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Effect of ionically conductive supports on the catalytic activity of platinum and ruthenium nanoparticles for ethylene complete oxidation

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ABSTRACT

The effect of the support nature on the catalytic activity of platinum and ruthenium nanoparticles is investigated for ethylene complete oxidation in the temperature range of 25–220 °C. The nanoparticles (NPs) were deposited on ionically conductive supports: yttria-stabilized zirconia (YSZ) and samarium-doped ceria (SDC), and on non-ionically conductive supports: carbon black (C) and gamma-alumina (γ-Al_2O_3) to give $\leq$0.7 wt% loading and an average particle sizes of 1.9–2.9 nm depending on the support. The presence of O^{2-} ionic conductivity greatly enhanced Pt and Ru catalytic activity compared with the same metals deposited on non-ionically conductive supports for C_2H_4 complete oxidation. The light off temperatures of Pt/SDC and Ru/SDC were 60 °C and 70 °C, respectively, whereas for the same NPs deposited on the high surface area carbon, the higher temperatures of 90 °C for Pt/C and 130 °C for Ru/C were obtained. The same trend was observed with activation energies, which were 22 and 35.1 kJ/mol for Pt/SDC and Ru/SDC compared with 31 and 52.4 kJ/mol for Pt/C and Ru/C, respectively. It is proposed that metal–support interaction (MSI), in particular, the electronic effect between NPs and ionic conductors is responsible for the high catalytic activity. The electronic effect is manifested by the oxygen ion exchange in the vicinity of the three-phase boundary similar to the electrochemical promotion mechanism, which is thermally self-induced in the case of Pt and Ru NPs deposited on SDC and YSZ.

1. Introduction

Understanding the oxidation reactions of simple volatile organic compounds (VOCs), e.g., such as ethylene on supported metal or metal oxide nanoparticle catalysts, creates a fundamental basis for the investigation of more complex hydrocarbon molecules and/or the oxidation of gas mixtures [1–3]. Elucidation of the effect of the nano-catalyst size, structure, morphology, shape and its interaction with the support on the performance of the supported catalyst represents a central topic in heterogeneous catalysis.

The general concept of catalytic oxidation of VOCs involves the use of two types of catalysts: metal oxides and noble metals [2]. Both were found to be active for many deep oxidation reactions. The mechanism of deep catalytic oxidation of VOCs involves lattice and surface oxygen for metal oxides and reduced metal sites for supported noble metals [2].

Metal–support interaction is a well-known phenomenon in heterogeneous catalysis, where the catalyst support enhances the catalytic activity and in some cases the selectivity of the catalyst via either the geometric or electronic effect. It was reported that supports with high surface area increase the dispersion of the catalyst and prevent nanoparticles from agglomeration, hence enhancing its catalytic activity [4]. Other effects were related to the presence of oxygen vacancies and reducibility of mixed ionic conductive supports such as TiO_2 and CeO_2 vs. non-ionic conductive supports such as Al_2O_3 [5].

Ionic conductive materials are found in many applications such as sensors, separators, solid oxide fuel cells (SOFC), heterogeneous catalysis [6,7] and in electrochemical promotion of catalysis (EPOC) [8–10]. Solid-state oxygen-ion conductors are solid solutions of oxides of divalent or trivalent cations (Y_2O_3, CaO, Yb_2O_3) in oxides of tetravalent metals (ZrO_2, ThO_2, CeO_2). Their O^{2-} conductivity is due to the oxygen ion vacancies created in the lattice of the tetravalent metal oxide after the doping [6].

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Yttria-stabilized zirconia (YSZ) is one of the most studied solid electrolytes in SOFC and gas sensors and its good O^{2-} conductivity is due to the presence of oxygen vacancies inside its crystallographic structure. It found a particular interest as a solid-electrolyte in EPOC studies, where the catalytic activity and sometimes selectivity of metals or metal oxides interfaced with solid electrolyte is enhanced reversibly or in some cases irreversibly via potential or current application. The increase in the catalytic rate can be several orders of magnitude higher than that anticipated from Faraday's law due to the backspillover of ionic conductive species ($O^{\delta-}$ in case of YSZ) over the gas-exposed catalyst surface [8].

