



Structural changes of nano-Pt particles during thermal ageing: Support-induced effect and related impact on the catalytic performances

J.P. Dacquin^a, M. Cabié^b, C.R. Henry^b, C. Lancelot^a, C. Dujardin^a, S.R. Raouf^c, P. Granger^{a,*}

^a Unité de Catalyse et de Chimie du Solide UMR 8181, Université de Lille1, Bâtiment C3, 59655 Villeneuve d'Ascq, France

^b Centre Interdisciplinaire de Nanoscience de Marseille, CNRS UPR 3118, Associated to Aix-Marseille Université, Campus Luminy, 13288 Marseille, France

^c Khartoum University, College of Engineering, Chemical Engineering Department, P. Box 321, Khartoum, Sudan

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ABSTRACT

The simultaneous reduction of NO and N₂O has been investigated on Pt-based catalysts supported on γ -Al₂O₃ and perovskite materials (LaFeO₃). Particular attention has been paid to the catalyst resistance to thermal sintering processes occurring under reaction conditions at elevated temperature in the presence of oxygen and water. Bulk and surface modifications have been examined using appropriate physicochemical techniques (H₂-TPR, XPS, and HRTEM) and have been tentatively correlated to the catalytic performances in terms of activity and selectivity. It has been found that a significant particle growth occurs on 4 wt.% Pt/ γ -Al₂O₃ having a strong detrimental effect on the conversion of N₂O at high temperature. On the other hand, 4 wt.% Pt/LaFeO₃ exhibits a higher resistance to thermal sintering. Such a behaviour has been explained by the occurrence of strong metal/support interactions highlighted by high resolution TEM observations. The formation of epitaxially oriented Pt particles on the LaFeO₃ crystal lattice during thermal activation, still observable after thermal ageing would partly explain the best resistance of 4 wt.% Pt/LaFeO₃ to deactivation towards the conversion of N₂O at high temperature. Hence, supported catalysts on LaFeO₃ with lower Pt loading were prepared. It has been finally found a striking enhancement of the catalytic performances, opening a new practical interest for minimising the noble metal loading.

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1. Introduction

Noble metal-modified perovskites have been recently developed for post-combustion applications particularly under three-way conditions [1]. In those typical cycling conditions, involving alternative reductive and oxidative atmospheres, reversible changes may occur at least at the surface with a partial reduction of LaBO₃ (with B = Fe, Co) into La₂O₃ and BO_x followed by the restoration of the structural properties of the perovskite [1–3]. The most important issue was presumably related to the consequences of those structural changes on the chemical environment and the oxidation state of noble metals. It was pointed out that noble metal cations, localised in B sites of the perovskite structure, might go out and segregate into metallic nanoparticles under rich conditions, whereas reverse oxidation/re-dispersion processes with partial inclusion of oxidic Pd species into the bulk perovskite would preferentially occur under lean atmosphere. Those transformations have been essentially characterised on Pd/LaCoO₃ and Pd/LaFeO₃-Co_{1-x}O₃ [1–6] with the stabilization of oxidic palladium species in unusual oxidation states. It was found that those modifications

are activated at the surface at mild temperature ($T = 300^\circ\text{C}$) and induce significant improvements on the catalytic performances (particularly the durability in three-way conditions) [1] because the particle growth of noble metals is inhibited under such conditions contrarily to usual observations on conventional alumina supports. As previously explained, the importance of those phenomena is mostly governed by the sensibility of perovskites under reductive atmosphere and, also, the sensibility of noble metals to oxidation under lean conditions. Recently, it was found that both aspects determine the extent of re-dispersion of Pd impregnated on LaCoO₃. Pre-activation thermal treatments under successive reductive and oxidative atmospheres lead to significant re-dispersion of oxidic Pd species during the reconstruction of the perovskite structure [5–7]. Recently, similar tendencies have been reported on Pt/CeO₂ [8] with the formation of surface nanocomposite oxide that involves the formation of a Pt–O–Ce bond, which stabilises Pt against sintering and redisperses agglomerated Pt particles under oxidative conditions. Herein, we have examined the behaviour of Pt supported on LaFeO₃ in terms of catalytic performances and resistance to particle sintering under reaction conditions. It will be found that the catalytic performance in the reduction of NO and N₂O by hydrogen strongly depend on the pre-activation thermal treatment, which might originate different

* Corresponding author. Fax: +33 320 436 561.

E-mail address: pascal.granger@univ-lille1.fr (P. Granger).