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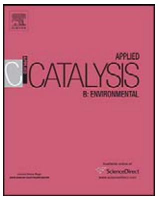

Effect of Pt/Pd ratio on catalytic activity and redox behavior of bimetallic Pt–Pd/Al_2O_3 catalysts for CH_4 combustion

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ABSTRACT

In the present work CH_4 combustion activity and reduction/oxidation behavior of bimetallic Pt–Pd/Al_2O_3 catalysts with constant Pd loading (2%, w/w) and different Pt/Pd atomic ratios (0, 0.10, 0.25 and 1) are investigated in the presence of alternated CH_4 lean combustion/CH_4-reducing pulses at 350 °C. In the fresh samples, according to XRD and CH_4-TPR measurements, Pd is always totally present as PdO and the CH_4 combustion activity is progressively promoted by Pt addition. On the other hand the reactivity scale is substantially changed ($Pt/Pd = 0.10 \geq Pt/Pd = 0 > Pt/Pd = 0.25 \gg Pt/Pd = 1$) after a conditioning treatment consisting of several reduction/oxidation cycles in CH_4-containing atmosphere, which has a progressively positive effect on decreasing the Pt content. Indeed, such a treatment results in a 20-fold catalytic activity enhancement for the monometallic sample (Pt/Pd = 0), whereas it has different effects on the bimetallic catalysts depending on the Pt/Pd ratio: for Pt/Pd = 0.10 the activity markedly increases up to the highest level among the tested catalysts (fresh and conditioned); for Pt/Pd = 0.25 the activity is substantially unchanged while for the Pt/Pd = 1 it is completely suppressed after the first CH_4-reducing pulse.

Such different behavior is mainly related to the influence of Pt on bulk reduction/re-oxidation properties of palladium; TPO data indicate a strong inhibition of Pt on Pd oxidation, which is completely suppressed for the Pt/Pd-1 catalyst, thus explaining the wide loss of activity after reduction for Pt/Pd-1 and confirming that PdO is the most active phase. In the case of the samples with Pt/Pd = 0.25 and Pt/Pd = 0.10 the inhibiting effect of Pt on Pd oxidation is progressively reduced, resulting in a fraction of PdO formed at the end of the conditioning process equal to 35% and 85% of total Pd, respectively.

In line with a Mars van Krevelen redox mechanism controlled by PdO surface reduction by CH_4, for the monometallic sample the activity enhancement upon conditioning is associated with an increase of bulk PdO reducibility, as determined by CH_4-TPR experiments. Such a correlation is not observed in bimetallic samples possibly due to the ability of metallic Pt to activate CH_4 under net reducing conditions (CH_4-TPR), which is suppressed under net oxidizing conditions (lean combustion).

1. Introduction

Lean burn natural gas vehicles (NGVs) represent a promising alternative to conventional diesel and gasoline vehicles thanks to the higher H/C ratio of the fuel which results in lower CO_2 emissions, and to the reduction of many pollutants [1] in the exhausts. Nevertheless, NGVs may suffer from the emissions of unburned CH_4, a strong greenhouse gas; in this context, catalytic combustion represents a promising way to reduce CH_4 emissions from NGVs' exhausts.

In the specific conditions of the exhausts (low temperature, 300–400 °C; presence of 10–15% of H_2O; large excess of O_2, low CH_4 concentrations, 500–1000 ppm) Pd supported catalysts are widely recognized as the most active in CH_4 combustion [1–4]; nevertheless, Pd catalysts suffer from deactivation problems due to the prolonged exposure to reaction conditions containing both H_2O and S-containing compounds which are strong poisons for Pd-based systems [2–14]. Some literature reports [15–18] suggest that the addition of Pt to Pd-containing catalysts leads to an improvement of catalyst stability under reaction conditions with respect to the Pd monometallic catalyst.

However, the influence of Pt on the catalytic activity of Pd–Pt bimetallic catalysts is still a debated issue. Some authors [15,16,19,20] claim that the addition of platinum to palladium results in increasing catalytic activity while for others [17,21] the effect of Pt is not straightforward. Persson et al. [17] found that the

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activity of the fresh Pt–Pd is lower compared to the activity of the monometallic Pd samples containing the same molar amount of palladium, although upon treatment under lean reaction conditions the two systems achieve similar activity levels. Testing catalysts with constant total metal loading (2.5%, w/w) and varying amounts of Pt and Pd, Strobel et al. [21] also observed a detrimental effect of Pt on fresh catalysts prepared via flame pyrolysis. Upon temperature cycles under reaction conditions up to 1000 °C, a reverse behavior was observed, the samples with small amounts of Pt being more active than the monometallic sample. This was attributed to the ability of Pt in increasing the sintering resistance of Pd particles. On the other hand a negative effect on activity was observed at high Pt loading, although in this case the corresponding decrease of Pd load might play some role. A promoting effect of Pt on Pd dispersion was also reported by Narui et al. [16].

In our previous works on Pd/Al_2O_3 catalysts [5,22], we found a positive effect of alternated reduction/re-oxidation cycles which resulted in a marked increase of the catalytic activity of the as-prepared samples up to a high and stable level and in recovering the activity losses during prolonged operation under H_2O and S-containing atmosphere.

In this work, we investigate Pt–Pd bimetallic catalyst with different Pt/Pd atomic ratios but constant Pd loading (2%, w/w). The effect of Pt/Pd ratio on catalytic activity in CH_4 combustion was investigated in the presence of alternated reduction/re-oxidation cycles; attention was focused on the correlation between the catalytic activity evolution during the repeated cycles and the influence of platinum amount on palladium reduction–oxidation behavior.

