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Total oxidation of propane on $Pt/WO_x/Al_2O_3$ catalysts by formation of metastable $Pt^{\delta+}$ species interacted with WO_x clusters

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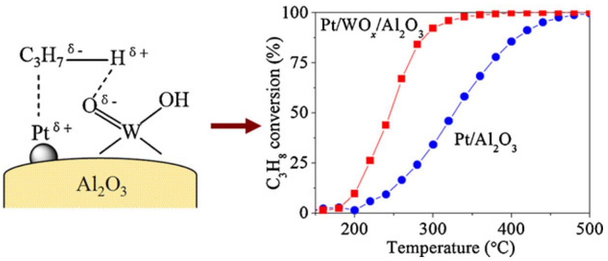
HIGHLIGHTS

- ► The activity of Pt/Al_2O_3 catalyst for C_3H_8 oxidation is promoted by WO_x addition.
- ► The $Pt^{\delta+}/Pt$ ratio increases with WO_x surface density.
- ► The reducibility of metastable $Pt^{\delta+}$ species correlates with the catalytic activity.
- ► simple redox model is presented involving the initial C—H bond activation.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of Pt/Al_2O_3 catalysts with various tungsten oxide loadings were prepared by a stepwise wet impregnation method. The catalysts were characterized by X-ray diffraction, nitrogen physisorption, Raman, UV–vis diffuse reflectance, transmission electron microscopy and infrared spectroscopy of adsorbed probe molecules (CO, NH_3 or C_3H_8). The propane oxidation activity of Pt/Al_2O_3 catalyst is significantly improved by the addition of tungsten oxide. The tungsten oxide overlayer is presented as monomeric/polymeric WO_x clusters and WO_3 crystals depending on the loading amount. The most active catalyst occurs at an intermediate surface tungsten density corresponding to the maximum of polytungstate species. The electronic interactions between Pt and WO_x clusters lead to the generation of more reducible $Pt^{\delta+}$ species which are suggested to be active sites for propane oxidation. Basically, a simple model is proposed involving the initial C—H bond activation at the platinum–tungsten oxide interface.

1. Introduction

Diesel engine vehicles have been rising rapidly in worldwide due to their high fuel efficiency, reliability and durability compared to gasoline cars [1]. Consequently, diesel exhaust pollutions are leading to increasingly stringent emission standards. Besides particulate matter (PM) and nitrogen oxides (NO_x), diesel emissions also contain a large share of unburned hydrocarbons (HC) presented in both the gas and particle phases [2]. These compounds when oxidized produce a wide variety of oxygenated products including aldehydes, ketones, alcohols, phenols, etc. most of which have been proven toxicity, and play a significant role in ozone production in the presence of nitrogen oxides [3]. For the reduction of HC emission as well as CO and the soluble organic fraction (SOF) of PM, Pt/Al_2O_3 system as a typical diesel oxidation catalyst (DOC) has been widely applied in current commercial oxidation catalysts installed in diesel driven vehicles [4]. Almost 60–80% of total hydrocarbon emissions are produced in the cold-start period [5]. Generally, the efficient oxidation of saturated hydrocarbons on Pt/Al_2O_3 catalyst requires relative high temperatures. It is therefore important to find routes to improve the low-temperature oxidation activity of platinum catalysts.

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The oxidation activity of Pt catalysts is found to depend strongly on the oxidation state and dispersion of platinum, both of which can be affected by the supports and additives. H. Yoshida's group investigated the effect of supports (MgO, La_2O_3, Al_2O_3, ZrO_2, SiO_2, SiO_2–Al_2O_3 and SO_4^{2-}–ZrO_2) on the low-temperature propane combustion over platinum catalysts [6–8]. They found that the turnover frequency is improved with the increase in the acid strength of support materials at the same dispersion of platinum. Kim et al. also ascribed the large different activities of Pt/ZrO_2–SiO_2 and Pt/ZrO_2–SiO_2–H_2O_2 catalysts, despite their close platinum dispersion, to the effect of the acidity generation on propane combustion [9]. On the other hand, Burch's group found that the alumina modified with fluorine is more acidic than that with sulfur dioxide, but its combustion activity is not higher than the latter one [10]. Similarly, Hubbard et al. reported no enhanced activity with sulfated zirconia even though the acidity increased by 11 orders of magnitude [11]. So it seems that the total acidity of the support is not the only important factor in determining the propane combustion activity of platinum catalysts.

