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Activation process of Pd/Al_2O_3 catalysts for CH_4 combustion by reduction/oxidation cycles in CH_4-containing atmosphere

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ABSTRACT

In this work, the effect of a conditioning process, consisting of several alternated CH_4-lean combustion/CH_4-reducing pulses at 350 °C, was investigated over Pd/Al_2O_3 catalysts with different Pd loadings (1, 2 and 4 w/w%) prepared from Cl-free precursors. Such a treatment resulted in a one order of magnitude activity enhancement and in the achievement of stable catalytic performances in all the investigated systems. The activity enhancement was associated with an increase in PdO reducibility, as revealed by the comparison of CH_4-TPR profiles before and after the conditioning process. Characterization studies showed that negligible or minor (for the 1% w/w Pd sample) modifications of Pd dispersion occurred upon conditioning, thus ruling out a significant effect of particle size variations on the observed activity enhancement. TPR, FT-IR and XRD measurements showed that palladium is completely oxidized upon conditioning, PdO is less crystalline than in the fresh catalyst likely due to the low oxidation temperature in the conditioning cycles but high activity was retained upon re-crystallization of PdO at 600 °C. FT-IR characterization revealed that conditioning results in a weakening of Pd–support interactions, which possibly originated from the interaction of the acidic Pd precursor with basic hydroxyls of the alumina surface, which acts as germination center during the impregnation step. Such a weakening of Pd–support interactions is likely responsible for the observed activity/reducibility enhancement.

1. Introduction

Natural gas vehicles (NGVs) operated under lean burn conditions guarantee a higher combustion efficiency and minimize the typical products of incomplete combustion, such as soot, CO and volatile organic compounds (VOCs) in addition to CO_2 emissions [1,2]. On the other hand, CH_4 is a strong green house gas, with a global warming potential higher than that of the CO_2; thus, large emissions of CH_4 would represent an environmental problem. Catalytic combustion of methane represents a promising way to reduce unburned CH_4 from the NGVs emissions. In the exhaust conditions, i.e. low temperatures, low CH_4 concentrations and presence of varying concentrations of O_2, H_2O, CO_2, NO_X and SO_X [3], the superiority of Pd-based catalysts has been widely recognized and their performances have been extensively investigated [4]. Nevertheless, many factors controlling the CH_4 combustion activity of Pd-supported catalysts are still debated [1–4].

Several studies [5–13] mentioned large enhancements of the activity of Pd-supported catalysts with time on stream before achieving a steady state behavior. It is now widely admitted that some activation periods reported in the early studies [5–8] are related to the slow removal from the catalyst of residual chlorine, coming from Pd salt precursors or from the support impurities [14–16], which has a strong deactivating effect on Pd catalysts [14,17]. However, chlorine removal is not the only cause of activity enhancement since time-dependent activation phenomena were reported also for chlorine-free catalysts. Garbowski et al. [9] correlated the increase in the catalytic activity of Pd/Al_2O_3 catalysts, observed after reaction tests at 600 °C under both fuel-rich and fuel-lean CH_4/O_2 mixture, to a surface reconstruction of palladium particles under the influence of the reactants; on the basis of spectroscopic techniques, they observed that the Pd(1 1 1) planes, prevailing on the fresh catalysts, disappear after reaction while Pd(1 0 0) and Pd (1 1 0) planes form.

Some authors [18,19] attributed the activation of palladium catalysts to the roughening of the surface occurring during reaction conditions. Others reported that CH_4 combustion activity is influenced by palladium particle size [1–5,20]; a high dispersion of palladium oxide, giving an intimate contact with the support, stabilizes PdO against decomposition and reduction leading to a lower specific activity according to a Mars–Van Krevelen redox mechanism for CH_4 oxidation [20].

As a whole, the effect of the presence of contaminants (chlorine), Pd reconstruction, metal–support interactions and Pd particle size may be responsible for the wide variation in TOFs

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reported in the literature [5,20–25] for CH_4 combustion, spanning more than two orders of magnitude [24].

Such a lack of quantitative understanding of the factors controlling CH_4 combustion activity of palladium catalysts can bias investigations into the role of preparation variables such as the choice of the support. Besides, from a practical point of view, uncontrolled detrimental effects can result in relatively poor CH_4 conversion performances of palladium catalysts.

In this respect, in previous works [3,26], we have mentioned alternated reduction/re-oxidation cycles under CH_4-containing atmosphere as an effective activation method to obtain high conversion performances over conventional Pd/Al_2O_3 catalysts prepared by a simple dry impregnation technique. Such a conditioning treatment resulted in a marked enhancement of the catalytic activity of the fresh samples, up to the achievement of steady state behavior; the final TOFs reported in Ref. [3] are comparable to the highest TOF values reported in the literature by Ribeiro et al. [24].

In this work, we investigated in detail the conditioning process of Pd/Al_2O_3 catalysts, consisting of alternated CH_4-lean combustion/CH_4-reducing pulses at 350 °C. The scope was to gain insight into the modifications responsible for the activity enhancement, thus providing a rational to develop practical activation methods. Three catalytic systems having different Pd loadings (1, 2 and 4% wt) were prepared starting from Cl-free Pd precursors. The activity evolution during the conditioning process was carefully monitored, and the different samples were characterized before and after the conditioning process by H_2 chemisorption, CH_4-TPR, XRD and FT-IR techniques.

