

Vapour phase deep oxidation of chlorinated hydrocarbons catalyzed by pillared bentonites

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Abstract

A natural sodium bentonite was pillared with aluminum, aluminum–iron, aluminum–ruthenium and aluminum–chromium polyoxocations. The clays were characterized by X-ray diffraction, ESCA and nitrogen adsorption. All the clays resulted to varying degrees in active catalyst for the deep oxidation of volatile chlorinated hydrocarbons (CVOCs) in the 300–400°C temperature range. The chromium pillared clay was by far the most active and stable catalyst, with more than 99% hydrocarbon conversion at 300°C. The catalytic activity trend is discussed as a function of the Brønsted acidity and of the oxidizing power of the metallic couple.

Keywords: Aluminium; Bentonite; Chlorinated hydrocarbons; Chromium; Deep oxidation; Oxidation; Polyoxocations

1. Introduction

Concern has been growing in recent years, that chlorinated hydrocarbons are harmful to health and the environment [1]. Chlorinated volatile organic compounds CVOCs (methylene chloride, trichloroethylene and carbon tetrachloride) constitute a major portion of the hazardous solvent wastes produced by industry. Social and economic pressures are forcing a change in mind-set from pollution control to pollution prevention and consequently strategies for reducing pollution at the source are gaining ground. In accord with US Environmental Protection Agency (EPA) guidelines, chlorinated pollutants reduction can be accomplished by material substitution, product

reformulation, process modification and recycling [2]. Much effort has been devoted to finding effective substitutes for the chlorinated solvents, but the use of these compounds will continue for years and their disposal/destruction will remain an important ecological problem. Combustion is effective to decompose volatile chlorinated organics but the present technology requires temperatures as high as 1000°C since incomplete combustion can lead to harmful products such as phosgene and formaldehyde [3]. Nevertheless high temperature combustion requires a large amount of energy and therefore is impractical for large-scale use, especially when lean exhaust gases containing chlorinated hydrocarbons are treated. Catalytic combustion is effective in decomposing chlorinated organics and can be carried out at lower temperatures. However investi-

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gations on the catalytic combustion of chlorinated hydrocarbons have scarcely been carried out until recently because chlorine can react with the transition metals which are used as combustion catalysts causing a decrease of their activity [4–8]. On the other hand, transition metal oxides have been found to be highly active and much more resistant to poisoning.

Deep oxidation, i.e. total combustion of chlorinated hydrocarbons, results in carbon dioxide and hydrochloric acid as the final products. It has been reported that the reaction involves both acid and redox catalysis [5], so oxides with acidic properties or zeolites were studied as catalysts [5,7,8].

Pillared clays are recently developed layered materials, prepared by substituting the small mono and divalent charge-compensating cations, normally found between the natural smectite clay layers, with large polyoxocations of various elements. On heating, the cationic pillars form oxide clusters that permanently prop open the clay layers, creating a well defined two dimensional pore structure with high specific surface area. The properties of these materials have been described in recent review articles [9–11]. The catalytic properties of a pillared clay strongly depend on the chemical composition of the pillars and on the nature of the cations present in the interlayer space. Both Brønsted- and Lewis-type acidity sites have been found in pillared smectites [9,12]. The more thermally stable, easily prepared by reproducible methods, and extensively studied are smectites pillared with polyoxoaluminum cations [9–11]. The catalytic activity of a clay pillared with hydroxy-aluminum oligomers can be modified by exchanging the residual interlayer alkali cations with other metallic ions or doping the pillaring solution with transition metal ions to obtain mixed-metal pillars [13–16]. In this way it is possible to modify the surface acidity of the clay and to add to the material the catalytic properties of the metal ion. In a recent paper we demonstrated that bentonites pillared with aluminum polyoxocations doped with transition metals or pillared with aluminum and exchanged with transition

metal ions can act as polyfunctional catalysts [17]. The clays in fact were found to be active catalysts of the acid catalyzed propene hydration to isopropanol and of the successive oxidative dehydrogenation of the alcohol to acetone. Some of the clay catalysts were found to catalyze above 300°C the total oxidation of the reagents to carbon dioxide and water. Therefore we decided to extend the use of these catalysts to the catalytic deep oxidation of volatile chlorinated hydrocarbons (CVOCs). In this paper we will discuss the preliminary results of this study.

2. Experimental

2.1. Characterization methods

Adsorption/desorption experiments using N₂ were carried out at –196°C on a C. Erba Sorptomatic 1900 Porosimeter. Prior to each measurement the samples were outgassed at 150°C for six hours. The N₂ isotherms were used to determine the specific surface areas (S_A), the mesopore surface area (S_{meso}), the micropore volume (V_{micro}), the mesopore volume (V_{meso}) and the pore size distribution of the samples. Surface areas were obtained using the full BET equation. The α -plot method was used to calculate the surface area of the mesopores, the micropore volume and the mesopore volume. The unpillared clay (Detercol P1) was used as reference material [18]. The micropore size distribution was determined using the method developed by Horvath–Kawazoe [19].

