



Effect of acid and base modification on the catalytic activity of Pt/Al₂O₃ for propene oxidation



Jie Wan, Rui Ran, Min Li, Xiaodong Wu, Duan Weng*

Key Laboratory of Advanced Materials of Ministry of Education, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

ARTICLE INFO

Article history:

Received 5 August 2013

Received in revised form 6 December 2013

Accepted 16 December 2013

Available online 22 December 2013

Keywords:

Pt/Al₂O₃
Propene oxidation
Adsorption
CO poisoning
Active oxygen

ABSTRACT

BaO and SO₄²⁻ modified Pt/Al₂O₃ catalysts were prepared by a two-step wetness incipient method. The textural properties were characterized by BET, XRD, *ex situ* FTIR. Propene oxidation activity under various redox ratio ($S = [O_2]/4.5[C_3H_6]$) was evaluated. The oxidation process and intermediate species were studied by detailed *in situ* FTIR experiments including propene adsorption CO IR and propene TPO. It is observed that the addition of BaO promotes the catalytic oxidation of propene over Pt/Al₂O₃, while sulfation results in the deactivation of Pt/Al₂O₃. The good activity of Pt/BaO/Al₂O₃ is ascribed to the weakened propene adsorption, the formation of reactive enolic species and easy oxidation of intermediate CO by active oxygen at Pt–Ba interface. On the contrary, the strong adsorption of propene as well as the intermediate CO poisoning are proved to be the main reasons for the deactivation of Pt/SO₄²⁻/Al₂O₃. A general reaction scheme is proposed based on these results.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Hydrocarbon is one of the major pollutants in automotive emissions. In particular propene is recognized as highly polluting molecules because of its high POCP (Photochemical Ozone Creativity Potential) [1–4]. Catalytic oxidation is the most widely used methods for hydrocarbon elimination due to its superiority in versatility and economical efficiency for mobile emission purification [5–12]. Two categories of catalysts are generally employed for hydrocarbons oxidation: (1) noble metal catalysts (such as Pt, Pd, Au, *etc.*) supported on high-surface-area supports (Al₂O₃, TiO₂, SiO₂, ZrO₂, *etc.*); and (2) transition metal oxides (Co₃O₄, Fe₂O₃, V₂O₅, *etc.*) catalysts [13–20]. The noble metal based catalysts, in spite of their more expensive costs, are widely used because of their high specific activity, resistance to deactivation and ability to be regenerated. Among them, Pt/Al₂O₃ catalysts attract the most attentions for the total oxidation of hydrocarbons [21–27].

According to the literatures [28–32], the activity of Pt/Al₂O₃ catalysts for hydrocarbon total oxidation depends not only on the preparation methods and loading amount of Pt, but also on their surface acidity/basicity. For propane oxidation, the effect of surface acidity has been widely studied. It was reported that the addition of SO₂, either by presulfation or by feeding in gaseous phase,

could remarkably promote the oxidation of saturated HCs such as propane due to formation of sulfates on the support oxides [33,34]. Burch *et al.* [35] and Skoglundh *et al.* [36] reported that the propane oxidation activity of Pt/Al₂O₃ was promoted by pre-sulfation and ascribed it to the formation of the Pt/Al₂O₃ interfacial sulfate species, which were more active than the Pt sites for propane oxidation. Lee *et al.* [37] found that the sulfate species formed on alumina support and Pt facilitated the dissociative chemisorption of propane. On the other hand, for propene oxidation, studies related with surface acidity/basicity are very rare to date. Some researchers [38–40] reported that the addition of alkali (earth) element enhanced the activity for propene total oxidation and C₃H₆ assisted SCR reaction (Selective Catalytic Reduction of NO_x). The opposite results of propene oxidation compared to propane oxidation are probably due to different reaction pathways of propene oxidation under different surface acid/base properties. However, few of these previous studies are involved in this point of view. Thus, it is necessary to figure out the role of the surface acid/base sites in the reaction pathways and intermediate species of propene oxidation on Pt/Al₂O₃ catalysts.

