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The addition of alkali and alkaline earth metals to Pd/Al_2O_3 to promote methane combustion. Effect of Pd and Ca loading

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ABSTRACT

Methane catalytic combustion was studied on Pd/Al_2O_3 catalysts modified with alkali and alkaline earth metals (K, Na, Ca and Ba). Temperature-programmed reactions were performed in flow reactor on washcoated monolithic samples. CO chemisorption was carried out and BET surface area was measured in order to characterize the catalysts. Addition of alkaline metals was either beneficial or detrimental for methane oxidation, depending on the catalyst composition and pretreatment. High loading of alkaline modifiers and cooling in reaction mixture increased the light-off temperature of methane oxidation. However, promotion was achieved by doping with calcium after cooling in inert atmosphere. Furthermore, calcium doping was more beneficial in presence of NO, which inhibits the methane oxidation. Higher Pd loading enhanced CH_4 oxidation, whereas the effect of calcium depends on Ca and Pd loading. Indeed, the promotion by calcium was more pronounced on catalysts with 5% Pd than with 2.5% Pd. On 2.5% Pd catalyst, high Ca loading was detrimental for CH_4 oxidation. In contrary, on 5% Pd catalyst, even 1.51 wt% calcium (the highest loading used) induced promotion, which demonstrates a correlation between Ca:Pd ratio and promotion/inhibition effect. Samples with a mass ratio of 0.15 showed the best activity.

1. Introduction

Methane is a convenient fuel used as power source due to its relative abundance and low combustion emissions. Catalytic methane combustion has been widely studied in relation to gas turbine application. The development of vehicles powered by natural gas (NGV) has led to new interest and new challenges for this reaction. Emission of traces of methane must be as low as possible since methane is a powerful greenhouse gas. The high stability of the methane molecule and the low exhaust gas temperature of NGV make the task complicated. Despite a low sulfur tolerance, Pd-based catalysts received a lot of attention due to their high activity [1]. Since many studies identified palladium oxide as the active species, one of the challenges to maintain high activity of Pd/Al_2O_3 is to keep the palladium in its oxidized form. The addition of oxygen storage compounds such as cerium oxide has proven to facilitate reoxidation of Pd and to increase the temperature of decomposition of PdO [2,3]. The Pd oxidation state is also strongly influenced by the nature of the support [4,5]. In presence of oxygen, the oxidation degree of Pd is higher when Pd is supported on basic support such as ZrO_2, MgO than on acidic support such as SO_2-ZrO_2, SiO_2-Al_2O_3. However these studies demonstrated the non-monotonic relation between PdO stability and CH_4 oxidation activity. Instead, highly stable PdO formed on highly basic support is less reactive than PdO formed on moderately basic support such as Al_2O_3. PdO stability, which can be tailored by the acido-basic property of the support, should be enhanced in order to improve CH_4 oxidation but should not exceed an optimum level. Indeed, some studies have shown that a too strong Pd-O bond was detrimental for methane oxidation [5,6]. The approach in this work was to add alkali and alkaline earth metal in the catalyst formulation in order to generate a higher electron density on the palladium and to enhance the stability of PdO. The electronic promotion by alkali and alkaline earth metals is a technique that can modulate the noble metal-adsorbate interaction strength and was applied successfully to various reaction such as NO reduction by propene [7–9], selective hydrogenation of phenol [10] and anthraquinone [11], oxidation of CO [12] and water gas shift reaction [13,14] among others. The excess of electron brought by the alkaline dopant decreases the interaction of the noble metal with electron donor species and conversely increases the interaction of the metal with electron acceptor species, like oxygen. Various elements can be considered as electro-promoter with different alkalinity and reactivity, which offers a lot of possibility to control the PdO stability. In addition, the promoter content can readily be adjusted to

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tune the Pd-O strength.

In this study, several metals (K, Ca, Ba, Na) were incorporated to a 5 wt% Pd/Al_2O_3 catalyst in the same molar proportion and the study was extended with samples containing various Ca and Pd loadings. Catalysts were tested in flow reactor for the complete oxidation of methane and their performances were compared. The effect of the presence of NO, which competes with CH_4 for catalytic sites, was also studied.

2. Experimental

2.1. Catalyst preparation

Pd/Al_2O_3 was prepared by wet impregnation and freeze-drying. Alumina (Puralox SBa-200, Sasol) was calcined in air for 2.5 h at 750 °C and mixed with pure water (Advantage A10, Millipore) ($\approx 16\ mL_{water}/g_{alumina}$). The pH of the alumina slurry was adjusted to 4 with diluted HNO_3. The palladium precursor $Pd(NO_3)_2$ (Heraeus GmbH) was added in appropriate amount to obtain a loading of either 2.5 wt% or 5 wt% to 40 mL of pure water. The obtained precursor solution was added drop wise to the stirred alumina slurry. After ca. 2 h of stirring, the slurry was frozen with liquid N_2 and dried under vacuum (Scanvac Coolsafe, Labogene). The catalyst powder was then calcined in air at 550 °C for 2 h.