2. Experimental

2.1. Catalysts preparation

Bimetallic Pt–Pd catalysts with constant Pd loading (2%, w/w) and different Pt/Pd atomic ratios (0, 0.10, 0.25, 1) were obtained by a dry co-impregnation technique of a commercial Al_2O_3 (Sasol Puralox SBA 140) calcined at 950 °C for 10 h (S.A. = 100 m^2/g, specific pore volume 0.49 cm^3/g, phase composition θ-Al_2O_3 phases with traces of γ): the procedure consists in the preparation of a water solution containing both the $Pd(NO_3)_2$ and the $Pt(NO_3)_2$ in appropriate amounts to achieve the nominal loading in a single step impregnation; a volume of the prepared solution equal to the total pore volume of the calcined alumina was then dropped on the support. The catalysts were dried at 110 °C for 2 h and calcined at 600 °C in air for 10 h.

In the following the investigated samples are identified as Pt/Pd-*X*, with *X* = 0, 0.10, 0.25, 1, accordingly to the nominal Pt/Pd atomic ratios.

2.2. Catalysts characterization

The experimental Pd and Pt loadings were determined by atomic absorption method on a Varian AA110 apparatus. XRD patterns were recorded on a Philips (PW 10507/70) powder diffractometer using a vertical goniometry and the Cu Kα radiation ($\lambda_{K\alpha}$ = 0.1518 nm). Specific surface areas were determined by nitrogen adsorption at 77 K using a Micromeritics Tristar apparatus according to the Brunauer–Emmet–Teller (BET) method. Metal dispersion was measured by H_2 chemisorption analysis, carried out on a Micromeritics AutoChemII instrument; the catalysts were reduced in 50 N cm^3/min of H_2 in Ar at 500 °C for 1 h; after a 2 h Ar purge the temperature was decreased. 5% H_2 in Ar pulses (0.961 ml loop) were injected at regular interval time at 70 °C to avoid the problem of Pd-hydrides formation [23]. A H/Pd = 1/1 and H/Pt = 1/1 stoichiometry were assumed for H_2 chemisorption on palladium and platinum.

2.3. Catalytic activity tests

The prepared catalysts were tested in a fixed bed tubular quartz microreactor (I.D. = 7 mm) operating at atmospheric pressure, placed within an electrically heated furnace. The catalytic bed consists of 60 mg of fine catalytic powder (74–105 μm) diluted with 60 mg of quartz powder of the same particle size. The temperature was monitored by a K-type thermocouple placed inside the catalytic bed. Composition of reactants and products at the outlet of the reactor was determined by a mass spectrometer with quadrupole detector (Balzers QMS 422) and was periodically verified through a HP6890 GC system. N_2 was used as an internal standard for gas-chromatographic analyses.

The investigated catalysts were tested according to the following experimental procedure:

> Alternated lean combustion/CH_4-reducing pulses at constant temperature (350 °C): the catalysts were operated for 30 min under lean combustion conditions (0.5% CH_4, 4% O_2, 1% H_2O, 2% N_2, He at balance, 150 N cm^3/min, GHSV = 150,000 Ncm^3/g/h) at 350 °C; then a 30–40 s purge (He + 5% N_2) was performed to allow the desorption of species adsorbed on catalytic surface and to purge the dead volumes. After the purge the reaction atmosphere was switched to reducing conditions (0.5% CH_4, 1% H_2O, He at balance, 150 Ncm^3/min, GHSV = 150,000 Ncm^3/g/h) for 120 s, keeping constant the temperature at the same level. After another purge, the lean combustion conditions were finally restored. Water was added to the feed by saturation of a stream of helium, its concentration was controlled by GC and regulated through the He flow rate to the saturator to compensate for temperature and pressure variations. Argon was always fed with CH_4 and used as a tracer to clearly identify the actual switch between the lean combustion conditions or the CH_4-reducing pulse and the purge. In the following samples underwent to the multiple alternated reduction/re-oxidation cycles according to the explained procedure will be named *conditioned* catalysts while the as-prepared samples will be referred as *fresh* catalysts.

2.4. Reduction/oxidation tests

The reduction/oxidation behavior of the investigated catalysts was studied by means of the following procedures:

(i) CH_4 temperature programmed reduction (CH_4-TPR): the catalysts were exposed to reducing atmosphere (0.5% CH_4, 1% H_2O, He at balance, 150 Ncm^3/min, GHSV = 150,000 Ncm^3/g/h) Gas composition at the outlet of the reactor was determined by a mass spectrometer with quadrupole detector (Balzers QMS 422) and periodically verified through a HP6890 GC system.

(ii) Temperature programmed oxidation (TPO): four cycles of TPO were performed on a Micromeritics AutoChemII instrument, exposing the catalysts to a 2% O_2, in He atmosphere, cycling the temperature between room temperature and 900 °C.

(iii) Oxidation under reactions conditions at constant temperature 350 °C, i.e. the same temperature of the activity test: the catalysts were exposed to lean combustion conditions (0.5% CH_4, 4% O_2, 1% H_2O, 2% N_2, He at balance, 150 Ncm^3/min, GHSV = 150,000 Ncm^3/g/h) for different time intervals, ranging from 0 s to 30 min; the amount of PdO formed was revealed by a CH_4-TPR (as described at point (i)) up to 350 °C, performed after a rapid quenching in inert atmosphere down to 200 °C.

Quantification of PdO was performed assuming the following stoichiometry:

$$4PdO + CH_4 \rightarrow 4Pd + CO_2 + 2H_2O \quad (1)$$