Support-mediated alkane activation over Pt–SO₄/Al₂O₃ catalysts

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Sulphate-promoted alkane combustion has been investigated over a series of Pt/Al₂O₃ catalysts using pre-sulphated alumina supports. Catalyst sulphation greatly enhanced ethane combustion over Pt/Al₂O₃, and also improved methane and propane light-off performance. Catalyst activity increased with Pt loading, however the magnitude of sulphate promotion was independent of Pt loading under oxidising conditions, but scaled with alkane chain length. Propane combustion activity was directly proportional to the surface coverage of aluminium sulphate sites; support-mediated alkane activation is the dominant process in sulphate promotion.

KEY WORDS: catalysis; platinum; alumina; oxidation; sulphate; alkane; ethane.

1. Introduction

The development of catalytic materials for the efficient combustion of light alkanes is of fundamental importance for automotive pollution control, and control of emissions produced from bio-fuel combustion [1,2]. While there are many detailed studies of methane and propane (for reviews see [3–5]) oxidation kinetics over supported platinum group metals (PGM), there are fewer investigations focussed on ethane combustion [6–12].

The rate-limiting activation step in alkane combustion is determined by the energy required to cleave the weakest C–H bond. Thus the relative reactivity would be expected to follow the order methane < ethane < propane, in accord with their respective C–H bond energies of 440, 420 and 401 kJ mol⁻¹. Indeed over PGM foils [13], the combustion light-off temperature for C₁–C₄ alkanes follows this trend, with the activation energy for combustion of C₄ alkanes observed to be invariant of chain length [10]. In addition under fuel-lean conditions enhanced combustion activity is also correlated with low metal–oxygen bond strength with light off temperatures observed to increase from Pt < Pd < Rh < Ir. The optimum air fuel ratio thus depends on the relative sticking probability of O₂ and the corresponding alkane.

A recent study of sol–gel prepared Pt/Al₂O₃ catalysts has shown enhanced ethane combustion occurs over larger metallic Pt crystallites [12], which is in accord with trends observed for methane [14], and propane [15] combustion where higher catalytic activity is observed when the metallic phase prevails. Ethane combustion has largely been studied in conjunction with methane for control of emissions from Natural Gas Vehicles, and has concentrated on the use of Pd based catalysts, which are more active than Pt in methane oxidation under air:fuel ratios typically employed, but also prone to sulphur poisoning [16].

Since the original report of SO₂-promoted propane combustion over Pt/Al₂O₃ [17] this phenomenon has been explored over both dispersed Pt catalysts [18–21] and model single-crystal systems [22–24]. However catalyst sulphation (ex situ or in situ) affects numerous physico-chemical changes, including the Pt oxidation state/particle size [25], Pt dispersion [20] and the support crystallinity [18,9,25] and porosity [25], hence various models have been advanced to explain this promotion. To date there have been no systematic efforts to isolate the respective roles of support and metal, and in particular identify which plays the dominant factor in sulphate-promoted alkane combustion. Here we address these issues using a range of well-defined Pt/SO₄–Al₂O₃ catalysts, and report the first observation of sulphate-promoted ethane combustion.

2. Experimental

2.1. Catalyst preparation

Sulphated aluminas were prepared by incipient wetness impregnation of 1 g of γ-Al₂O₃ (Degussa Aluminium Oxide C) with a 10 cm³ solution of 0.01–2.5 M H₂SO₄ (Fisher 98%). The resultant slurry was dried at 80 °C in air for 12 h and then calcined in flowing O₂ at 550 °C for 3 h. Samples were subsequently stored in air. Platinum was added via the incipient wetness technique using 1 cm³ of (NH₄)₂PtCl₆ (Johnson Matthey, 55.24 wt% Pt assay) as an aqueous solution per gram of support. The resultant paste was air-dried at 80 °C for 12 h and then calcined in flowing O₂ at 500 °C for 2 h. Catalysts were then reduced in flowing H₂ at 400 °C for 2 h.