Recently, Vernoux et al. [11] proposed the functionally similar concept, termed "self-induced electrochemical promotion of catalysis", which is a MSI effect observed between NPs and purely ionic conductive support, e.g., YSZ. Vernoux and co-workers found that MSI in this case is manifested by the spontaneous backspillover of ionic species from the support to the gas-exposed catalyst surface. The backspillover is thermally induced without any electrical polarization, which is required in the conventional electrochemical promotion studies [8–10]. The "self-induced EPOC" was first demonstrated over Pt NPs of 10 nm average size deposited on YSZ for propane deep oxidation and more recently over the similar system but with Pt average size of 3 nm for CO and toluene oxidation [12–14]. It was found that for both CO and toluene oxidation, Pt/YSZ outperformed Pt deposited on carbon and γ-Al_2O_3 catalysts despite the much higher specific surface area of the two latter materials.

Ruthenium was extensively studied for carbon monoxide oxidation [15–17]. However, the application of Ru-based catalysts in the alkanes/alkenes combustion is limited. Toluene, propane and orthoxylene oxidation were studied over Ru/CeO_2 [18] and on Ru/γ-Al_2O_3 [19], propylene oxidation was studied over RuO_2/CeO_2 [20], low temperature oxidation of butane, ethyl acetate, acetaldehyde, and toluene oxidation were investigated over Ru supported on CeO_2, ZrO_2, SnO_2 and Al_2O_3 [21,22]. Furthermore, ethylene oxidation was investigated over a 1 mm thick film of RuO_2/YSZ electrochemically promoted catalysts and it was found that RuO_2 is a good catalyst for this reaction and the rate of ethylene oxidation can be further increased by a factor of ten via anodic polarization (supply of $O^{\delta-}$ promoters to the catalyst surface) and by a factor of three via cathodic polarization (removal of $O^{\delta-}$ from the catalyst surface) [23,24].

In this paper, Pt and Ru colloidal nanoparticles of 1.8–1.9 nm average size were synthesized using modified polyol process with ethylene glycol (EG) as a reducing agent. The colloidal nanoparticles were then deposited on yttria-stabilized zirconia (YSZ), samarium-doped ceria (SDC), gamma-alumina (γ-Al_2O_3) and carbon black (C) resulting in ≤0.7 wt% of Pt and Ru on each support with a resulting nanoparticle average sizes ranging between 1.9 and 2.9 nm depending on the support. First, the kinetics of ethylene oxidation over Ru/YSZ NPs is investigated by varying C_2H_4 and O_2 partial pressures at 150 °C. Then the effect of the support for complete ethylene oxidation reaction at constant P_{O2} and P_{C2H4} was carried out in the temperature range of 25–220 °C in fuel lean conditions. Furthermore, C_2H_4 oxidation over Pt/YSZ and Ru/YSZ in the absence of oxygen in the gas feed was performed.

2. Experimental

2.1. Synthesis and characterization of supported nanoparticles

Platinum and ruthenium nanoparticles were synthesized using a modified polyol reduction method, described in details elsewhere [25,26]. In short, first, Pt and Ru nanoparticles in the form of colloids were synthesized in ethylene glycol (Anhydrous 99.8% Sigma–Aldrich) at 160 °C, starting from $PtCl_4$ (Alfa Aesar, 99.9% metals basis) and $RuCl_3$ (Alfa Aesar, 99.99% metals basis) precursor salts respectively using a sodium hydroxide (EM Science, ACS grade) concentration of 0.08 M as described previously [13]. An appropriate amount of the resulting dark brown solution of Pt and Ru nanoparticles in ethylene glycol were deposited on 1.5 g of 8 mol% Y_2O_3-stabilized ZrO_2 (Tosoh, specific surface area (a_s) = 13 $m^2\,g^{-1}$), SDC (Fuel Cell Materials, a_s = 35 $m^2\,g^{-1}$), carbon black (Vulcan XC-72R, Cabot Corp. a_s = 254 $m^2\,g^{-1}$) and γ-Al_2O_3 (Alfa – Aesar, a_s = 120 $m^2\,g^{-1}$). The mixture of the supported nanoparticles was left to stir over night at room temperature to achieve high dispersion of the metal nanoparticles on each support. The supported NPs were extensively washed with deionized water (18 MΩ cm) and separated by centrifugation, then dried in air at 60 °C resulting in ≤0.7 wt% of metal on the support as confirmed by inductive coupled plasma measurements using (ICP-OES Varian Vista-Pro CCD spectrometer).

