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Electrochemical promotion of platinum impregnated catalyst for the selective catalytic reduction of NO by propene in presence of oxygen

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Abstract

The effect of electrochemical promotion for the selective catalytic reduction of NO by propene was investigated, for the first time, on a Pt impregnated catalyst film directly deposited onto a $Na–\beta''-Al_2O_3$ solid electrolyte. The effect of sodium promoters on the activity and N_2 selectivity was evaluated at 240 °C under different oxygen concentrations (0.5, 1 and 5%). The presence of promoters still enhanced the selectivity to N_2, even under large excess of oxygen (5%), where the N_2 reaction rate was increased by a factor of 1.8. Nevertheless, the promotional effect of sodium on the overall catalytic activity for NO removal was progressively lowered with increasing oxygen concentrations, as a result of a strong inhibition of propene adsorption and a relative increase of the oxygen coverage. Characterization by cyclic voltammetry supported these results, providing useful information about the chemisorption of reactant species under the different reaction conditions.
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1. Introduction

The combustion of fossil fuels unavoidably leads to the formation of nitrogen oxides (NO_x) which, if released to the atmosphere, can lead to acid rain, detrimental interactions with ozone and the harmful impact of NO_x on the respiratory system of human beings. While three-way catalysts have been optimized to reduce NO_x emissions in rich-burn exhaust as from consumer automobiles, these catalysts are ineffective under lean-burn conditions, as usually observed with stationary sources or diesel engines. Recently, the selective catalytic reduction (SCR) of NO_x with injected hydrocarbon, is believed to be a possible way to solve this problem, and has been extensively studied [1–4]. Among many investigated catalysts formulations for SCR, supported platinum-based catalysts have shown an excellent catalytic performance, especially using propene as the reductant. This catalytic system presents high de-NO_x activities in the low temperature range (200–350 °C), significant resistance to poisons contained in car-exhaust, and high thermal stability. The main drawbacks of Pt-based catalysts are the narrow operation temperature window for an effective NO_x removal, as well as the low-selectivity to N_2 producing large amounts of N_2O. Considerable effort has recently been expended on enhancing the catalytic properties of Pt-group metals by additives (promoters) in order to overcome these limitations [5]. The phenomenon of electrochemical promotion (EP) [6,7] provides an alternative approach to the improvement of catalyst performance, because it allows in situ control of the promoter concentration at the surface of a working metal catalyst [8]. This new phenomenon, discovered and developed by Vayenas et al. [9,10], occurs when catalytic reactions take place on a variety of metal films in contact with a solid electrolyte, where the latter acts as a source of electrochemically controlled promoter species that directly modify the behaviour of the catalyst film (working electrode). Several authors have used EP to investigate the efficacy of promoters for the nitric oxide reduction by propene in presence of oxygen using Pt [11,12], Rh [13–17] and Rh–Ag [18] as active phases, deposited on different solid electrolytes such as YSZ, $Na–\beta''-Al_2O_3$ and NASICON. In these studies, the catalyst films were prepared using two typical methods: application of thin coatings of metal pastes and sputtering. The

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first one is a very simple method to form a thin layer onto a solid electrolyte but the compositions of these commercial pastes are usually unknown. Furthermore, this procedure needs very high temperatures of calcination (above 800 °C), for the decomposition of the paste, which produces very high metal particle sizes and thus very low metal dispersion (typically less than 10^{-4}) [10,19]. The sputtering technique presents many unique characteristics as compared to the first one. For example, it provides a very simple control of thickness of the deposit film, the surface cleaning by reverse sputtering, and the good adhesion to the support. But the main advantage of this technique is that it leads to a high dispersion of the catalyst-working electrode, comparable to supported commercial catalyst, which is one of the major goals for the practical utilization of EP. Hence, one of the most important advances for the practical application of NEMCA effect has been the development of a novel electrochemically promoted reactor [20,21] using Rh/YSZ/Pt sputtered plates with high metal dispersions (13–51%). On the other hand, this physical deposition technique requires very costly equipments and cannot be used for deposition of thin catalysts films into channels of typical industrial supports such as monolithic ones or diesel particulate filters ones. The use of typical monolith or particulate filters is still questionable, although conceptually very favourable, since it allows treating high flow rates with high catalytic performance, and leads to a cell configuration easily adaptable to the existing catalytic devices. One could envisage the elaboration of monolith or diesel particulate filter (DPF) from electrolyte materials. However, suitable deposition techniques have to be developed in order to achieve thin catalyst films with high active area inside the monolith or DPF channels. The deposition in the vicinity of channels is not possible by PVD, and film preparation from metallic paste generates very low dispersion. Thus, from a practical point of view, it is interesting to develop other methods to form porous active films that can be electrochemically promoted. Marwood and Vayenas [22] reported that Pt, prepared by a wet impregnation on a porous Au film, can be electrochemically promoted for C_2H_4 oxidation. On the other hand, Fóti et al. [17,23–27] promoted electrochemically working electrodes directly deposited onto solid electrolytes, prepared by wet impregnation of suitable precursors ($RuCl_3$, H_2IrCl_6 and $RhCl_3$). This method led to a porous catalyst film by a simple procedure which does not need high temperatures for the thermal decomposition of the precursor and allows to easily controlling the metal loading of the electrochemical catalysts. Furthermore, porous catalytic films can also be deposited onto tubes or channels [17,23,25]. Therefore, some of these advantages make this method a suitable technique for the practical application of the NEMCA effect.