In this work, we modify the surface acidity/basicity of Pt/Al₂O₃ catalysts by impregnating barium oxide and SO₄²⁻. The effect of BaO and sulfation on the reaction pathway of propene oxidation is investigated by *in situ* diffuse reflectance infrared transform (DRIFT) spectroscopy. By combining the results of *in situ* DRIFT and structural characterizations, a primary reaction scheme involving the role of the surface acid/base sites is proposed.

* Corresponding author. Tel.: +86 10 62785986; fax: +86 10 62785986.
E-mail address: duanweng@mail.tsinghua.edu.cn (D. Weng).

2. Experimental

2.1. Catalyst preparation

$\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ and $\text{BaO}/\text{Al}_2\text{O}_3$ supports were prepared by incipient wetness method, with $\gamma\text{-Al}_2\text{O}_3$ (BASF A150, $S_{\text{BET}} = 150 \text{ m}^2 \text{ g}^{-1}$), sulfuric acid solution (98%, Yili) and aqueous solution of barium acetate (AR, Xilong). The nominal loading amount of H_2SO_4 and BaO were both 5 wt.%. The impregnated supports were dried at 110°C for 6 h and calcined at 500°C for 2 h. The blank Al_2O_3 was also calcined under same procedure to ensure the comparability. Then the Pt supported catalysts were prepared by impregnating $\text{Pt}(\text{NO}_3)_2$ (27.82 wt.%, Heraeus) on the three different supports. The nominal loading amount of Pt was 2 wt.%. The impregnated powders were dried at 110°C overnight and calcined at 500°C for 2 h to obtain the $\text{Pt}/\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ (PSA), $\text{Pt}/\text{BaO}/\text{Al}_2\text{O}_3$ (PBA) and $\text{Pt}/\text{Al}_2\text{O}_3$ (PA) catalysts.

2.2. Structural and surface properties characterizations

The powder XRD experiments were performed on a Japan SHIMADZU XRD-7000 X-RAY Di-Fractometer using monochromic $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) operating at 40 kV and 30 mA. The diffractograms were recorded at 0.01° intervals in the range of $20^\circ \leq 2\theta \leq 80^\circ$ with a scanning velocity of $6^\circ/\text{min}$ (continuous scan). The crystalline phases were identified with the help of the JCPDS cards.

The specific surface area of the samples was measured using the N_2 adsorption at -196°C by the four-point Brunauer–Emmett–Teller (BET) method on an automatic surface analyzer (F-Sorb 3400, Gold APP Instrument). Prior to the measurements, the samples were degassed in vacuum at 200°C for 2 h.

The *ex situ* diffuse reflectance IR spectra were collected using a Nicolet 6700 FTIR spectrometer equipped with a MCT detector cooled by liquid nitrogen in conjunction with an *ex situ* diffuse reflection chamber. Dry KBr powders (AR, Xilong) were used as blank background spectra. IR spectra of the as-received samples were recorded at RT by accumulating 32 scans at a resolution of 4 cm^{-1} .

Ammonia temperature-programmed desorption (NH_3 -TPD) experiments were carried out with an MKS Multigas 2030 IR spectrometer. Before the experiment, 0.1 g catalyst was pretreated at 500°C in N_2 for 30 min. After cooling down to RT, the sample was exposed to 1% NH_3/N_2 for 30 min and flushed with N_2 for 30 min. The experimental runs were recorded in N_2 while heating from RT to 500°C with a heating rate of $10^\circ\text{C min}^{-1}$.

CO_2 temperature-programmed desorption (CO_2 -TPD) experiments were performed in a fixed-bed reactor with the effluent gases monitored using a quadrupole mass spectrometer (MS). 0.1 g catalyst was pretreated at 500°C in Helium gas for 30 min, then cooled down to RT in the same atmosphere. Then the sample was exposed to 2% CO_2/He for 30 min and then flushed with He for 30 min. Finally, the reactor temperature was raised to 500°C in He with a heating rate of $10^\circ\text{C min}^{-1}$ and CO_2 desorption was monitored by MS.

