

Influence of co-metals on bimetallic palladium catalysts for methane combustion

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Abstract

The catalytic combustion of methane has been investigated over eight different bimetallic palladium catalysts, comprising the co-metals Co, Rh, Ir, Ni, Pt, Cu, Ag, or Au. The catalysts were characterized by TEM, EDS, PXRD, and temperature-programmed oxidation (TPO). It was found that a catalyst containing both Pd and Pt was the most promising, as it had a high activity that did not decline with time. The catalyst containing Pd and Ag was also a promising candidate, but its activity was slightly lower. For PdCo and PdNi, the co-metals formed spinel structures with the alumina support, with the result that the co-metals did not affect the combustion performance of palladium. For PdRh, PdIr, PdCu, and PdAg, the co-metals formed separate particles consisting of the corresponding metal oxide. These catalysts, except PdRh, showed a stable activity. For PdPt and PdAu, the co-metals formed alloys with palladium, and both catalysts showed a stable activity. © 2005 Elsevier Inc. All rights reserved.

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1. Introduction

During the last decades emission standards for combustion-related emissions have become more and more stringent. Hence, it has become increasingly important to find new ways of abating such emissions. Since it is difficult to decrease the pollutants to desirable levels with conventional flame combustion techniques, catalytic combustion has become a highly attractive combustion technique. Catalytic combustion is especially promising for decreasing emissions from the combustion of gaseous fuels such as natural gas or methane in gas turbines [1–3]. The low operation temperature accomplished by this combustion technique results in almost no thermal NO_x and ultra-low emission of CO and hydrocarbons.

The catalysts employed in catalytic combustion for gas turbine applications must be able to ignite the fuel at a temperature as low as 350 °C, which requires very ac-

tive catalysts. Supported palladium catalysts have an excellent activity for methane oxidation and have therefore been extensively used for catalytic combustion purposes [2,4]. However, palladium catalysts have some drawbacks. At 700–800 °C, depending on the support material and the atmosphere, palladium oxide decomposes into metallic palladium. When the catalyst is cooled, palladium oxide is reformed at a lower temperature than the decomposition temperature. This induces instabilities in the performance of the catalytic combustor. Other disadvantages with palladium catalysts have been observed at temperatures lower than the decomposition temperature. Even though the initial activity is high at these temperatures, the catalyst is not able to maintain the high conversion level during extended time periods; that is, the activity is not stable [5–7]. For this reason, the ignition of the methane will be increasingly difficult. Since palladium-based catalysts have such a high initial activity for methane combustion, it is desirable to improve the stability of the catalytic activity.

One way to increase the stability of the palladium catalysts could be to include a second metal in the catalysts,

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forming a bimetallic catalyst. Bimetallic catalysts have been used for several applications other than catalytic combustion and have been established to improve both the activity and selectivity of a great number of reactions [8,9]. The right combination of metals is important for producing the desirable effect. Coq et al. [10] explain the changed behavior of a bimetallic catalyst as an electronic effect, geometry effect, and/or a result of the presence of mixed sites, depending on the co-metal, the metal, and the reaction. However, it is still not fully understood how a bimetallic catalyst works.

Lately, bimetallic catalysts have been given more attention in catalytic combustion applications. Most reports consider methane oxidation over PdPt catalysts. The addition of platinum to a palladium catalyst has been shown to prolong the activity for methane combustion compared with monometallic palladium catalysts [5–7,11–13]. Likewise, PdAg has been reported to maintain its activity over time [5]. Narui et al. [6] attributed the superior combustion stability of PdPt to higher dispersion of supported particles and suppression of particle growth. Whether the activity is higher for the PdPt catalyst compared with the palladium-only catalyst is a debated question. Several authors have also considered the combination of Rh and Pd. However, the opinion regarding the catalytic properties of this catalyst is also divided. Ahlström-Silversand et al. [14] reported positive results for a PdRh catalyst in the temperature range of 300–400 °C, but Ryu et al. [15] and Oh and Mitchell [16] found that rhodium did not noticeably improve the catalytic activity of palladium in methane combustion. Addition of copper to the palladium catalyst has been reported to improve the resistance to sulfur [17].