2. Experimental

2.1. Catalysts preparation

Palladium supported on alumina catalysts were prepared starting from a commercial alumina (Sasol Puralox SBA140) calcined at 950 °C for 10 h in air in order to stabilize structural and morphological properties. A θ-Al_2O_3 (with traces of γ) phase was obtained with a specific surface area of 100 m^2/g and a pore volume of 0.49 cm^3/g. Different palladium loadings (1, 2 and 4 w/w%) were added by a dry impregnation technique, starting from an aqueous solution containing the $Pd(NO_3)_2$ precursor (Alfa Aesar) in appropriate amounts. The prepared catalysts were dried at 110 °C for 2 h and treated at 600 °C for 10 h in air before any testing.

2.2. Catalysts characterization

The experimental Pd loadings were determined by atomic absorption analysis (AAS) on a Varian AA110 apparatus. Palladium dispersion was estimated by H_2 chemisorption measurements on a Micromeritics AutoChemII instrument: the catalysts were first reduced in 5% H_2 in Ar stream at 500 °C for 1 h; then, after a 2-h Ar purge at 500 °C, the temperature was decreased to 70 °C and 5% H_2 in Ar pulses (0.961 ml) were injected at regular interval times. A H/Pd = 1/1 stoichiometry was assumed. Palladium dispersion was estimated for both the *fresh* samples, i.e. the calcined at 600 °C in air sample before any testing, and the catalysts underwent repeated redox cycles at 350 °C, according to the procedure illustrated in the next section, hereafter called *conditioned* catalysts.

The mean Pd particle diameters d_P (nm) were estimated from dispersion data using the following expression derived from hemispherical particles [22]:

$$d_P = \frac{6 \cdot C_a \cdot PM \times 10^9}{\rho \cdot D \cdot N_{av}}$$

with C_a concentration of surface metal atoms, equal to 1.27×10^{19} atoms/m^2, PM Pd atomic mass, ρ Pd volumetric mass equal to 12.02×10^6 g/m^3, D metal dispersion and N_{av} Avogadro number [22].

XRD patterns were recorded on a Philips (PW 1050/70) powder diffractometer using a vertical goniometer and the Cu Kα radiation ($\lambda_{K\alpha}$ = 0.1518 nm). XRD patterns were collected on the fresh and conditioned 2% Pd/Al_2O_3 sample and over the conditioned sample subsequently exposed to dry lean reaction conditions (0.5% CH_4, 4% O_2, N_2 at balance) at 600 °C for 5 h (called conditioned-600).

FT-IR experiments were performed on the fresh 2% Pd/Al_2O_3 catalyst and on the same conditioned sample. For FT-IR studies, pure alumina support and 2% Pd on alumina-powdered catalysts were pressed in self-supporting disks (average weight 20 mg), outgassed at 500 °C, or reduced in pure hydrogen (400 torr) and outgassed at 500 °C directly in the IR cell connected to a gas manipulation apparatus. CO adsorption was performed at liquid nitrogen temperature (around 10 torr CO gas, "full coverage"). FT-IR spectra were recorded, outgassing at increasing temperature in the range −130 °C to room temperature at decreasing CO coverage.

2.3. Catalytic activity test

Catalytic activity tests were performed in a fixed-bed quartz microreactor (ID = 7 mm) placed inside an electrically heated furnace. The reactor was loaded with 60 mg of fine catalytic powder (74–105 μm) diluted with quartz of the same particle size, with a different dilution ratio depending on Pd loadings (Pd/quartz equal to 1 for the 1% and 2% Pd catalysts and to 3 for the 4% Pd sample in order to minimize temperature gradients). The catalyst temperature was monitored using a K-type thermocouple located in the center of the catalytic bed. Composition of the reactants and products at the outlet of the reactor was monitored by a mass spectrometer with a quadrupole detector (Balzers QMS 422). Periodical GC analyses were performed with a HP6890 Systems in order to calibrate CH_4, CO_2 and O_2 MS signals and to more precisely quantify CH_4 conversion.

The following experiments were performed on the prepared samples:

- alternated redox cycles under CH_4-containing atmosphere at constant temperature (350 °C): the catalysts were operated for 30 min under CH_4-lean combustion conditions (0.5% CH_4, 4% O_2, 1% H_2O, 2% N_2 and He at balance, GHSV = 150,000 $Ncm^3/g_{cat}/h$, atmospheric pressure); then, after a 30–40 s inert purge (5% N_2 in He), performed to allow the desorption of species from the catalytic surface, the reaction atmosphere was switched to rich conditions, exposing the catalysts for 2 min to a CH_4-reducing stream (0.5% CH_4, 1% H_2O, He at balance, GHSV = 150,000 $Ncm^3/g_{cat}/h$, atmospheric pressure); after another purge, the lean conditions were restored. The procedure was repeated several times during the conditioning process.
- CH_4-TPR: the catalysts were exposed to a reducing stream (0.5% CH_4, 1% H_2O, He at balance, GHSV = 150,000 $Ncm^3/g_{cat}/h$, atmospheric pressure), and the temperature was raised up to 500 °C and down to RT at 15 °C/min.

3. Results

3.1. Conditioning process

Fig. 1 shows the time evolution of CH_4, CO_2 (ppm) and H_2 (a.u.) outlet concentrations during one typical lean combustion/