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Effect of the metal loading on the catalytic combustion of propene over palladium and platinum supported on alumina-pillared clays

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ABSTRACT

The aim of this work was to study the effect that the structural properties and metal content of various pillared-clay-supported catalysts may have on the oxidation of propene. Thus, a montmorillonite was intercalated and pillared with alumina, then used as a support for palladium and platinum with metal contents of between 0 and 2 wt.%. The resulting materials were tested in the oxidation of propene. The results obtained suggest that the nature of the metal and the metal content are the main factors governing the oxidation of propene over these catalysts.

1. Introduction

Thermal combustion is the most widely used technology for the abatement of volatile organic compounds (VOCs). However, as this process must be performed at high temperatures, usually above 1000 °C, it requires the use of additional fuel and temperature-resistant materials and generates by-products such as NOx. Catalytic combustion is a better solution for the elimination of low concentrations of VOCs as it offers several environmental advantages compared to thermal combustion, including the ability to operate at lower temperatures and less by-product formation [1]. Noble metals and transition metal oxides are commonly used as catalysts for the combustion of VOCs.

The synthesis of porous solids from clay materials with a controlled pore structure is of great interest because of the potential applications of these materials in catalysis, purification and sorption-based processes [2]. Pillared interlayered clays (PILCs), for example, are one of the most attractive groups of porous solids due to their controllable pore dimensions and catalytic properties, which can be varied by changing the type of silicate layers and pillaring agents used [3]. The incorporation of metal ions during either pillar formation or through a post-pillaring treatment has extended the field of application of pillared clays to cover several environmental processes, including the destruction of hazardous gaseous pollutants by complete oxidation. Pollutants are usually present in air streams at low concentrations, therefore highly efficient technologies that ensure total oxidation whilst avoiding the formation of harmful by-products are required.

Propene is widely used as an alkylation or polymer-gasoline feedstock for octane improvement, with large quantities also being used during the manufacture of plastics and chemicals [4]. It is considered to be a highly reactive VOC as it is involved in the formation of ground-level and tropospheric ozone, and therefore in photochemical smog [5]. It has anaesthetic properties and can cause asphyxiation at high concentrations, and it is flammable under normal atmospheric conditions [4]. In light of these characteristics, there is an increasing interest in controlling its presence in gaseous emissions.

Propene oxidation over several different catalysts has been studied by various groups [6–14]. Indeed, we have studied the oxidation of propene using chromium [15] and cobalt [16] pillared clay catalysts. The results of these studies showed that the catalytic performance of these materials is independent of the method used to incorporate the chromium [15] but is controlled by the acid–base and adsorption properties of the support in the case of cobalt oxide catalysts [16].

The present work, which forms part of our systematic study of the preparation of metal catalysts supported on pillared clays, focuses on the effect that the metal loading of pillared-clay-supported noble metals may have on the catalytic propene oxidation behaviour.

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2. Experimental

2.1. Catalyst preparation

The starting material was a montmorillonite from Tsukinuno, supplied by The Clay Science Society of Japan, which was pillared with alumina according to a conventional pillaring procedure [17] and then used as the support in all sample preparations. Metal catalysts were prepared by wet impregnation of the support with solutions of palladium ($Pd(NO_3)_2$) and platinum ($[Pt(NH_3)_2](NO_2)_2$) salts. Thus, the metal salt/clay slurries were evaporated under reduced pressure in a rotary evaporator and the resulting solids dried at 120 °C for 16 h then calcined in air at 500 °C for 4 h to form the final supported catalysts, which had metal contents of between 0 and 2 wt.%.

2.2. Catalyst characterization

Adsorption experiments with nitrogen (Air Liquide, 99.999%) at −196 °C and carbon dioxide (Air Liquide, 99.998%) at 0 °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 and a pressure lower than 0.133 Pa beforehand. The Langmuir surface area (S_{Lang}) was calculated from nitrogen adsorption data over the relative pressure range 0.01–0.05. The total pore volume (V_{p}) was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The micropore volumes ($V_{\mu\mathrm{p}}$) were calculated using the Dubinin–Radushkevich equation [18] over the relative pressure range 0.01–0.05.

Chemisorption of CO (Praxair, 99.99%) was performed at 35 °C using the static volumetric apparatus mentioned above. All samples were reduced at 360 °C for 6 h then cooled to the adsorption temperature. CO adsorption data were collected in the pressure range 50–300 mmHg. After this first adsorption experiment, the samples were degassed for 0.5 h at 35 °C and new adsorption data collected in the same pressure range. The volume of CO adsorbed was calculated from the difference between these two adsorptions.