The purpose of this study was to investigate the catalytic combustion of methane over a range of different compositions of bimetallic catalysts, which all consist of palladium as one of the active components. The co-metals were taken from groups 9–11 in the periodic table. The activity and the ability to maintain a stable activity for methane combustion of the various catalysts have been evaluated. Characterization techniques such as TPO, TEM, EDS, BET, and PXRD have been used to determine the change in morphology, element distribution, and thus properties when a second metal has been incorporated into the palladium catalyst.

2. Experimental

2.1. Catalyst preparation

Different palladium-based catalysts were prepared for this study; they are described in Table 1. All bimetallic catalysts were calculated to have a loading of 470 μmol metal/g catalyst powder, corresponding to the 5 wt% Pd in the reference catalyst (Pd-ref). Furthermore, the bimetallic catalysts were formulated to contain equal molar amounts of palladium and the co-metal, Co, Rh, Ir, Ni, Pt, Cu, Ag, or Au. Three monometallic catalysts, in addition to Pd-ref, have

Table 1
The nomenclature and the BET surface area of the different catalysts

Sample	Composition	BET surface area (m ² /g)
Pd-ref	5 wt% Pd//Al ₂ O ₃	102
PdCo	1:1 Pd:Co//Al ₂ O ₃	112
PdRh	1:1 Pd:Rh//Al ₂ O ₃	97
PdIr	1:1 Pd:Ir//Al ₂ O ₃	106
PdNi	1:1 Pd:Ni//Al ₂ O ₃	111
PdPt	1:1 Pd:Pt//Al ₂ O ₃	107
PdCu	1:1 Pd:Cu//Al ₂ O ₃	107
PdAg	1:1 Pd:Ag//Al ₂ O ₃	106
PdAu	1:1 Pd:Au//Al ₂ O ₃	97
½ Ni	Ni//Al ₂ O ₃	–
½ Pd	2.5 wt% Pd//Al ₂ O ₃	–
½ Pt	Pt//Al ₂ O ₃	–

also been prepared, ½ Pd, ½ Pt, and ½ Ni. These catalysts consist of only half the molar amount of metal (235 μmol metal/g catalyst powder), representing the concentration of the corresponding metal in the bimetallic catalysts. The amounts of metals in the catalysts were confirmed by EDS analysis. All catalysts were supported on γ -Al₂O₃ (Condea, PURALOX HP-14/150).

The alumina powder was impregnated with the metal/metals by the incipient wetness technique. The bimetallic catalysts were manufactured by co-impregnation of the two metals, through a mixture of a solution of Pd(NO₃)₂ with a solution containing a salt of the co-metal, Co(NO₃)₂, Rh(NO₃)₃, IrCl₃, Ni(NO₃)₂, Pt(NO₃), Cu(NO₃)₂, AgNO₃, or AuCl. The metal solution was dripped onto the alumina and was carefully mixed. This procedure was repeated twice, with a drying step at 300 °C for 4 h in between. The resulting samples were thereafter calcined at 1000 °C for 1 h and cooled at a rate of 20 °C/min to room temperature.

The catalyst powders were mixed with ethanol, and the resulting slurries were ball-milled for 24 h. Cordierite monoliths (400 cpsi, Corning), with ϕ 14 mm and length 10 mm, were then immersed in the slurry, followed by a drying step at 100 °C. This procedure was repeated until 20 wt% catalyst material was fixed on the monolith. The coated monolith was then calcined at 1000 °C for 2 h and cooled at a rate of 2 °C/min to room temperature.

2.2. Characterization

The surface areas of all catalyst powders were measured by nitrogen adsorption at liquid N₂ temperature in a Micromeritics ASAP 2010 instrument. The surface area was determined according to the Brunauer–Emmett–Teller theory. The samples were degassed in vacuum for at least 2 h at 250 °C before analysis.

The crystalline phases in the various catalysts were monitored by powder X-ray diffraction (PXRD), with the use of a Guiner–Hägg camera with a radius of 40 mm. The powder X-ray photographs were evaluated with the program package Scanner System [18] and obtained *d*-values associated

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