As prepared, Ru is mostly present in the oxidized form, i.e., RuO_x ($x \leq 2$) while partial surface oxidation was found for Pt [4]. Therefore, before catalytic measurements, all supported Pt and Ru catalysts were reduced in H_2 (Linde, 99.99%) at 300 °C for 3 h then tested immediately.

The morphology and particle size of the resulting Pt and Ru colloids were characterized by TEM (JEOL JEM 2100F FETEM) operating at 200 kV. A drop of the colloidal solution was deposited on a copper grid (Electron Microscopy sciences, CF-300). The size distribution and mean particle size were performed using the imaging software MeasureIt (Olympus Soft Imaging Solutions) by measuring at least 200 nanoparticles from TEM images.

Dispersion of the supported Pt and Ru nanoparticles was determined using the CO titration technique [27–30]. In brief, carbon monoxide (Linde, 1000 ppm CO in He) with a flow rate of 15 $ml\,min^{-1}$ for Pt and 20 $ml\,min^{-1}$ for Ru was adsorbed on the catalyst surface at 140 °C and 180 °C for Pt and Ru, respectively. The reactor was then purged with He (Linde, 100%) at the same temperature and flow rate of 100 $ml\,min^{-1}$. An oxygen flow of 30 $ml\,min^{-1}$ (Linde, 99.997%) was then passed through the reactor and the amount of CO_2 formed was measured using gas chromatograph and an online non-dispersive infrared (NDIR) CO_2 analyzer (HORIBA VA-3001). This procedure was repeated for different purging times ranging from 5 to 20 min, and the maximum reactive CO uptake was obtained by extrapolating to time equals zero. The CO/Pt ratio is assumed to be unity [10,30,31] but the CO/Ru ratio is taken as 2.3 for Ru nanoparticle of 2.5 nm size [16,32].

Calculation of the supported catalyst particle size was estimated using TEMs or using the following equation [33]:

$$d_{nm} = \frac{MW \times 600}{\rho \times \text{dispersion}\quad(\%) \times a \times N_a} \tag{1}$$

where MW is the molecular weight of Pt = 195.08 $g\,mol^{-1}$ or Ru = 101.07 $g\,mol^{-1}$, a is the atomic surface area = 8.06×10^{-20} $m^2\,atom^{-1}$ for Pt and 1.96×10^{-19} $m^2\,atom^{-1}$ for Ru, ρ = 21.09 $g\,cm^{-3}$ for Pt and 12.2 $g\,cm^{-3}$ for Ru, N_a = Avogadro's number.

2.2. Catalytic activity

The catalytic activity measurements of the supported nanocatalysts for ethylene oxidation were carried out at atmospheric pressure in a continuous flow U-shaped quartz reactor. Approximately 50 mg of catalyst was placed into the reactor. The reactive mixture was composed of 909 ppm C_2H_4 (Linde, 5% in He), 3.5% O_2 (Linde, 99.997%) and balance He (Linde, 100%) as a carrier gas. The total gas flow rate was 4.62 $L\,h^{-1}$ unless otherwise stated. For the oxidation experimental part in absence of oxygen in the gas phase, the reactive mixture composed of 909 ppm C_2H_4 (Linde, 5% in He) and balance He (Linde, 100%) as a carrier gas.