



The promoting effect of cerium on the characteristics and catalytic performance of palladium supported on alumina pillared clays for the combustion of propene



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ABSTRACT

The aim of this work was to study the effect of the presence of various amounts of cerium on palladium supported on an alumina pillared clay for the catalytic oxidation of propene. For this purpose, a montmorillonite clay was intercalated and pillared with alumina, then used as a support for palladium. The palladium loading was selected on the basis of previous findings from our group. Cerium loadings of between 0 and 1 wt.% were added after the incorporation of palladium onto the support. The resulting catalysts were characterized by nitrogen physisorption at -196°C , X-ray powder diffraction (XRD), temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS). The results obtained suggest that the added Ce partially blocks the microporous volume of the metal catalyst and interacts with the Pd to form new metallic species that enhance the behavior of the initial catalyst in the oxidation of propene.

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1. Introduction

The increasing demand for green energy and the coming into force of more stringent regulations regarding exhaust emissions have been the driving force behind much of the recent research into catalytic combustion technologies. The benefits of catalytic combustion with respect to its traditional thermal counterpart are well established and consist mainly in the formation of lower amounts of by-products due to the lower operating temperatures and higher efficiency [1]. In this respect, although noble metal-based catalysts are well-known for their high performance in the catalytic combustion of hydrocarbons, several studies have investigated the possibility of enhancing the performance of supported noble metal catalysts by adding suitable promoters [2,3].

Pillared InterCalated Clays (PILCs) are an interesting class of two-dimensional microporous materials that can be prepared by the intercalation of inorganic or organic compounds between the silicate layers of clay minerals, which results in an increased basal spacing, pore volume and specific surface area. Due to their textural properties and acidity characteristics, these solid materials are very attractive for adsorption and catalytic applications [4]. Unfortunately, PILCs are not sufficiently stable and tend to collapse, with a resulting loss of textural properties and catalytic performance, at

high temperatures. As such, the thermal stability of the pillars must be increased to avoid the sintering of pillared clays. One way to achieve this goal is to introduce mixed-oxide pillars, such as Al–Ga, Al–Si, Al–Zr, Al–Fe, and Al–Cu, amongst others [5]. Another appropriate way to overcome this problem is to add a rare earth metal. Thus, Sterte [6] found that the incorporation of lanthanide elements during preparation of the intercalating agent resulted in materials whose basal spacing was greater than that of conventional materials. Likewise, an improvement in the thermal stability of Al-pillared clays was reported by Tokarz and Shabtai [7], who prepared pillared clay catalysts by first exchanging the clay with Ce^{3+} or La^{3+} , then exchanging these clays with refluxed, partly hydrolysed Al(III) solutions. The addition of a rare earth metal improves both the thermal stability and the adsorptive and catalytic properties of the pillared materials. CeO_2 has been reported to be able to store and liberate oxygen as a result of the redox properties of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ pair, which can result in good performance for the combustion of Volatile Organic Compounds (VOCs). Supported palladium catalyst is known to be effective for the combustion of VOCs and many research works investigate the possibility of enhancing the catalytic activity by using CeO_2 as suitable support or adding this oxide as promoter to the supports. The properties of the supports are modified by the presence of CeO_2 . Farrauto et al. [8] reported a beneficial effect of the presence of CeO_2 as support on the stabilization of PdO. The effect of CeO_2 addition to alumina-support is studied by various authors [9–13] on supported catalysts for the methane combustion. Similarly, various authors have reported that the presence of Ce in Pd/Al-pillared clays produces a substantial decrease in the

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temperature required for the complete oxidation of benzene [14,15]. In all these studies the properties of the supports are modified and after wet impregnation with a palladium solution, new catalysts are obtained. In the present work, various amounts of cerium are added to a supported palladium catalyst and the characteristics and catalytic performance on the combustion of propene studied. The catalyst was selected from a previous work [16] considering the possibility of modification of the catalytic behavior by the presence of a promoter.

2. Experimental

2.1. Catalyst preparation

The starting material was a montmorillonite from Tsukinuno, supplied by the Clay Science Society of Japan. The raw clay was pillared with alumina according to a conventional pillaring procedure [17], then used as catalytic support. The supported palladium catalyst was prepared by wet impregnation of the support with a solution of palladium ($\text{Pd}(\text{NO}_3)_2$, palladium(II) nitrate solution, 10 wt.% in 10 wt.% HNO_3 , Sigma–Aldrich) to obtain a material with a metal loading of 0.1 wt.%. The metal salt/clay slurry was evaporated under reduced pressure in a rotavapor and the resulting solid dried at 120 °C for 16 h before being calcined in air at 500 °C for 4 h to form the final supported catalyst. The modified catalysts were prepared by treating 5 g of the Pd catalyst with 50 cm^3 of aqueous $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solutions (99.99%, Sigma–Aldrich) to obtain loadings of between 0 and 1 wt.%. The metal salt/catalyst slurries were evaporated under reduced pressure in a rotavapor and the resulting solids dried at 120 °C for 16 h before being calcined in air at 500 °C for 4 h to form the final modified catalysts. The catalytic series are referred to as wt. CePd, where wt. indicates the cerium content.

