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Sulphate-promotion and structure-sensitivity in hydrocarbon combustion over Rh/Al_2O_3 catalysts

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Abstract

A series of Rh/Al_2O_3 catalysts have been prepared using untreated or pre-sulphated alumina supports. The effect of support sulphation on catalyst activity towards propene and propane combustion has been explored as a function of Rh loading. Light-off temperatures for the total oxidation of both hydrocarbons decrease with increasing Rh content, associated with a transition from small oxidic clusters to large metallic Rh particles. Sulphate promotes both propene and propane combustion equally, with the magnitude of promotion exhibiting only a weak loading dependence. Enhanced catalytic performance is accompanied by Rh reduction and sintering.

Keywords: Rhodium; Sulphate; XPS; Propane; Propene; Combustion

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1. Introduction

Rhodium is a ubiquitous component of the modern three-way catalyst (TWC) employed for automotive pollution control applications [1], where its principal role is the direct reduction of NO to N_2. The other primary functions of TWCs are the combustion of unburned hydrocarbons and CO to form "environmentally benign" CO_2 and H_2O. These latter reactions have been extensively explored over platinum and palladium [2,3], the other precious metal constituents of catalytic convertors, however little is known about the corresponding combustion chemistry of Rh. Despite the advent of low S fuels, it has long been known that even trace SO_2 formed in situ from thiophene/mercaptane derivatives during gasoline/diesel combustion can profoundly influence hydrocarbon combustion over Pt/Al_2O_3 catalysts via catalyst sulphation [4]. Indeed propane combustion is dramatically promoted by either gas-phase sulphation of conventional Pt/Al_2O_3 catalysts [5], or sulphate pre-treatment of the alumina support [6], while propene (and CO) combustion is suppressed [5]. Propane combustion over commercial $Pt–Rh/CeO_2–Al_2O_3$ catalyst formulations is also promoted by SO_2 under oxidising conditions [7]. Although the origin of this promotional phenomenon has been extensively investigated over Pt/Al_2O_3 catalysts [8–11], nothing is known regarding the impact of sulphate on hydrocarbon combustion over their rhodium counterparts.

The main studies on the effect of SO_2 on Rh/Al_2O_3 catalysts are concerned with the selective catalytic reduction (SCR) of NO with propene, for which there are conflicting reports. Early work by Summers et al. show Rh to be more tolerant towards SO_2 poisoning than Pt or Pd [12] but report that SO_2 inhibits NO reduction by propene in all cases. In contrast, addition of only 200 ppmv SO_2 to a 2 wt% Rh/Al_2O_3 catalyst is reported to promote propene oxidation during NO_x SCR [13,14].

Surprisingly little is known regarding structure–activity relations in hydrocarbon oxidation over Rh/Al_2O_3, with only a few studies of propane or propene combustion reported [3,15–17]. The excellent steam reforming activity of Rh makes it effective for catalysing hydrocarbon conversion under fuel rich conditions [18,19]. However under highly oxidising conditions Rh is inferior to Pt and Pd,

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with propene [3] and propane oxidation [17] inhibited, possibly due Rh_2O_3 formation [20]. Propene combustion over Rh/Al_2O_3 is also sensitive to catalyst pre-calcination temperature [16,21,22]. Low temperatures (<800 °C) favour small reducible rhodium oxide clusters which are active in propene combustion under oxygen rich conditions. Combustion activity decreases with increasing calcination temperature, with little difference in activity reported between catalysts containing 0.1% or 1 wt% Rh [16]. Higher temperature calcination induces a strong metal-support interaction forming irreducible Rh clusters and decreasing the titratable Rh sites (attributed to Rh substitution into alumina lattice [22]).

Here we report on the loading dependent activity of Rh/Al_2O_3 and $Rh/SO_4–Al_2O_3$ catalysts in propene and propane combustion, and reveal that combustion activity of both hydrocarbons is promoted by support pre-sulphation.