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2.2. Catalyst characterisation

Porosity and surface area measurements were performed following the N\textsubscript{2} adsorption on a Micromeritics ASAP 2010 instrument. Surface areas were calculated using the BET equation over the pressure range \(P/P_0 = 0.02–0.2\), where a linear relationship was maintained. The final sulphur content was determined by elemental analysis using a Carlo Erba 1108 CHN/S instrument (quoted percentages refer to total S levels).

Pt loadings were measured using a Perkin-Elmer P40 emission ICP-MS instrument. XRD spectra were acquired using a Siemens D5000 diffractometer and CuK\textsubscript{α} radiation. S 2p XP spectra were also measured using a Kratos AXIS HSi instrument, equipped with charge neutraliser and MgK\textsubscript{α} X-ray source, to identify the S species present in the final fresh catalysts. Two point energy referencing was employed using adventitious carbon at 285 eV and the valence band, and in all instances only SO\textsubscript{4} groups were observed with a characteristic binding energy of 170 eV.

2.3. Catalyst testing

Catalyst testing was performed in a fixed-bed quartz reactor using 100 mg catalyst. The total gas flow rate was 21 cm\textsuperscript{3} min\textsuperscript{−1} and stoichiometric mixtures were employed using 1 cm\textsuperscript{3} min\textsuperscript{−1} of alkane together with the appropriate oxygen flow with helium added as an inert diluent. This equated to gas mixes of 5 vol% HC and 10–25 vol% O\textsubscript{2} in He. Gases used were CH\textsubscript{4} (E&W 99.995%), C\textsubscript{2}H\textsubscript{6} (E&W 99.5%) and C\textsubscript{3}H\textsubscript{8} (E&W 99.9%). Light-off measurements were performed with a ramp rate of 5 °C min\textsuperscript{−1} with the catalyst bed temperature measured with a coaxial thermocouple. Reaction was monitored on-line using a VG 200 amu quadrupole mass spectrometer. The sole reaction products were CO, CO\textsubscript{2} and H\textsubscript{2}O. The systematic error in conversion was ±2%. Blank runs showed negligible gas-phase contributions to alkane combustion below 700 °C.

3. Results and discussion

The effect of sulphate on alkane combustion was first investigated using Pt-doped catalysts prepared from a SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} support pre-sulphated with 0.1 M H\textsubscript{2}SO\textsubscript{4}. Figure 1a compares the resulting light-off curves for methane, ethane and propane combustion over Pt/Al\textsubscript{2}O\textsubscript{3}. The alkane light-off temperatures decrease in the order propane < ethane < methane over the unsulphated catalyst as expected; C–H bond activation is widely accepted as rate-limiting in alkane oxidation over Pt/Al\textsubscript{2}O\textsubscript{3}. Alumina pre-sulphation reduced the light-off temperature for all light alkanes, with the magnitude of

![Figure 1. (a) Light-off curves for C1–C3 alkanes over 0.05 wt% Pt/Al\textsubscript{2}O\textsubscript{3} and Pt–SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} catalysts. (○) Alumina pre-sulphated with 0.1 M H\textsubscript{2}SO\textsubscript{4}; (□) unsulphated alumina. (b) Light-off curves for C1–C3 alkanes over 5 wt% Pt/Al\textsubscript{2}O\textsubscript{3} and Pt–SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} catalysts. Alumina pre-sulphated by 0.1 M H\textsubscript{2}SO\textsubscript{4}; (○) alumina pre-sulphated with 0.1 M H\textsubscript{2}SO\textsubscript{4}; (□) unsulphated alumina.](image)

ethane [18] and methane [8] under fuel-lean conditions. Apparent activation energies derived over the kinetic (low conversion) regime are also in accord with previous estimates (table 1). These show a progressive rise in \(E_{\text{act}}\) with chain length, supporting C–H cleavage as the rate-limiting step.

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![Table 1 Kinetic parameters for alkane combustion over a 0.05 wt% Pt/Al\textsubscript{2}O\textsubscript{3} catalyst](image)