

The effect of potassium on the Ir/C₃H₆ + NO + O₂ catalytic system

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Abstract

The C₃H₆ + NO + O₂ reaction has been studied in a wide range of temperatures (ca. 250–400 °C) and oxygen concentrations (0–5% O₂) over potassium-modified Ir surfaces. The *in situ* electrochemical controlled concept of catalysts promotion was used by interfacing a polycrystalline Ir thin film with a potassium β''-Al₂O₃ solid electrolyte disc, a K⁺ conductor. At low oxygen concentrations (i.e., at reducing conditions), the effect of potassium on the Ir activity and selectivity is negligible. However, at higher oxygen concentrations (oxidizing conditions), strong K-induced poisoning on both propene and NO turnover consumption rates, as high as ~85% and ~65%, respectively, were recorded. Significant reduction on the system selectivity towards N₂ was also recorded under these conditions (from 100% over K-free Ir surface to ~70% on K-modified Ir surfaces). The performance of Ir under alkali promotion is dramatically different to that reported in the literature for Pt or Pd under similar conditions, where strong promotional effects have been found. This very different behaviour may be understood in terms of the electronic influence of co-adsorbed potassium on the adsorption strengths of the neighbor reactants on the Ir surface.

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1. Introduction

Pollution control of NO_x, CO and hydrocarbons mainly produced by vehicles, but also by stationary sources, is the central environmental object. Although, three-way catalytic converters (TWCs) have been highly successful in controlling conventional engines' emissions that operate close to stoichiometric conditions, they are no longer efficient in controlling NO_x emissions from lean-burn or diesel engines [1], which operate at net-oxidising conditions and are therefore related to excess oxidant concentrations in their exhaust gases (typically 350–1200 ppm NO, 2–12% O₂ [1]). The latter engines may be considered more promising compared to stoichiometric gasoline engines since they are related to significant lower fuel consumption. For NO_x abatement in the presence of excess O₂, the selective catalytic reduction (SCR) of NO_x by NH₃ over V₂O₅–WO₃–TiO₂ catalytic systems is a well-implemented

technology for stationary sources. Overcoming the problems related to mobile sources, the NH₃-SCR technology is currently commercially available for trucks in the EU and for cars close to commercialization in the US. Another, convenient for mobile source, alternative technology for NO_x abatement under excess oxygen that has recently gathered significant research efforts is the SCR of NO_x with hydrocarbons [1,2]. A variety of catalyst formulations have been tested for this process, including primarily ion-exchanged zeolites based catalysts [2,3] and Pt-group metal supported catalysts [4–23].

Recent studies have shown that electropositive promotion, by alkalis or alkaline earths, induces significant enhancements in both activity and selectivity of Pt-group metals for the NO reduction by propene [10–18] or CO [17–20] in the absence [10–15] or in the presence of oxygen at lean-burn [16] or simulated stoichiometric TWC [17–20] conditions. Among the three noble metals Pt, Pd and Rh, studied up to now under electropositive promotion, the promotion was found to be more effective over Pt (up to two orders of magnitudes increases in NO reduction rate, accompanied by up to ~30–50 percentage points improvements in N₂-selectivity) [12–14,16,17], followed by Pd (up to one order of magnitude increases in NO

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reduction rate, accompanied by up to ~20–30 percentage points improvements in N_2 -selectivity) [11,18], while on Rh, promotion was less effective and appeared only in the absence of oxygen (in the presence of oxygen, electropositive promoters were found to poison the NO reduction efficiency of Rh) [18]. Besides NO reduction by propene or CO, the oxidation of CO and hydrocarbons were also found to be significantly promoted over electropositive-modified Pt, Pd and Rh noble metals [16–18,21–23].

Iridium is an element of the noble metals family, which is currently under high research interest for the SCR of NOx [24–33]. Since now, there are only few preliminary studies concerning the influence of electropositive or electronegative promoters on its de-NOx chemistry: Vernoux et al. [32] have used the electrochemical promotion concept (or NEMCA effect, proposed by Vayenas et al. [34]) to show that the Ir-catalysed propene-SCR of NO under stoichiometric (2000 ppm C_3H_6 , 2000 ppm NO, 1 vol.% O_2) and excess oxygen (2000 ppm C_3H_6 , 2000 ppm NO, 5 vol.% O_2) conditions is subjected to moderate promotional effects with electronegative O^{2-} species, supplied to Ir catalyst via an YSZ solid electrolyte interfaced with it. Wögerbauer et al. [33] studied the lean NOx reduction at a specific simulated exhaust gas mixture (300 ppm NO, 1800 ppm C_3H_6 , 450 ppm CO, 8 vol.% O_2 , 10 vol.% H_2O , 10.7 vol.% CO_2) over electropositively modified by sodium Ir-black catalysts. However, since now, there are not any reports concerning the effect of electropositive promoters (alkalis) on Ir-catalysed NO reduction by hydrocarbons over a variety of oxygen concentrations and/or of promoter loading to the catalyst; note that the other noble metals (Pt, Pd and Rh) have shown very spectacular responses, strongly depended by these two factors.