Catalyst acidity was determined by adsorption of NH_3 (Air Liquide, >99.995%) using a dynamic pulse method on a Micromeritics TPR/TPD 2900 instrument with approximately 0.2 g of catalyst. All samples were pre-treated at a heating rate of 10 °C/min, under a He (Praxair, 99.999%) flow of 30 mL/min, up to 400 °C for 3 h and then cooled to 70 °C in the same stream. Ammonia pulses (0.5 mL) were injected at 70 °C until the area of consecutive eluted pulses was constant.

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 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 mL/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 total volume of the catalytic bed, were about 20,000 h^{-1}. Prior to the catalytic tests, the catalysts were pre-treated *in situ* by heating for 2 h at 150 °C in 100 mL/min of air. The reactant and product streams were analyzed using an Agilent 6890 GC system.

3. Results and discussion

The characterization results for the palladium and platinum catalysts are presented in Table 1. The intercalation-pillaring of the montmorillonite was successful in all cases, and subsequent impregnation with the aqueous solution of metal resulted in a loss of surface area and pore volume. The specific surface area (S_{Lang}) and the specific micropore volume calculated from N_2 adsorption ($V_{\mu\mathrm{p}}(N_2)$) for the metal catalysts remained practically unchanged up to a metal content of 2 wt.% for Pd and 1 wt.% for Pt.

Nitrogen and carbon dioxide adsorption measurements provided complementary characterization information for these microporous materials [3]. Nitrogen adsorption characterizes pores between 0.5 and 200 nm, whereas pores with diameters in the range 0.4–1.5 nm can be measured using CO_2 [19] as a result of the smaller kinetic diameter and higher kinetic energy of CO_2 [3]. The results presented in Table 1 show that, according to the CO_2 measurements, Al-PILC has the same micropore volume as all the metal-containing samples, thereby suggesting that pore diameters of between 0.4 and 1.5 nm are not influenced by the presence of metal species. In contrast, the micropore volume obtained from the N_2 measurements differs between the various samples, probably due to the presence of metal species in the micropore range characterized by N_2 adsorption.

The acid properties remain practically unchanged as the metal content increases (see Table 1), thus indicating that metal species do not contribute significantly to the acidity of the pillared clay and that the most important contribution is that from the clay support.

Table 1

Surface area, pore volume, acid properties, metal dispersion and metal content derived from nitrogen and carbon dioxide adsorption at −196 °C and 0 °C, respectively, ammonia adsorption at 70 °C, carbon monoxide adsorption at 35 °C, and chemical analyses.

Catalyst	S_{Lang}[a] (m^2/g)	V_{p}[b] (mL/g)	$V_{\mu\mathrm{p}}(N_2)$[c] (mL/g)	$V_{\mu\mathrm{p}}(CO_2)$[c] (mL/g)	$V(NH_3)$[d] (mL/g)	D(CO)[e] (%)	Metal content[f] (wt.%)
Al-PILC	212	0.113	0.080	0.054	6.14	–	–
0.1Pd	162	0.086	0.061	0.055	6.54	29.7	0.08
0.5Pd	168	0.090	0.063	0.054	6.56	9.6	0.50
1Pd	156	0.085	0.059	0.052	7.23	5.6	1.06
2Pd	151	0.066	0.057	0.050	6.67	4.5	2.03
0.1Pt	150	0.083	0.056	0.055	6.58	29.9	0.09
0.5Pt	150	0.087	0.057	0.054	6.04	19.0	0.49
1Pt	128	0.076	0.048	0.051	6.32	17.6	0.99
2Pt	74	0.050	0.028	0.053	4.28	12.8	2.01

[a] Specific surface area calculated using the Langmuir equation.
[b] Specific total pore volume.
[c] Specific micropore volume.
[d] Ammonia adsorption volume.
[e] Metal dispersion.
[f] Metal content.