Transmission electron microscope (TEM) images were taken on a FEI Tecnai G20 with an acceleration voltage of 200 kV. The average particle size of the platinum crystallites was determined by measuring 200 particles for each sample.

2.3. Activity measurement

The catalytic activity for propene oxidation was tested in fixed bed reactor made of stainless steel (i.d. 18 mm). 0.1 g of catalyst powders (diluted by coarse quartz particles to 1 ml), sandwiched

between two quartz wool layers, were inserted into the reactor. The gases used included pure N_2 (99.99%), pure O_2 (99.99%) and 1% $\text{C}_3\text{H}_6/\text{N}_2$ ($1 \pm 0.02\%$ C_3H_6 in N_2). After a pretreatment at 500°C in N_2 for 30 min and cooling down to room temperature (RT), the reactor was then heated in the designed gas mixture from RT to 500°C at a rate of $10^\circ\text{C min}^{-1}$. The gas mixture consisted of 800 ppm C_3H_6 , 2% O_2 and N_2 as balance gas with a total flow of 1 L min^{-1} . The outlet gas concentrations were analyzed by an MKS Multigas 2030 IR spectrometer.

Effect of different reaction atmosphere on the propene oxidation was also verified by conducting similar activity tests under different redox ratios ($S = [\text{O}_2]/4.5[\text{C}_3\text{H}_6]$). The theoretical value would be $S = 1$ according to the propene total oxidation equation (Eq. (1)). Various S ratios were obtained by changing the O_2 concentration in the gas mixture, from O_2 -deficient condition ($S = 0.27$) to O_2 -rich condition ($S = 5$).



2.4. In situ DRIFT experiment

The *in situ* diffuse reflectance IR spectra were collected using a Nicolet 6700 FTIR spectrometer equipped with a MCT detector cooled by liquid nitrogen in conjunction with an *in situ* diffuse reflection chamber. Successive experiments were carried out as follows:

Propene adsorption: Samples were pretreated in N_2 (100 ml min^{-1}) at 500°C for 30 min. After being cooled down to 150°C , the samples were first exposed to 1% $\text{C}_3\text{H}_6/\text{N}_2$ (100 ml min^{-1}) for 20 min and the purged with pure N_2 for 20 min. IR spectra with time evolution were recorded both before and after purging by accumulating 32 scans at a resolution of 4 cm^{-1} .

Propene oxidation: Two kinds of propene oxidation DRIFT experiments were conducted as (1) propene oxidation after pre-adsorption and (2) *in situ* propene and O_2 gas mixture TPO.

- (1) For propene oxidation after pre-adsorption, the samples were first subjected to propene adsorption as described above at a constant temperature of 150°C . After the adsorption the gas mixture consisting of 2% O_2 and N_2 as balance gas was introduced into the reflection chamber with a total flow of 100 ml min^{-1} . Time evolved IR spectra with of both adsorption and oxidation were recorded by accumulating 32 scans at a resolution of 4 cm^{-1} .
- (2) For *in situ* propene and O_2 gas mixture TPO, samples were pretreated in N_2 (100 ml min^{-1}) at 500°C for 30 min. After being cooled down to RT, the samples were then heated in reaction gas mixture (800 ppm C_3H_6 , 2% O_2 and N_2 , total flow rate 100 ml min^{-1}) from RT to 250°C at a rate of $10^\circ\text{C min}^{-1}$. IR spectra were collected by accumulating 32 scans at a resolution of 4 cm^{-1} .

CO adsorption: Samples were pretreated in He (100 ml min^{-1}) at 500°C for 30 min. After being cooled down to room temperature (RT), the samples were first exposed to 1% CO/He stream (diluted from 4% CO/He by pure He) with a flow rate of 100 ml min^{-1} for 20 min and then purged with pure He stream for 20 min. IR spectra were recorded under pure He stream by accumulating 32 scans at a resolution of 4 cm^{-1} .

Download English Version:

<https://daneshyari.com/en/article/65606>

Download Persian Version:

<https://daneshyari.com/article/65606>

[Daneshyari.com](https://daneshyari.com)