus Chimie (2017), http://dx.doi.org/10.1016/j.crci.2017.08.004