Pt-Containing Pillared Clay Catalysts for CO Oxidation

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Abstract—Platinum has been introduced into pillared clay as a complex with the organosilicon amine N'-[3-(trimethoxysilyl)propyl]diethyltriamine, as a complex with the organosilicon amine and zirconyl chloride, as an ammine complex, and by impregnation with a chloroplatinic acid solution followed by hydrogen reduction. The catalytic activity of the Pt-containing clays in CO oxidation in excess hydrogen was also studied. The last procedure yields the most active Pt-containing pillared clay. Calcium has been introduced into pillared clay by ion exchange, and it was found that the catalytic activity of the clay decreases with increasing Ca content.

The removal of CO from hydrogen is of great industrial importance. In recent years, there have been studies aimed at solving this problem by selective CO oxidation with oxygen in excess hydrogen. This purification method has afforded special-purity hydrogen for fuel cell applications [1]. The oxidation of CO is catalyzed by platinum supported on ceria [2], iron oxide [2], alumina [2–6], and activated carbon [7, 8]. Besides platinum, other platinum-group metals are used as catalysts, including Ru [8], Pd [8], Rh [9], and Au [10–12]. A promising support for these catalysts is pillared clay [13]. This material is prepared by exchanging alkali and alkaline-earth cations in the interlayer space of clay for inorganic polyoxo(hydroxo)cations [14–16]. High-temperature treatment of a clay containing bulky polyoxo(hydroxo)cations in its interlayer space results in the removal of the adsorbed water and in the partial dehydroxylation of the clay surface. The inserted polyoxo(hydroxo)cations are also dehydroxylated, yielding metal oxide clusters tightly bonded to aluminosilicate layers through oxygen bridges [17, 18]. These metal oxide clusters, which are called pillars, prevent clay layers from coming closer together, resulting in a porous two-dimensional structure in which the spacing between aluminosilicate layers may be as large as 20 Å.

In the study reported here, we used different methods to synthesize pillared clays and load them with platinum. The purpose of our work was to see how the activity of the resulting catalysts in selective CO oxidation with oxygen in the presence of hydrogen depends on the synthetic method and platinum content.

EXPERIMENTAL

The starting chemicals were montmorillonite (Montmorillonite K 10 purchased from Aldrich; pH 4 in a 1 wt % suspension), zirconyl chloride (ZrOCl$_2 \cdot$ 8H$_2$O, Fluka), calcium nitrate tetrahydrate (Ca(NO$_3$)$_2 \cdot$ 4H$_2$O, pure grade) as a 0.05 mol/l solution, N'-[3-(trimethoxysilyl)propyl]diethyltriamine ((CH$_3$O)$_3$Si(CH$_2$)$_3$NH(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$, Aldrich), and a solution of chloroplatinic acid (H$_2$PtCl$_6 \cdot$ 6H$_2$O, Aldrich) containing 3.4 g of Pt per 100 ml.

Preparation of Pillared Clays

Synthesis of pillared clay. Pillared clay was synthesized by a standard procedure [19]. Montmorillonite (10 g) was dispersed in water (500 ml) under vigorous stirring. ZrOCl$_2 \cdot$ 8H$_2$O (8.86 g) was dissolved in 50 ml of water, and the solution was added to the suspension at room temperature under continuous stirring. Next, the temperature was raised to 70°C over a period of 1 h, and the mixture was stirred at this temperature for 32 h. Thereafter, the mixture was centrifuged and the precipitate was thrice washed with water and air-dried. The resulting solid was heated to 550°C at a rate of 10 K/min and was calcined at this temperature for 2 h. This yielded a clay containing ~15.2 wt % Zr. Hereafter, this clay is called specimen *1*. It was used as the starting material in the preparation of catalysts. According to X-ray powder diffraction data, specimen *1* (after calcination at 550°C) is characterized by d_{001} = 1.8 nm. In the original montmorillonite, d_{001} = 1.3 nm. The difference of 0.5 nm is explained by the increased aluminosilicate layer spacing in the clay [13].