2. Experimental

2.1. Catalyst synthesis

Sulphated aluminas ($SO_4–Al_2O_3$) were prepared as previously described by incipient wetness impregnation of γ-Al_2O_3 (Degussa aluminium oxide C) with an aqueous 0.5 M H_2SO_4 (Fisher 98%) solution and subsequent drying and calcination [23]. The strength of H_2SO_4 sulphating solution was chosen to be just below that required to induce major crystallisation and pore-collapse of the parent alumina [23]. Rhodium was subsequently added via the incipient wetness technique to either untreated or sulphated alumina, using 1 cm^3 of an aqueous $RhCl_3$ (Johnson Matthey) solution per gram of support to generate Rh loadings ranging from 0.05 to 5 wt%. The resultant paste was air-dried at 80 °C for 12 h and then calcined in flowing O_2 at 500 °C for 2 h (10 $cm^3\ min^{-1}$) followed by a 2 h reduction in flowing H_2 (10 $cm^3\ min^{-1}$) at 400 °C.

2.2. Catalyst characterisation

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS HSi photoelectron spectrometer with a charge neutraliser and Mg Kα excitation source (1253.6 eV). Energy referencing was employed using adventitious carbon at 284.5 eV. Peak analysis was performed using CasaXPS version 2.3.5 software, with all spectra Shirley-background subtracted prior to fitting. A common lineshape was adopted for each element, based on a Gaussian–Lorentzian mix, with FWHM = 3.0 (O 1s), 2.6 (Rh 3d) and 3.0 (S 2p), and Lorentzian contribution = 30% (O), 0% (Rh) and 30% (S), respectively. Surface compositions were determined using the respective atomic sensitivity factors for O (0.736), S (0.723), Rh (5.155) and Al (0.257). Metal loadings were determined by ICP-MS. Surface area measurements were performed on a Micromeritics ASAP 2010 porosimeter. The acidity of the parent and sulphated Al_2O_3support materials were determined by Hammett acidity measurements and found to lie in the range $H_0 \geqslant +2.8$ and $-3.0 \geqslant H_0 \leqslant -5.6$, respectively [23]. Rhodium dispersion was measured by pulsed H_2 chemisorption at room temperature using a Micromeritics Pulse Chemisorp 2700 gas adsorption system; samples were pre-reduced at 400 °C for 2 h under flowing hydrogen.

2.3. Catalyst testing

Reactions were performed in a fixed-bed quartz reactor using 100 mg catalyst. The total gas flow rate was 46.5 $cm^3\ min^{-1}$ and stoichiometric mixtures were employed using 2.5 $cm^3\ min^{-1}$ of hydrocarbon (C_3H_6-E&W 99.9% or C_3H_8-E&W 99.9%) together with the appropriate oxygen flow with helium added as an inert diluent. This equated to gas mixes of 5 vol% HC and 24–27 vol% O_2 in He. Light-off measurements were performed with a ramp rate of 10 °C min^{-1} with the catalyst bed temperature measured with a coaxial thermocouple. Reaction was monitored via on-line mass spectrometry (VG 200 amu QMS) with CO_2 and H_2O the sole reaction products observed. The overall error in conversion was ±4%. Blank runs with alumina and sulphated-alumina supports showed negligible contributions to combustion below 470 °C (C_3H_6) and 530 °C (C_3H_8), respectively.

3. Results and discussion

3.1. Physical properties

A series of 0.05, 0.25, 1 and 5 wt% Rh-doped Al_2O_3 and $SO_4–Al_2O_3$ samples were prepared. Elemental analysis confirmed the incorporation of both Rh and sulphur into the bulk and surface of the samples (Table 1). The bulk rhodium content of all materials were in excellent agreement with their nominal loadings. The corresponding surface Rh loadings of the Rh/Al_2O_3 series, as determined by XPS, were consistently higher than their bulk values, as expected from the surface impregnation preparation method. Although a similar rhodium surface enhancement was seen for the lower loading $Rh/SO_4–Al_2O_3$ samples, the extent of this was reduced, indeed the surface Rh content of the 5 wt% $Rh/SO_4–Al_2O_3$ sample is comparable to its bulk value. These observations are consistent with the dramatically lower Rh dispersions and increased particle sizes of the pre-sulphated materials, which reduce the amount of rhodium visible by XPS. The bulk sulphur content of the $Rh/SO_4–Al_2O_3$ series remained unchanged following Rh impregnation at ~3.7 wt% S, however the surface sulphur loading fell significantly, particularly for Rh loadings above 1 wt%, consistent with partial screening of the underlying sulphated support decorated by rhodium clusters. This rhodium agglomeration is not associated with significant textural changes or pore-collapse of the alumina support, since surface area measurements (Table 1) confirm that BET areas remain ~100 $m^2\ g^{-1}$ for both bare and pre-sulphated alumina and the Rh impregnated materials. The