X-ray diffraction spectra were measured with a Philips diffractometer using the Cu-K α radiation. The samples were thin oriented films of clay mounted on glass slides or disc shaped pressed powders.

XPS spectra were run on a Vacuum Generators Escalab spectrometer, equipped with an hemispherical analyzer operated in the fixed analyzer transmission (FAT) mode, with a pass energy of 20 eV. Al-K α photons were used to excite photoemission. The binding energy (BE) scale was cal-

ibrated by taking the Au $4f_{7/2}$ peak at 84.0 eV. Correction of the energy shifts due to static charging of the samples was accomplished by referencing to the C 1s line from the residual pump-line oil contamination, taken at 285.0 eV. The accuracy of the reported BEs is ± 0.2 eV and the reproducibility of the results was within these values. The spectra were collected by a DEC PDP 11/83 data system and processed by means of VG 5000 data handling software.

The catalytic tests were carried out in a tubular stainless-steel flow reactor interfaced to a gas chromatograph (HP 5890) equipped with FI and TC detectors. Methylene chloride was vaporized into the carrier gas stream (He) using a thermostated saturator. Typical experiment conditions: 500 mg of clay, total flow of reactants (air and chlorinated hydrocarbon in helium) = 90.0 ml/min, chlorinated hydrocarbon concentration 10000 ppm, and total pressure = 101.3 kPa (space velocity = 12000 h^{-1}). The reaction was monitored determining by GC the remaining chlorinated hydrocarbon with a 25 m wide bore column 50% phenylmethyl silicone working at 120°C with a carrier gas flow of 10 ml/min. The formation of CO and CO₂ was periodically determined by GC. Hydrochloric acid was determined by titration. Partial oxidation products (phosgene and formaldehyde) and chlorine (formed by the Deacon reaction) were never found by usual detection methods.

2.2. Pillared clays syntheses

The clay used as starting material was a natural Na⁺-bentonite (Detercol P1) supplied by C.Laviosa SpA (Leghorn, Italy) with a CEC of 85 mequiv./100 g.

All the chemicals were reagent grade and used without further purification. APA is a clay pillared with aluminum polyoxocations, AFPA is pillared with aluminum pillars doped with Fe, ARuPA and ACrPA contain aluminum pillars doped with Ru and Cr. APA, AFPA, ARuPA, were obtained by a slight modification of the method described in a previous paper [17] and are highly microporous.

A pillaring solution of Chlorhydrol and Cr(NO₃)₃·3H₂O (Al/Cr = 20) was used in the preparation of ACrPA.

3. Results

Surface areas, pore volumes, X-ray data and transition metal content of the prepared pillared clays are presented in Table 1.

The Fe 2p_{3/2} and Ru 3d_{5/2} binding energies are analogous to those reported for similar clays in our previous paper [17]. The Al/Cr clay (ACrPA) showed a Cr 2p peak at 579.2 ± 0.2 eV that can be attributed to the Cr⁶⁺ ion (lit. CrO₃ 580.1 eV). This value remained substantially unchanged after the catalytic experiments suggesting the formation of stable Al/Cr mixed pillars.

Fig. 1 describes the behaviour of the clay catalysts in the deep oxidation of methylene chloride in the 300–400°C temperature range. Methylene chloride was chosen because it is one of the more refractory halocarbons. It is known, in fact, that compounds with carbon-carbon linkages or increasing numbers of halogen atoms can be destroyed at lower temperatures.

Of all the pillared clays used in this study, the chromium doped one ACrPA afforded the best results: essentially complete destruction of methylene chloride at 10000 ppm in air on 0.5 g of catalyst at 300°C, was obtained. No methylene chloride is detected in the effluent gas stream: the GC detector sensitivity sets the maximum possible [CH₂Cl₂] in the effluent at 40 ppm.

Table 1
Surface areas, pore volumes, X-ray and metal content of pillared clays

	%(w/w)	<i>d</i> ₀₀₁ Å	<i>S</i> _A m ² /g	<i>V</i> _{micro} cm ³ /g	<i>V</i> _{meso} cm ³ /g	<i>S</i> _{meso} m ² /g
APA	Fe 1.7	18.2	388.5	0.17	0.005	14.6
AFPA	Fe 3.7	18.2	349.3	0.15	0.007	20.5
ARuPA	Ru 1.0	18.4	407.9	0.18	0.005	14.6
ACrPA	Cr 1.3	18.2	350.2	0.15	0.005	13.8

Deep oxidation of CH_2Cl_2

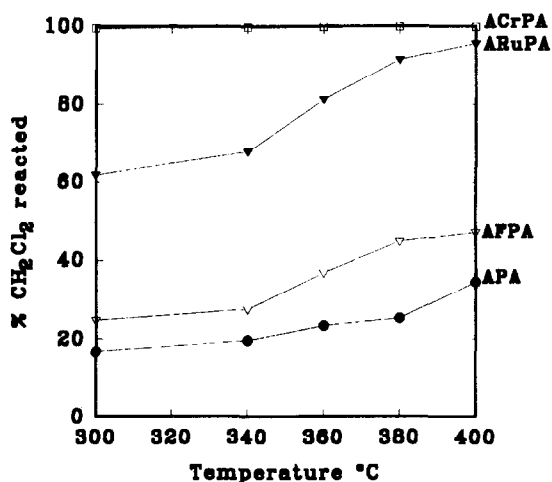


Fig. 1. Deep oxidation of CH_2Cl_2 catalyzed by some pillared bentonites.