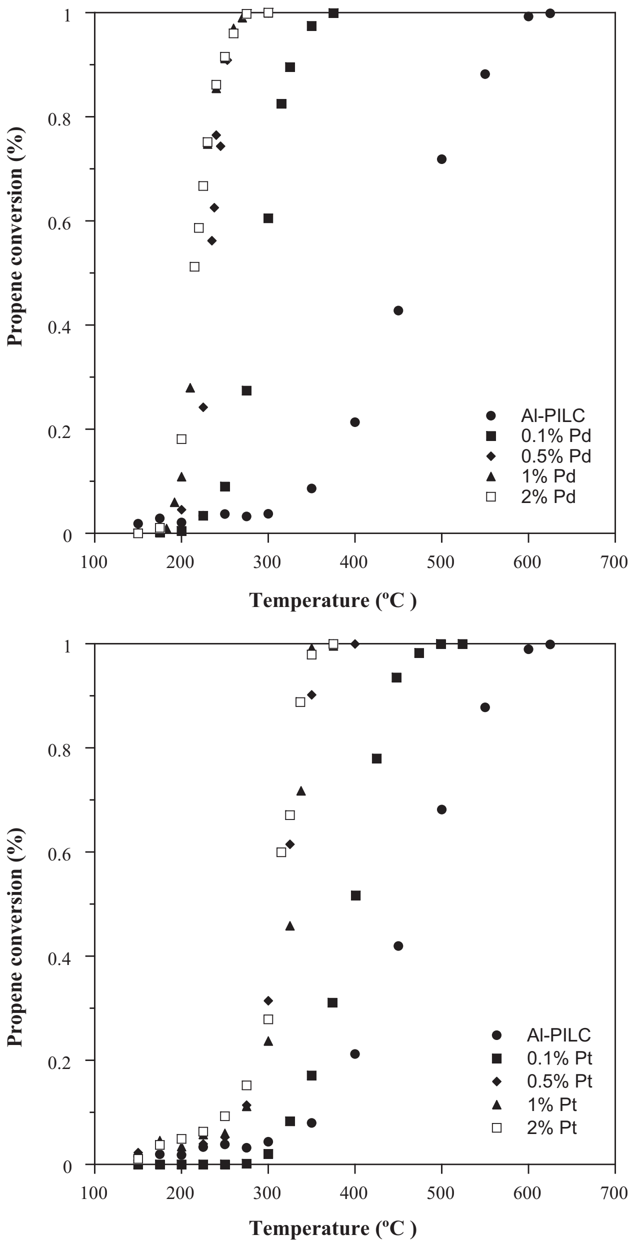

Fig. 1. Conversion of propene over palladium- and platinum-containing alumina pillared catalysts.

Propene conversion using the studied catalysts is presented in Fig 1 together with that for Al-PILC for comparison. The samples were heated to the reaction temperature at a rate of 5 °C/min under reactant flow. Care was taken to ensure that the temperature stabilized rapidly and then remained constant during the reaction at all temperatures studied. The points included in Fig. 1 correspond to the steady state, which was usually reached after 120 min of reaction. As expected, the main products of the reaction were carbon dioxide and water along with very small quantities of carbon monoxide depending on the sample and the conversion. The catalytic performance increased up to 0.5 wt.% metal content then remained unchanged up to 2 wt.%. A comparison of the two metals shows that the temperatures required for propene oxidation are lower for the palladium catalysts than for their platinum counterparts. A similar behaviour was found by Burch and Loader [20] for alumina-supported catalysts for the combustion of methane under oxygen-rich atmospheres.

The metal dispersion *D*(CO), as calculated from the chemisorption results assuming a stoichiometry of one carbon monoxide molecule adsorbed per surface metal atom [21], was also considered to explain the observed catalytic behaviour. The two series of catalysts show a metal dispersion of about 30% for an initial metal content of 0.1 wt.%, whereas this value decreases for metal contents in the range 0.5–2 wt.%, more notably so for the palladium catalysts. However, the temperatures required for propene oxidation with these catalysts are lower than that required for the catalyst with a higher dispersion. These results suggest that the nature of the metal has the most important effect on propene oxidation. The metal content is also important, although no improvement in catalytic performance is observed beyond 0.5 wt.%.

4. Conclusions

Metal doping produces an initial loss of the textural properties of the alumina-pillared clay, which then remains constant up to a metal content of 2 wt.%. The metal species are incorporated into the micropore region characterized by N_2 adsorption, and pores with diameters of between 0.4 and 1.5 nm are not affected by the presence of metal species.

The palladium catalyst supported on alumina-pillared clays is more active for the oxidation of propene than its platinum counterpart, although an improved catalytic performance was observed upon increasing the metal content from 0 to 0.5 wt.% for both metals.

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