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Short Communication

Performance of Pd supported on mesoporous molecular sieves on methane combustion

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ABSTRACT

The performance of Pd-based catalysts supported on mesoporous molecular sieves with different pore arrangement (MCM-41 and MCM-48) was investigated for methane combustion. All molecular sieves showed to be thermally stable, evidencing the suitability of these materials as support for high temperature processes and motivated the efforts to exploit their use. Reaction data showed that silicate-based samples rendered more active catalysts than those prepared on aluminosilicate; activity was affected by monodimensional or three-dimensional pore arrangement. The use of molecular sieves in proton form led to an increase in the reaction rate in relation to the sodium form.

1. Introduction

Catalytic combustion of methane is an effective route for energy production from natural gas as well as for the reduction of polluting gases [1]. In the latter case, the process is tremendously advantageous to decrease the NO_x emission levels from natural gas-fueled gas turbines as the reaction is allowed to proceed at a lower temperature if compared to the conventional flame combustion. Furthermore, catalytic combustion is also suitable to abate unburned methane from natural gas vehicles (NGV), which is rather relevant considering that methane is a powerful greenhouse gas [1].

A wide variety of catalysts have been tested over the last decade but palladium-based systems have been found to be the most active [2,3]. Despite the good performance achieved over catalysts prepared on conventional oxide supports, especially alumina, other materials have been studied. The extensive investigations currently presented in the literature are not only motivated by the need to overcome some process requirements, particularly those related to thermostability, but also to better understand the factors that determine the catalytic reaction. The contributions dedicated to exploit ordered materials revealed that the use of zeolites produces very active systems for methane combustion at low temperatures. Mordenite, ZSM-5, SAPO-5, SAPO-11, SAPO-34 can be listed among those evaluated so far [4–9]. Relevant experimental and theoretical studies carried out with ZSM-5 indicated that their acid properties may promote the activation of methane by facilitating the cleavage of C–H bond.

Mesoporous molecular sieves, on the other hand, have attracted less attention so far but some studies on the behavior of SBA, HMS and MCM-41 as catalyst supports for methane combustion have been reported elsewhere [4,10–13].

We have reported that both silicate and aluminosilicate MCM-41 are adequate supports for methane oxidation catalysts but that the addition of lanthanides decreases the catalytic activity [11]. Nevertheless, any influence of the structural arrangement of mesoporous molecular sieves on the catalysts performance has not been addressed in the open literature while some recent studies claim that the surface acidity may play an important role in determining their activity [12].

This contribution aims at evaluating the performance of Pd-based catalysts supported on mesoporous molecular sieves with different porous structures for methane combustion, particularly MCM-41 and MCM-48. Attention is also given to the possible effects brought about by their pore arrangement and the use of molecular sieves in their protonic form.

2. Experimental

2.1. Molecular sieve syntheses

The MCM-41 and [Al]-MCM-41 molecular sieves were synthesized according to the method described by Pastore et al. [14,15].

Cetyltrimethylammonium bromide (CTABr) was used as structure's template, sodium silicate (Nuclear, $Na_2SiO_3 \cdot 5H_2O$) and aluminum isopropoxide ($Al[OCH(CH_3)_2]_3$, 98+% Alfa Aesar) were, respectively, the

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silicon and aluminum source; the pH (10.80) was adjusted with acetic acid (98% Merck). The gels composition were:

Na_2O: SiO_2: $0.25(CTA)_2O$: 0.5HBr: $100H_2O$

Na_2O: $0.0167Al_2O_3$: SiO_2: $0.25(CTA)_2O$: 0.5HBr: $100H_2O$

The template of the molecular sieves as synthesized was eliminated in a Soxhlet system with 0.30 mol L^{-1} HCl solution in 50/50 ethanol/heptane at 363 K, over a period of 40 h. Next, the samples were thermally treated at 773 K, following a heating rate of 5 K min^{-1}, under dry argon. After reaching the calcination temperature, the treatment was then maintained for 20 h under dry oxygen.

After calcination, a part of the [Al]-MCM-41 and MCM-41 was ion-exchanged three times with NH_4OH (0.03 mol L^{-1}, 10 mL solution per g of molecular sieve) at 333 K by 24 h, to prepare the proton form (H-[Al]-MCM-41 and H-MCM-41).

MCM-48 was synthesized following the procedure described by Xia and Mokaya [16]. In this case, the structure template was cetyltrimethylammonium hydroxide (CTAOH), prepared in the laboratory from cetyltrimethylammonium bromide (CTABr), and the silica's source (silica Aerosol 200, Degussa) was added slowly under magnetic stirring. The gel composition was:

SiO_2: 0.28CTAOH: $42H_2O$

This gel was aged under stirring at room temperature by 2 h. Then, it was transferred to a Teflon-lined stainless steel autoclave and submitted to a hydrothermal treatment at 408 K by 24 h. The solid was washed with distilled water until washings were neutral. The template was eliminated by calcination at 773 K, following a heating rate of 5 K min^{-1}, under dry oxygen flow by 10 h.

A commercial sample of γ-Al_2O_3 (238 m^2/g) was taken as reference support to prepare Pd-based catalysts. Prior to use, alumina was calcined in air at 823 K for 3 h.