Table 2

Deep oxidation of some chlorinated hydrocarbons at two different temperatures catalyzed by some pillared bentonites

Catalyst	Temp. °C	CCl_4 % reacted	$\text{C}_6\text{H}_5\text{Cl}$ % reacted
ARuPA	300	99.7	89.0
	400	99.9	99.9
ACrPA	300	99.9	99.9
	400	99.9	99.9

The clay was found to maintain a constant activity up to 400°C and a good durability (a sample of ACrPA was used continuously for more than three days at 380°C without any detectable decrease in activity). All the other tested catalysts were found to be less active and only the Ru doped ARuPA catalyst showed, but only above 400°C, an activity close to that of the chromium clay (95% CH_2Cl_2 conversion). Consequently only the ruthenium and chromium clays, were tested further in the deep oxidation of other halocarbons (carbon tetrachloride and chlorobenzene). The results are presented in Table 2.

4. Discussion

The deep oxidation mechanism of halocarbons is not well understood, but it was proposed that

the acidic properties and oxygen adsorption capacity of the catalyst are involved in a probably multi-step process [7]. This model involves adsorption of the hydrocarbon on Brønsted acid sites and of oxygen on metal ion sites [7]. Experiments with deuterated reagents suggested that C–H bond cleavage is involved in the rate determining step [8]. A natural clay is essentially a mesoporous material. Mesoporosity is generally attributed to three-dimensional random ‘card-house’ structure which is a common form of aggregates in fine clay particles. Microporosity and further mesoporosity is created by the pillaring process inducing a considerable increase of the specific surface area. The (micro)texture of these materials is controlled by the synthetic procedure and, to a large extent, by the drying method. The activity of a bifunctional catalyst depends from a delicate balance of the two active functions (in this case Brønsted acidity and oxidizing power). There is a general agreement to impute the main source of Lewis acidity of an Al pillared clay to the pillars [12,20–22]. The location of Brønsted sites is more controversial. It seems that Brønsted acidity sites are dependent on the parent clay and some are situated on the pillars and some on the tetrahedral layer [12,20–23]. The transition metal ions added as dopants to the pillaring solution modify the final pillar chemical composition and consequently the strength and nature of the acid sites.

The redox metallic couples present in the clay structure are the most likely active catalytic sites for the hydrocarbon oxidation in air.

The aluminum pillared clays contain a variable amount of iron ions in the octahedral layer depending on the natural clay used in the synthesis. These sites, buried in the octahedral layer, are inaccessible to reagents and that can explain the low activity of these clays in the catalytic oxidation, as reported in a preceding paper [17]. Nevertheless it was reported that strongly acid Y type zeolites or mordenite, in absence of any transition metal cation, are able to catalyze to a certain extent the complete oxidation of halocarbons [7]. Also the iron doped AFPA clay was found to be a mod-

est catalyst of the title reaction in spite of the almost doubled iron content. The pillar structure of iron–aluminum pillared clays has been accurately studied recently [14,23]. The structure of a pillar with $\text{Fe}/\text{Al} < 0.5$ was proposed to be a Keggin structure similar to that of the aluminum pillars [23] where iron ions partially substitute aluminum ions. It was demonstrated that iron incorporation in the alumina pillars causes a decrease of the acid strength of the surface and of the amount of Brønsted acid sites [23]. This reduced acidity is the most likely cause of the low catalytic activity of the Al/Fe clays. The ARuPA clay contains strong oxidizing centers but, in spite of that, showed a modest catalytic activity below 400°C . This behaviour can be also attributed to the low Brønsted acidity of Ru doped clays as was pointed out by us in a previous paper [17]. The very good catalytic performance of the chromium clay can be attributed to the low ionization potential, the availability of high oxidation states of the trivalent chromium ion and to the high Brønsted acidity generated by this cation on the clay surface [7]. This is not surprising because chromium based systems on acid supports have been already found to be very good CVOCs deep oxidation catalysts [7,8].

We can tentatively deduce from these preliminary data that the modest catalytic performance of the Al, Fe/Al and Ru/Al microporous pillared clays at low temperature can be mainly attributed to their low Brønsted acidity. Only at higher temperature (400°C), in the presence of a strongly oxidant system such as Ru ion, overcomes the drawback of the reduced Brønsted acidity, affording conversion values close to those shown by the Cr/Al clay. No efforts have been made up to now to optimize the catalytic performance of this clay with a view to practical use. Further investigation of the catalysts characteristics is presently under way along with the testing of other clay based systems.

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