Solid oxide additives are promising for preparing highly active platinum catalysts. For example, the propane oxidation turnover rate on Pt/V_2O_5/Al_2O_3 catalysts increases with the vanadium oxide loading, probably because the intrinsic Pt oxidation activity increases with the sample acidity in spite of increased Pt dispersion [12]. The increased activity for propane combustion on Pd/V_2O_5–Al_2O_3 catalysts is also related to the modified redox properties of the catalysts and in particular the high reducibility of vanadium species [13]. The promoting effect of tungsten oxide on the propane oxidation activity of platinum catalysts has been also reported. Yoshida's group [8,14] showed that the enhanced activity of catalysts is ascribed to less oxidized platinum by interaction with the electronegative additives used (W, V, P, Mo and Nb) under the oxidizing atmosphere. The stabilities of Pt/WO_x/Al_2O_3 and Pt/WO_x/TiO_2–SiO_2 are proved stable on the propane combustion tests at 750 °C for 1000 h [15] and at 350 °C for 400 h [16]. A similar promotion effect of tungsten oxide was found on Pt/Al_2O_3 catalyst for methane combustion [17]. Recently, Taylor's groups ascribed the enhanced catalytic activity of Pd/WO_x/TiO_2 catalyst to an increased concentration of highly reactive oxygen species on the new WO_x-decorated interface between PdO_x and TiO_2 particles [18]. They also found that there is significance in the order of impregnation of the noble metal and promoter on the final performance of for Pd/VO_x/Al_2O_3 catalysts [19]. The formation of active sites at the Pt/WO_x interface on titania was reported to facilitate the dissociation of surface intermediates for propane oxidation in our previous study [20]. Nevertheless, the catalytic behaviors of such catalysts are not fully understood; for example, the nature of the true active phase, metal or metal oxide, remains a matter of discussion. A detailed characterization study needs to be performed to elucidate the exact nature of the metal/support interaction between platinum and tungsten oxide and the corresponding effect on propane combustion activity.

In this study, the effect of different tungsten oxide loadings on the propane oxidation of Pt/Al_2O_3 was investigated by using structural characterizations and *in-situ* diffuse reflectance infrared transform (DRIFT) spectroscopy. The key factors controlling the activity of the catalysts were discussed from the viewpoint of Pt dispersion, Pt oxidation state and reactivity of Pt sites affected by tungsten oxide, and a simple reaction scheme was proposed.

2. Experimental

2.1. Catalyst preparation

The alumina supports modified with various weight percentages of tungsten oxide (10 wt.%, 20 wt.% and 30 wt.%, calculated in terms of WO_3/Al_2O_3) were prepared by the incipient-wetness impregnation of γ-alumina (BASF, Germany, $S_{BET} = 150\ m^2/g$) with ammonium metatungstate ($(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$, 99.5%, Yili, China). After drying at 110 °C for 12 h, the samples were calcined at 550 °C for 3 h in a muffle and the obtained WO_x/Al_2O_3 supports were denoted as *y*WAl (where *y* was the loading percentage of WO_3). For reference, pure tungsten oxide (derived by decomposition of ammonium metatungstate) and alumina were treated by the same calcination process.

The supported catalysts were prepared by impregnating the obtained supports (*y*WAl, Al_2O_3 and WO_3) with $Pt(NO_3)_2$ solution (27.82 wt.%, Heraeus) as the precursor. The nominal loading amount of Pt was 1 wt.%. The impregnation procedure was the same as described above. The impregnated powders were submitted to drying at 110 °C for 12 h and calcination at 500 °C for 3 h in static air. The received catalysts were denoted as *y*PtWAl, Pt/Al_2O_3 and Pt/WO_3, respectively.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns were determined by a Japan Science D/max–RB diffractometer employing Cu Kα radiation (λ = 0.15418 nm) operating at 40 kV and 30 mA.

Textural properties were determined by nitrogen physisorption at −196 °C using a JW-BK122F (Beijing JWGB, China) instrument. Prior to nitrogen physisorption measurement, the samples were degassed to 0.01 Pa at 220 °C. The specific desorption pore volume was assessed by the Barrett–Joyner–Halenda (BJH) method.

The Raman spectra of the samples were obtained at ambient condition on a confocal micro-Raman apparatus (LabRam HR 800, Horiba Jobin Yvon, France) with a CCD detector.UV–vis diffuse reflectance spectra (UV–vis DRS) of the samples were recorded on a Hitachi U-3010 (Japan) spectrophotometer equipped with an integrating sphere.

Transmission electron microscope (TEM) images were taken using a FEI Tecnai G^2 20 with an acceleration voltage of 200 kV.

Infrared (IR) spectra of CO adsorption were recorded on a Nicolet 6700 FTIR spectrometer equipped with a MCT detector. Successive experiments were carried out to collect the information of CO adsorption for the catalysts. After pretreating in He (100 ml/min) at 500 °C for 1 h, the as-received catalyst was cooled down to RT for CO adsorption. After the first CO adsorption, the catalyst was then treated in 5% O_2/He (100 ml/min) at 500 °C for 1 h to obtain the oxidized sample, and was cooled down to RT in He (100 ml/min) for the second CO adsorption. Similarly, the reduction treatment was then performed in 5% CO/He (100 ml/min) at 500 °C before the third CO adsorption. For each CO adsorption measurement, the sample wafer was first exposed to 1% CO/He stream (100 ml/min) for 20 min and then flushed with He for 20 min. IR spectra were recorded under He stream by accumulating 32 scans at a resolution of $4\ cm^{-1}$.

IR spectra of ammonia adsorption were recorded on the same apparatus. The catalyst was purged by nitrogen at 500 °C for 30 min. A gas mixture of 1000 ppm NH_3/N_2 was dosed in a diffuse reflectance IR cell at RT for 30 min, and then the catalyst was flushed with N_2. The spectra were collected by accumulating 32 scans at a resolution of $4\ cm^{-1}$.

IR spectra of propane oxidation were performed on the same apparatus. After pretreatment in nitrogen at 500 °C for 0.5 h, the catalyst was cooled down to 200 °C. The spectra were recorded at an interval of 50 °C after exposing the catalyst to 800 ppm C_3H_8/2% O_2/N_2. The heating rate was 10 °C/min.