Difference in Catalytic Combustion of Propane and Propene on Pt/Al_2O_3 Catalyst

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(Received April 21, 1999; CL-990316)

Propene combustion on Pt/Al_2O_3 catalysts was enhanced when partial pressure of oxygen in a feed increased, while propane combustion was found to be depressed when partial pressure of oxygen was higher than the stoichiometric pressure.

Catalytic combustion have been extensively studied partially because of the effective energy generation[1] and partially because of the removal of pollutants emitted from automobile engines and power plants.[2] It has been well accepted that precious metals such as platinum, palladium and rhodium are more active than base metals for hydrocarbon combustion.[3] In an early work by Yao,[4] a negative kinetic order was reported for oxygen during paraffin combustion on Pt/Al_2O_3, which was elucidated by competitive adsorption of paraffin with oxygen on the same metal sites. He has also studied olefin combustion on Pt/Al_2O_3,[5] and reported a positive kinetic order for oxygen and a negative for olefin, suggesting self-inhibiting by olefin during combustion. However, little attentions were paid to the stoichiometry of the combustion reactions, though the difference in the hydrocarbon combustion under fuel-lean and fuel-rich conditions has been growing concerns with emissions of unburned hydrocarbons and volatile organic compounds.[6] In this work, C_3H_8 and C_3H_6 combustion on Pt/Al_2O_3 was carried out to clarify the difference in catalytic combustion of paraffin and olefin under fuel-lean and rich condition. Stoichiometric concentrations of oxygen for C_3H_8 and C_3H_6 combustion are 1.5 and 1.35 vol%, respectively, when 3000 ppm of C_3H_8 or C_3H_6 was conducted. Catalysts used were Pt/Al_2O_3, prepared by conventional impregnation using alumina and aqueous solution of H_2PtCl_6, and Pt loading was 2 wt% of the catalysts. Catalysts were calcined at 873 K in air for 4 h, followed by reduction with 3 vol% H_2/Ar at 573 K for 4 h prior to combustion activity, CO adsorption and other measurements.

Propane and propene combustion was done using a flow reactor with 0.45 g catalyst. Gases were analyzed by gas chromatography using columns packed with Molecular Sieve 5A and Porapak Q. Reactant gases consisted of 3000 ppm hydrocarbons, and the concentration of oxygen was varied from 1 to 10 vol% in a feed gas, diluted by He with a space velocity of 50000 h^{-1}. Figure 1 shows the conversions of C_3H_8 and C_3H_6 as a function of combustion temperature in the presence of 3 or 5 vol% of O_2; under fuel-lean condition. The figure shows that C_3H_6 is more active than C_3H_8 for the catalytic combustion on Pt/Al_2O_3. It is also prone that C_3H_6 combustion is accelerated when the oxygen concentration increases, but C_3H_8 combustion is depressed with an increase in O_2 concentration under fuel-lean condition.

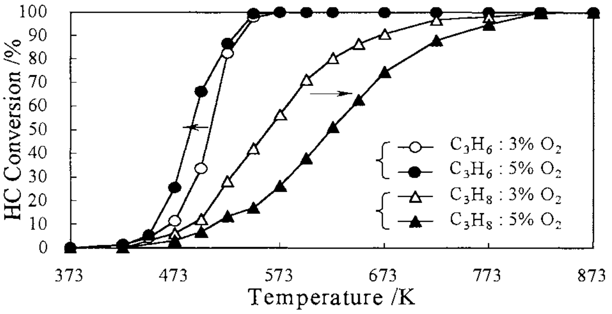

Figure 1. Catalytic combustion of C_3H_6 and C_3H_8 on Pt/Al_2O_3.

Figures 2 and 3 show the dependence of catalytic combustion of C_3H_6 and C_3H_8 on Pt/Al_2O_3 upon O_2 concentration. For C_3H_6 combustion the activity increases when O_2 concentration increases, but for C_3H_8 combustion the activity strongly depends on O_2 concentration. The activity for C_3H_8 combustion increases with O_2 concentration up to the stoichiometry, but decreases as O_2 concentration is beyond stoichiometry. Consequently, C_3H_8 combustion is enhanced as O_2 concentration increases in fuel-rich region, but is depressed in lean region. While C_3H_6 combustion is always accelerated as O_2 concentration increases.

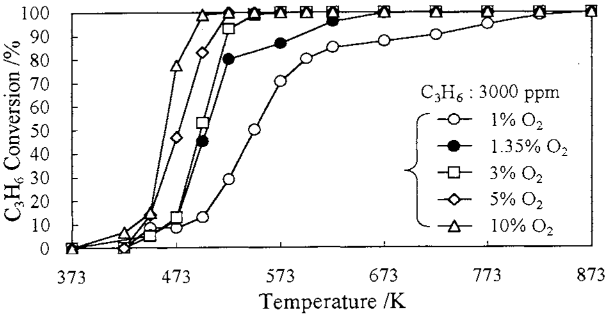

Figure 2. Combustion of C_3H_6 under various O_2 concentration.

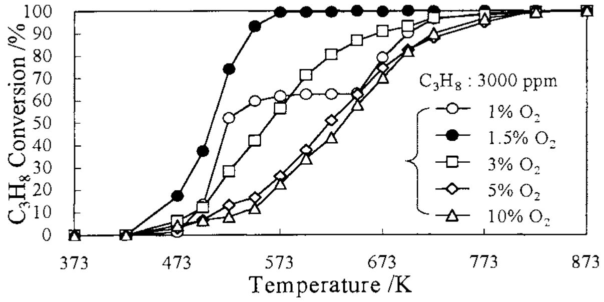

Figure 3. Combustion of C_3H_8 under various O_2 concentration.