2.2. Catalyst characterization

Nitrogen adsorption experiments (Air Liquide, 99.999%) at –196 °C were performed using a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyser). All samples (0.2 g) were degassed for 24 h at 200 °C at a pressure lower than 0.133 Pa. The Langmuir surface area (S_{Lang}) was calculated from nitrogen adsorption data over the relative pressure range 0.01–0.05, considering a nitrogen molecule cross-sectional area [18] of 0.162 nm^2 . The total pore volume (V_p) was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99, assuming that the density of the nitrogen condensed in the pores is equal to that of liquid nitrogen at –196 °C (0.81 g/cm^3) [18]. The micropore volumes ($V_{\mu\text{p}}$) were calculated using the Dubinin–Radushkevich equation [19] over the relative pressure range 0.01–0.034.

After extraction by acid digestion, the metal contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian Vista-MPX instrument. X-ray diffraction (XRD) patterns of nonoriented powder samples were obtained using a Siemens D-5000 diffractometer fitted with a Ni-filtered $\text{Cu K}\alpha$ radiation source, at 40 kV and 30 mA. Temperature-programmed reduction (TPR) studies were carried out using a Micromeritics TPR/TPD 2900 instrument. An initial pre-treatment with N_2 (Air Liquide, 99.999%) was carried out at 150 °C for 90 min, at a heating rate of 10 °C/min, under a flow of 30 cm^3/min , to condition the samples. TPR tests were then carried out from room temperature up to 800 °C, at a heating rate of 10 °C/min, under a total flow of 30 cm^3/min (5% H_2 in Ar, Air Liquide). Water and other compounds that might be formed during metal reduction and precursor decomposition were retained by a molecular sieve trap. Hydrogen consumption was measured using a thermal conductivity detector (TCD).

X-ray photoelectron spectroscopy (XPS) analyses were performed using an SSI X-probe (SSX-100/206) spectrometer from Surface Science Instruments (USA). The analysis chamber was operated under ultrahigh vacuum at a pressure close to 5×10^{-7} Pa, and the sample was irradiated with monochromatic $\text{Al K}\alpha$ (1486.6 eV) radiation (10 kV; 22 mA). Charge compensation was achieved using an electron flood gun adjusted to 8 eV and placing a nickel grid 3.0 mm above the sample. The pass energy for the analyzer was set at 150 eV for both wide and narrow scans, and an area of approximately 1.4 mm^2 was analyzed. Under these conditions, the full width at half-maximum (fwhm) of the $\text{Ag 3d}_{5/2}$ peak from a silver standard sample was about 1.6 eV. For these measurements, the binding energy (BE) values were referred to the C-(C,H) contribution of the C 1s peak at 284.8 eV. Data treatment was performed using the CasaXPS program (Casa Software Ltd., UK), and some spectra were deconvoluted using the least squares fitting routine incorporated in this software with a Gaussian/Lorentzian (85/15) product function and after subtraction of a non-linear baseline. Molar fractions were calculated using peak areas normalized on the basis of acquisition parameters and sensitivity factors provided by the manufacturer. The C 1s, O 1s, Mg 2s, Si 2p, Al 2p, Ce 3d and Pd 3d peaks were used for quantitative analysis. Based on the XPS analysis, the XPS surface ratio of a given element is defined as the atomic concentration of the element (%) with respect to the concentration of the major element of the support (Si) (%).

2.3. Catalytic performance

Propene combustion was carried out using an automated bench-scale catalytic unit (Microactivity Reference, PID Eng & Tech). The reactor was a tubular, fixed-bed, downflow type with an internal diameter of 0.9 cm. Catalyst samples were mixed with an inert material, at a weight ratio of 1:4, in order to dilute the catalyst bed and avoid hot spot formation. The propene concentration in the feed was 0.5% and the oxygen-to-hydrocarbon molar ratio was 20, with helium as the balance gas, up to a total feed flow of 150 cm^3/min . The catalyst was stabilized for 120 min at each temperature to ensure steady-state conversion. Space velocities (GHSV), calculated at standard temperature and pressure and based on the volume of the catalytic bed, were about 20,000 h^{-1} . Prior to the catalytic tests, one of the following pre-treatments were applied to the catalysts: (1) in flowing air (100 cm^3/min): heating to 150 °C at 2 °C/min, 2 h at 150 °C and cooling to room temperature, or (2) in flowing H_2 (Air Liquide, 99.999%) (100 cm^3/min): heating to 300 °C at 2 °C/min, 2 h at 300 °C and cooling to room temperature. The reactant and reaction product streams were analyzed online using an Agilent 6890 gas chromatograph system.

3. Results and discussion

The most important differences between the nitrogen adsorption isotherms of the samples are found at relative pressures lower than 0.10 (see Fig. 1), in other words in the micropore region. The textural properties of the materials obtained are presented in Table 1. The Al-PILC used as catalytic support in this work shows a specific surface area of 158 m^2/g . A comparison of the textural properties of the support, the Pd catalyst and the Ce-modified catalysts showed that the surface and volume accessibilities are affected by the presence of the metals, especially in the case of Ce. The loss of specific surface area caused by the presence of Pd is around 26%, with this value increasing to 53–63% in the presence of Ce. For 0CePd as well as for Ce-modified catalysts, the decrease in the microporous surface is much more significant than that in the external surface. These results are attributed to the presence of the smaller particles of palladium on the microporous region

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