The aim of this work is to demonstrate that a Pt film, directly deposit onto a Na–β″-Al_2O_3 disc by thermal decomposition of H_2PtCl_6 solution, can be electrochemically promoted for the NO reduction by C_3H_6 in presence of oxygen. This simple procedure to prepare porous catalyst-working electrodes, has not been reported before for Pt, and could be an approach for the future practical application of the NEMCA effect for the abatement of NO_x. The wet impregnation method could generate electrochemical catalysts with high metallic dispersion which could be effective at very low temperature (240 °C), compatible with the treatment of real diesel exhaust (200–350 °C). This temperature range would also preserve the lifetime of the cell, because the evaporation of the Na^+ ions promoters is almost negligible in this temperature window.

Potentiostatic catalytic behaviours of the cell were investigated under different oxygen concentrations at 240 °C. The observed behaviour is discussed on the basis of the reaction mechanism and the effect of sodium addition on the binding strength of chemisorbed reactant species. Furthermore, cyclic voltammetry was performed in a wide potential range, varying the composition of the gas mixture, in order to investigate the chemisorption properties of the Pt catalyst-working electrode under reaction conditions.

2. Experimental

2.1. Apparatus

The experimental setup (schematically illustrated in Fig. 1) consisted of a feeding unit, a reactor and an analytical system. The reaction gases were Praxair certified standards of 4% C_3H_6/He, 4% NO/He, O_2 (99.99% purity) and He (99.999% purity), which was used as the vector gas. The gas flow was controlled by a set of calibrated mass flowmeters (Brooks 5850 E and 5850 S). The feed composition was as follows: 2000 ppm NO, 2000 ppm C_3H_6, 0.5–5% O_2 and the balance He. The flow rate was 10 L/h. The products were analyzed simultaneously, using a micro gas-chromatograph (Varian CP-4900), and a chemiluminescence analyzer (Teledyne 9110 EH). Nitrogen and carbon mass balance always closed to within 3%.

The catalytic experiments were carried out in a tubular solid electrolyte cell reactor, as shown in Fig. 2. The cell reactor was made of a pyrex glass tube with appropriate feed-through and was operated at atmospheric pressure. The electrochemical cell was placed on a fritted glass with 21 mm of diameter, with the counter (C) and reference (R) electrode facing the fritted glass. An inner glass tube was pressed onto the Pt working electrode (W) to insure the electrical contacts. All the current collectors were made from gold. Note that in such a single-compartment reactor, the gold reference electrode is exposed to a varying gas composition. Hence, it must be regarded as a pseudoreference electrode. The temperature of the catalyst was measured with a K-type thermocouple (Thermocoax) placed inside the inner glass tube. The entire reactor was placed in a furnace (JH HEE.CC4) equipped with a heat control system (Conatec 4801).

Constant voltages across the cell were imposed using a potentiostat–galvanostat Voltalab 21 (Radiometer Analytical). All analyzers outputs, as well as the potentiostat–galvanostat outputs (I and V_{WR}) were continuously monitored and recorded.

The electrochemical experiments were carried out under potentiostatic mode by following the effect of the applied potential (V_{WR}) on the reactions rates. Initially, before the

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