2.2. Catalyst preparation

Palladium catalysts were prepared by wet impregnation. The molecular sieves were slurried with an acetone solution of the necessary quantities of the precursors in a rotary evaporator at room temperature for 6 h. Palladium acetate (Aldrich, 98%) was used as metal precursor; all catalysts were prepared so as to obtain a palladium loading of 1 wt.%. Afterwards, the excess of acetone was evaporated under vacuum. The powders were first dried overnight at 383 K and then calcined under dry oxygen flow at 773 K for 4 h, at a rate of 5 K min^{-1} [17].

The catalysts were labeled following their corresponding support: Pd/[Al]-MCM-41, Pd/H-[Al]-MCM-41, Pd/MCM-41, Pd/H-MCM-41, Pd/MCM-48 and Pd/Al_2O_3.

2.3. Characterization of the molecular sieves and catalysts

2.3.1. X-ray diffraction (XRD)

The samples, both supports and catalysts, were analyzed by powder X-ray diffraction (Shimadzu, XRD 6000), using Cu Kα radiation (λ = 1.5406 Å). The diffractometer was operated at 40 kV, 30 mA at a scan rate of 2° min^{-1} and a count time of 0.6 s. XRD patterns were recorded in the range of 1.4–50° (2θ).

The thermal stability of all catalysts was also analyzed by XRD following an in situ thermal treatment up to 1373 K.

Spent catalysts, which were collected after being used on methane combustion, were also additionally analyzed by XRD under the same experimental conditions previously used for the fresh catalysts.

2.3.2. Chemical analysis

The chemical composition was determined in a Perkin-Elmer 300DV inductively coupled plasma-atomic emission spectrometer (ICP-AES). A standard ICP torch and peristaltic pump were used for all measurements and deviation is considered in the order of 2 to 5%.

The sample decomposition consisted in heating the catalysts at 1073 K at a rate of 10 K min^{-1} for 6 h. Approximately 30 mg of catalysts were weighed in three different melters. The samples were dissolved in 3 mL HF (48 wt.%, Merk), 3 mL HNO_3 (65 wt.%, Quimex) and 2 drops of $HClO_4$ (70 wt.%, Aldrich) at 423 K. This process was repeated twice again after acid evaporation. Finally, the rest was dissolved in aqua regia and put aside until dryness. An aqueous solution of HNO_3 (1% v/v) was added in the materials and then transferred to a volumetric flask.

2.3.3. Porosity and surface area

The porosity of samples was characterized by nitrogen adsorption. The adsorption isotherms were determined at 77 K in a ASAP 2010 Micromeritics apparatus. Prior to analyses, the samples were degassed at 393 K, until a residual pressure of 10^{-4} Pa. The specific surface areas were determined by BET method while the pore size distribution and the average pore size were obtained using the BJH method.

2.3.4. UV-visible diffuse reflectance spectroscopy (DRS)

DR spectra of all catalysts were recorded in the 200–800 nm range in a Varian Cary 500 spectrophotometer, using the bare molecular sieves as reference.

2.3.5. Surface acidity (TGA)

The acidity properties were estimated by adsorption of *n*-butylamine [18,19]. Firstly, the samples were treated in situ at 773 K under a 30 mL min^{-1} nitrogen flow for 1 h and then cooled down to 423 K, temperature at which the alkylamine was admitted to the catalysts. Adsorption was allowed to occur for 30 min in order to complete saturate the acid sites of the samples. Finally, the reactor was purged at the same temperature with nitrogen aiming at removing the physically adsorbed amine. The quantification was performed by monitoring the mass loss during desorption in a thermobalance SDT Q600 from TA Instruments. The analyses were carried out following a heating rate of 20 K min^{-1} up to 800 K under nitrogen.

2.3.6. Catalytic activity

Methane combustion reaction was performed at atmospheric pressure in a conventional system with fixed bed reactor. Reaction products were monitored on-line by a HP 6890A chromatograph. The experiments followed the same protocol described elsewhere [11,20]. Basically, a reaction gas mixture with an $O_2/CH_4 = 4$ was fed into the catalyst at $W/Q = 0.06$ g s cm^{-3}. Prior to reaction, the catalysts were reduced in situ at 573 K for 2 h under pure hydrogen. The activity data were collected just after the catalysts have achieved the steady-state at 773 K. In order to avoid temperature gradients in the reactor, silicon carbide was added for dilution ($w_{cat}/w_{dil} = 1/10$). The temperature of the catalyst bed was measured by a thermocouple placed in a small cavity on the reactor outside wall.

3. Results and discussion

The XRD patterns of the synthesized samples are presented in Fig. 1. The material corresponding to Fig. 1a exhibits three low angle diffraction peaks, which can be indexed as the (100), (110) and (200) planes associated with the hexagonal arrangement of mesoporous molecular sieve MCM-41. However, the ion exchange by H^+ to prepare H-[Al]-MCM-41 (Fig. 1b) presented an X-rays diffractogram where only the first diffraction peak can be noticed, indicating that the structure was somewhat affected upon ion exchange step and, as a consequence, the hexagonal arrangement of pores is not perfectly organized. Finally, all samples presented an amorphous halo at Bragg angles within 15–30° attributed to the amorphous walls of the MCM-41 monodimensional channels. The peaks corresponding to the (110) and (200)