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Kinetics of methane combustion over Pt and Pt–Pd catalysts

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ABSTRACT

A kinetic study was performed over thermally aged and steam-aged Pt and Pt–Pd catalysts to investigate the effect of temperature, and methane and water concentrations on the performance of catalysts in the range of interest for environmental applications. It was found that both catalysts permanently lose a large portion of their initial activity as result of exposure to 5 vol.% water in the reactor feed. Empirical power-law and LHHW type of rate equations were proposed for methane combustion over Pt and Pt–Pd catalysts respectively. Optimization was used to determine the parameters of the proposed rate equations using the experimental results. The overall reaction orders of one and zero in methane and water concentration was found for stabilized steam-aged Pt catalyst in the presence and absence of water. The apparent self-inhibition effect caused by methane over Pt–Pd catalyst in the absence of water was associated with the inhibiting effect of water produced during the combustion of methane. A significant reversible inhibition effect was also observed over steam-aged Pt–Pd catalyst when 5 vol.% water vapor was added to the reactor feed stream. A significant reduction in both activity and activation energy was observed above temperatures of approximately 550 °C for steam-aged Pt–Pd catalyst in the presence of water (the activation energy dropped from a value of 72.6 kJ/mol to 35.7 kJ/mol when temperature exceeded 550 °C).

Keywords: Methane combustion; Platinum; Palladium; Kinetics; Optimization

1. Introduction

Natural gas, composed primarily of methane, offers the cleanest and most practical alternative to other fossil fuels. Natural gas readily forms homogenous air–fuel mixtures that can be ignited and burned over a wide flammability range (Liu et al., 2001). At the same time, the low carbon/hydrogen ratio of natural gas permits substantial reduction of carbon dioxide (CO_2) emissions, a problem of increasing preoccupation (Corbo et al., 1995). Operating under lean combustion atmosphere, natural gas fueled vehicles (NGV) typically emit not only less carbon dioxide (CO_2), but also considerably less carbon monoxide (CO), nitrogen oxides (NO_x) and soot emissions compared to diesel engines (Liu et al., 2001). However, these benefits are in part offset by unacceptable level of methane emissions in the exhaust of NGV. Although methane is chemically resistant and toxicologically inert, its removal is needed because it is a strong greenhouse gas with a global warming potential 23 times higher than that of CO_2. Methane emissions must be eliminated using catalytic converters. Although some attention has been paid to catalytic convertors for natural gas engines, this area has not been extensively researched.

The catalytic combustion of methane can be performed over either noble metals or transition metal oxides. Both families of catalysts have been extensively studied with a view to developing catalytic combustion applications (Gelin and Primet, 2002). The temperature of exhaust gases from NGV is relatively low (typically varying between 300 and 500 °C) (Ando et al., 2003; Zanoletta et al., 2009), therefore the abatement of methane emission in the exhaust of NGV requires high activity at low temperatures and a good resistance to poisoning. The main advantage of noble metals (especially Pt, Pd and their mixtures) over metal oxides is their superior specific activity, making them better candidates for low temperature methane combustion (Gelin and Primet, 2002).

Pd catalysts are commonly used for methane oxidation in catalytic combustion applications because of their excellent catalytic activity, however these catalysts have major weaknesses. Firstly, Pd catalysts often have a poor stability for

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