2.2. Preparation of promoted catalysts

The different alkaline promoters (K, Ca, Na, Ba) were introduced to the Pd/Al_2O_3 catalyst, prepared as described above, by incipient wetness method with solution of nitrate salts of K, Ca, Na and Ba respectively. The samples were dried overnight at 110 °C and subsequently calcined 2 h at 550 °C. The Ba loading was 5 wt.%, corresponding to 0.384 $mmol_{Ba}/g_{cat}$. Due to significant molar mass difference between promoters, the molar loading was identical for all promoted samples leading to different weight loadings, which are summarized in Table 1. Two sets of catalysts with various calcium loading, corresponding to a half and a quarter of the initial calcium loading were prepared.

2.3. Monolith preparation

For the flow reactor study, the prepared catalyst powders were deposited onto cordierite monoliths (length = 20 mm, Ø = 20 mm). The honeycomb-structured monoliths, with a channel density of 400 cpsi, were pre-calcined in air for 2 h at 600 °C. A slurry was prepared to dip and coat the monoliths. A binder (boehmite Disperal P2, Sasol) was mixed with the catalyst powder with a weight ratio of 20/80. The powder was then dispersed in a solution made of equal mass of pure water and ethanol. The solid-liquid ratio was initially 1–8 to obtain optimum solid particle concentration. The slurry was kept under vigorous stirring to allow homogeneous dispersion of the powder. The monoliths were dipped and dried slowly under a hot air flow. During this step, the monoliths were flipped and rotated to allow homogeneous wetting of the inner walls and homogeneous drying. After evaporation of the liquid and ensuring that no channel was clogged, the monoliths were dried under a hot air flow at 600 °C for 1 min. The dip-coating operation was repeated until a mass of ca. 550 mg washcoat was deposited.

Table 1
Summary and composition of the prepared catalysts.

Promoter	Name	wt.% Pd	Promoter loading (wt.%)	Promoter molar fraction (mmol/g Pd/Al_2O_3)
None	5Pd	5	0	0
Barium	5Pd-Ba	5	5	0.384
Calcium	5Pd-Ca	5	1.51	0.384
Potassium	5Pd-K	5	1.48	0.384
Sodium	5Pd-Na	5	0.87	0.384
Calcium	5Pd-Ca1/2	5	0.76	0.192
Calcium	5Pd-Ca1/4	5	0.38	0.096
None	2.5Pd	2.5	0	0
Calcium	2.5Pd-Ca	2.5	1.51	0.384
Calcium	2.5Pd-Ca1/2	2.5	0.76	0.192
Calcium	2.5Pd-Ca1/4	2.5	0.38	0.096

2.4. Catalyst characterization and CO chemisorption

The specific surface area was measured by N_2 physisorption at 77 K using the BET method. The powder sample was first degassed at 250 °C under vacuum for 3 h. The measurements were performed with a Micromeritics Tri-Star 3000 chemisorption instrument. CO chemisorption was performed after degreening on monolithic samples in a tubular quartz reactor (see below). After a reduction step at 450 °C for 30 min (2% H_2 in Ar, 1 L/min) the catalyst was cooled in argon to 25 °C. 100 ppm CO (1 L/min) was flown through the catalyst for 20 min and the effluent CO concentration was measured by a gas FTIR analyzer (Multigas 2030, MKS) at a frequency of 1 Hz allowing accurate integration of adsorbed CO. The adsorbed amount during the first pulse corresponds to weakly bound and chemisorbed CO. An argon flushing step of 8 min was performed to remove weakly bound CO and a second CO pulse was carried out (100 ppm, 10 min) to measure the amount of weakly bound CO that adsorb. The amount of chemisorbed CO was inferred from the two pulses as the amount adsorbed during the second pulse subtracted from the amount adsorbed during the first pulse.

2.5. Flow reactor setup

The flow reactor consists of a horizontal quartz tube electrically heated and wrapped in insulating quartz wool. The sample was placed in the back quarter of the tube (ca. 10 cm from the outlet) in order to facilitate homogenously mixed and heated inlet gas. Two K-type thermocouples were inserted through the back of the reactor. One was inserted inside the monolith to monitor the intra-monolith temperature. The other measured the temperature of the gas entering the sample, approximately 1 cm upstream of the monolith. The latter temperature was used as feedback for the temperature controller. A set of mass flow controllers (MFC) (Bronckhorst High Tech) was used to supply the gases. A controlled evaporator mixing system (Bronckhorst High Tech) was used to supply water vapor. The gas lines from the MFCs to the reactor inlet and from the reactor outlet to the analysis instruments were heated at 150 °C. The outlet gas passed through a Multigas 2030 FTIR analyzer (MKS) operating at 191 °C to analyze the effluent composition. The reactor operates at atmospheric pressure and argon was always used as carrier gas.

2.6. Catalyst degreening

All catalysts were pretreated in the flow reactor prior to CO chemisorption and activity test. However, the present work was divided in two stages that differ by catalyst degreening. The catalysts used for the promoter screening were first reduced for 30 min at 450 °C under a flow containing 2% H_2 in argon and then thermally aged to ensure the catalyst stability. The hydrothermal treatment carried out consisted of a lean-rich-lean cycle at 650 °C in presence of water vapor (5%). During the 1-h lean period, the gas flow (3 L/min) contained 500 ppm CH_4, 8% O_2 and 5% H_2O, balanced with Ar. Oxygen was turned off during the 30-min rich period (500 ppm CH_4, 5% H_2O in argon). This defines the degreening 1.

The catalysts used for the study focused on the effects of Pd and Ca