In order to understand the reason why C_3H_8 combustion was depressed with an increase in oxygen concentration in fuel-lean region, kinetics of C_3H_8 combustion were studied using 2 wt% Pt/Al_2O_3. The kinetic orders for oxygen during C_3H_8 combustion were determined in both fuel-rich and lean conditions, where C_3H_8 concentration was kept constant (4000 ppm) and oxygen concentration was varied from 500 to 2500 ppm for fuel-rich region, or from 2 to 4.5% for fuel-lean region. The reaction was carried out at 433 K and 513 K for fuel-rich and lean conditions, respectively, in order to control C_3H_8 conversion less than 10% for precise kinetic analysis. The kinetic order of C_3H_8 was also determined at 513 K by varying C_3H_8 concentration from 500 to 4,000 ppm at a constant oxygen concentration (3%). The results are summarized in table 1, with the results obtained for C_3H_6 combustion, studied in the similar manner as mentioned above.

Table 1. Kinetic orders for propane, propene and oxygen

	HC	O_2(fuel-rich)	O_2(fuel-lean)
Propane combustion	0.4	0.4	-0.9
Propene combustion	0.4	0.3	1.1

So far as the kinetic order for oxygen was concerned, it changed from 0.4 to -0.9 for C_3H_8 combustion at stoichiometric oxygen concentration (1.5%). This means that C_3H_8 combustion was inhibited by oxygen, presumably adsorbed on Pt, in fuel-lean region. While for C_3H_6 combustion, the kinetic order for oxygen was positive regardless of oxygen concentration, though the kinetic order changed from 0.3 to 1.1 at the stoichiometric condition. Consequently, the difference in C_3H_8 and C_3H_6 combustion on Pt/Al_2O_3 catalyst appeared in the kinetic order for oxygen under fuel-lean region; negative for C_3H_8 and positive for C_3H_6 combustion.

Why was C_3H_8 combustion inhibited by oxygen but C_3H_6 was not, even though the same catalyst was used? In order to discuss the question, adsorption of C_3H_8 or C_3H_6 on the catalyst was studied by TPO (temperature programmed oxidation) using a rapid type gas chromatography (P-200, MTI; Ohkura-Riken Co.). In the TPO measurements, C_3H_8 or C_3H_6, diluted by He to 1 vol%, was first conducted onto the catalyst (0.45 g) at 323 K for 1 h, and then the flow was switched to 20% oxygen, diluted by He, with rising the catalyst temperature at the rate of 10 K per min. Gases were monitored at the outlet of the reactor, and CO_2 released from the catalyst was analyzed every 3 min of the reaction, since no CO and negligibly small amounts of C_3H_8 and C_3H_6 were detected. In figure 4 are given the TPO profiles for C_3H_6 and C_3H_8 adsorbed on Pt/Al_2O_3 catalyst, respectively. The amount of C_3H_6 adsorbed on the catalyst was estimated to be 5.0 x10^{-5} mol/g catalyst from the amounts of CO_2 released.

Table 2. CO adsorption measurements on 2 wt% Pt/Al_2O_3

Amounts of sites	Dispersion	Surface area	Pt particle size
1.49x10^{21}/g Pt	0.48	119 m^2/g Pt	2.4 nm

This corresponds to 3.0x10^{19} molecule/g catalyst, suggesting that 6.0x10^{19} sites are necessary on 0.009 g Pt in the catalyst, based on the assumption that 2 sites on Pt surface are occupied by 1 C_3H_6 molecule. However, CO adsorption measurements, shown in table 2, revealed that only 1.3x 10^{19} sites are on 0.009 g Pt in the catalyst. This suggests that C_3H_6 molecule or its fragments move to the surface of Al_2O_3 when Pt surface is significantly covered. In figure 4, 3 peaks were observed for CO_2 formation; 423, 548 and 673 K. Though the assignments of the peaks are in further works, the first peak will be due to C_3H_6 combustion on Pt surface and the last one to the combustion on Al_2O_3 surface or at the interface of Pt particles and Al_2O_3 support.

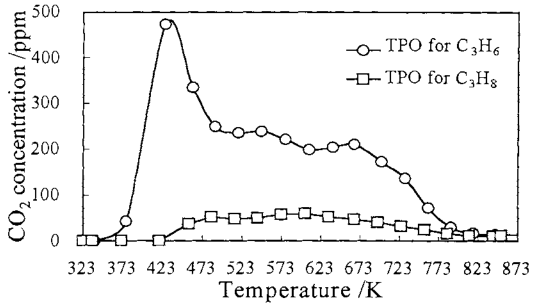

Figure 4. TPO spectra of C_3H_6 and C_3H_8 adsorbed on Pt/Al_2O_3.

On the contrary, the amount of C_3H_8 adsorbed on Pt/Al_2O_3 was estimated to be 1.0x10^{-5} mol/g catalyst, corresponding to one-fifth of the amount of C_3H_6 adsorbed. Three peaks were also detected for CO_2 formation at 473, 598 and 673 K, respectively. First peak will be due to C_3H_8 combustion on Pt and the last one to the combustion on Al_2O_3 surface. From the results, it is concluded that the number of sites for C_3H_8 adsorption is small both on Pt and Al_2O_3 surface in the catalyst. Discussion above likely leads us to the speculation that C_3H_6 molecules will decompose into oxidized fragments at the interface of Pt particles and Al_2O_3, then the fragments will move to sites provided on Al_2O_3 surface when excess amounts of oxygen are conducted to the catalyst, but that C_3H_8 will neither decompose nor move to Al_2O_3 surface. We believe this is the reason why C_3H_8 combustion on Pt/Al_2O_3 was depressed at O_2 concentrations more than the stoichiometry. Similar results were obtained for pentane and pentene combustion on Pt/Al_2O_3, and will be published in the near future.

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