In this study, we report on the influence of potassium on the Ir-catalysed NO reduction by propene in the presence of oxygen in a wide range of oxygen concentrations, including zero, around stoichiometric and excess O_2 conditions. The study was performed in a “single-pellet” type electrochemical reactor, where Ir catalyst in the form of thin film was interfaced with a potassium β'' - Al_2O_3 solid electrolyte disk, a K^+ ions conductor. In this way, the electrochemical promotion (or NEMCA) concept was applied in order to investigate the performance of the $C_3H_6 + NO + O_2$ reaction on a variety of potassium coverages on Ir surface. The results obtained on the K-modified Ir catalyst were found to be in complete contrast to those previously found for Pt and Pd [10–18] under similar conditions, where the benefits of electropositive promotion were found to be very substantial; alkali-modified Ir performance seems to be more close to that of alkali-modified Rh [18]. The results may be understood in terms of the electronic effect of co-adsorbed potassium on the adsorption strength of the various reactants on the Ir surface. The explanations given are consistent to those that explain the very different behaviour on the other noble metals, Pt and Pd.

2. Experimental methods

The “single-pellet” reactor configuration (Fig. 1, top), used in most previous electrochemical promotion (EP) studies (e.g.,

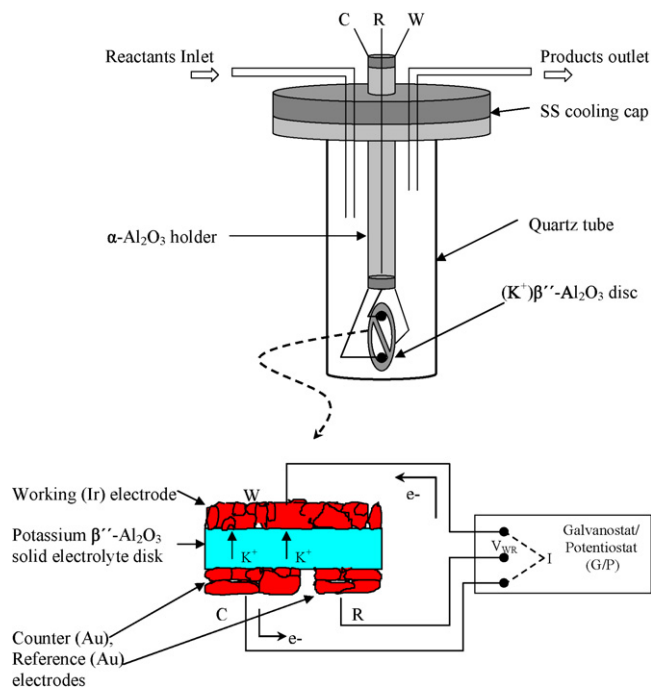


Fig. 1. Single pellet catalytic reactor and electrodes configuration.

[10,19,22]), was again applied in the present study: the potassium β'' - Al_2O_3 disc was suspended in a 25 cm³ quartz CST reactor with the three electrodes, i.e., working-catalyst electrode (Ir), counter (Au) and reference (Au) electrodes, all exposed to the reacting gas mixture (Fig. 1). The Ir catalyst film and the Au counter and reference electrode films were magnetron sputtered at the opposite sides of the beta alumina disc as schematically shown in Fig. 1 (bottom).

Before measurements were taken, the catalysts were operated for 1 day in air and for 1 day in a reactive gas mixture, 2000 ppm NO/2000 ppm C_3H_6 /5% O_2 at 420 °C in order to ensure stable operation (i.e., metal crystallite stabilization resulting from reaction or thermal sintering). The latter step is often used in Ir-catalysed de-NOx studies, since it has been documented that such a step activates the catalyst by establishing a certain ratio of Ir/IrO₂ (see for example Refs. [26,30,33]). After this pretreatment the true (active) surface area of Ir film was determined by m.s.-aided, CO temperature programming reaction (TPR) experiments, after CO adsorption at ambient temperature. This was found to be equal to 4.08×10^{-7} mol Ir or equivalently to 186 cm²; the latter value was based on an Ir surface atom density 1.3×10^{19} atoms/m².

He-diluted Air Liquide certified gas mixtures (10% C_3H_6 , 7.83% NO, 20.7% O_2 and 20% H_2) were used. After further dilution in ultrapure He (99.999%), in order to yield the required composition of 2000 ppm NO/2000 ppm C_3H_6 /0–5% O_2 , the gas mixture was delivered to the reactor by mass flow meters (MKS type 247) at 1 bar and a total flow rate of 140 cm³/min.

The reactor inlet and outflow were on line analysed using a chemiluminescence NOx analyser (Thermo Environmental Instr., 42C, for the analysis of NO and NOx = NO + NO₂) and a

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