Ion exchange between pillared clay and calcium nitrate. A suspension of pillared clay (16 g) was added to 160 ml of the calcium nitrate solution, and the mixture was vigorously stirred for 30 min. The pH of the solution was measured with a Checker pH meter (Hanna Instruments) calibrated against two buffers, namely, calcium hydroxide (Ca(OH)$_2$) with pH 12.45 and potassium phthalate (C$_8$H$_5$OK) with pH 4.01. the solution was settled for one week and then decanted. Thereafter, another 160 ml of the calcium nitrate solu-
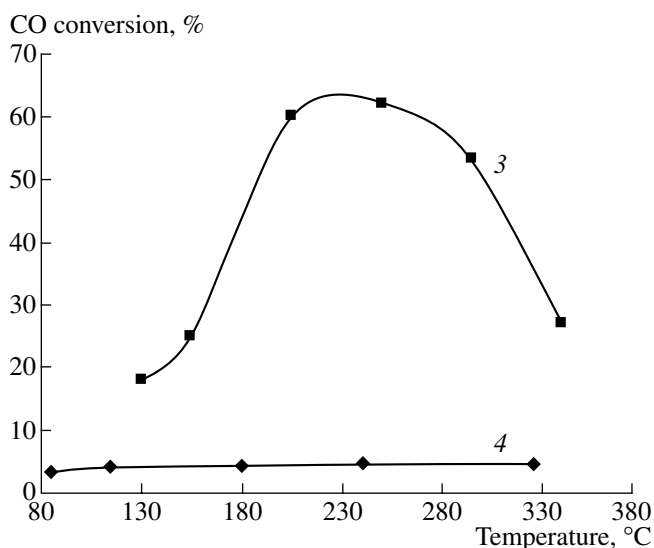
CO conversion, %

Fig. 1. CO conversion over specimens *3* and *4*.

tion was added, the mixture was vigorously stirred for 30 min, and the pH of the aqueous layer was measured. The suspension settled for 1 week. This procedure was repeated twice. After ion exchange with calcium nitrate, the precipitate was decanted, washed with water (measuring the pH of the washings), and air-dried at room temperature for 1 day and at 50°C for 2 h. Hereafter, the resulting solid is called specimen *2*.

Preparation of Pt-Containing Pillared-Clay Catalysts

Several procedures were developed for introducing platinum into pillared clay.

(1) A 20-fold excess of *N'*-[3-(trimethoxysilyl)propyl]diethyltriamine (8.24×10^{-4} mol) was added to a chloroplatinic acid solution containing 4.12×10^{-5} mol Pt. The mixture was magnetically stirred for 10 min. Next, pillared clay (2 g of specimen *1* or *2*) was impregnated with this mixture. All of the solution was taken up. The resulting clay was air-dried for 1 day and then calcined at 500°C for 2 h (heating rate, 10 K/min). This yielded specimen *3* (from specimen *1*) and specimen *4* (from specimen *2*).

(2) *N'*-[3-(Trimethoxysilyl)propyl]diethyltriamine (2.06×10^{-4} mol) was added to a chloroplatinic acid solution containing 2.06×10^{-4} mol Pt (Pt : amine = 1). This resulted in slight precipitation. Otherwise, a molar excess (11.05×10^{-4} mol) of amine was introduced. In this case, we observed the formation of a rich yellow solution. For partial hydrolysis of methoxysilane, this solution was heated to 50°C and stirred for 1 h. The resulting substrate was added to a stirred solution of $ZrOCl_2 \cdot 8H_2O$ (0.0275 mol) in 30 ml of water. The mixture was adjusted to 100 ml while vigorously stirring and was then combined with a suspension of montmorillonite (10 g) in water (500 ml). The product was air-dried at 70°C for 32 h under continuous stirring. For

the catalyst synthesized at Pt : amine = 1 and then air-dried (specimen *5*), $d_{001} = 1.9$ nm; in the case of excess amine (specimen *6*), $d_{001} = 1.7$ nm.

Specimen *7* was similar to specimen *6*, with the only difference that the solution of chloroplatinic acid and amine used in its synthesis was not hydrolyzed. For the air-dried specimen *7*, $d_{001} = 1.7$ nm.

(3) Pillared clay was loaded with platinum using aqueous ammonia. A multifold excess of 20% ammonia (1.23×10^{-3} mol) was added to a stirred mixture of a solution of chloroplatinic acid (6.18×10^{-5} mol) and pillared clay (3 g). The mixture was stirred, and another portion of aqueous ammonia was added. The resulting solid was calcined at 550°C for 2 h (specimen *8*).

(4) Chloroplatinic acid solutions containing 4.12×10^{-5}, 3.09×10^{-5}, 2.05×10^{-5}, and 1.03×10^{-5} mol Pt were mixed with pillared clay (2 g). The resulting wet powders were thoroughly homogenized, dried at 150°C for 1 h, and reduced in flowing H_2 (2 ml/min) at 400°C for 1 h. Specimens *9–12* were thus obtained, which contained 0.4, 0.3, 0.2, and 0.1 at % Pt, respectively.

Physicochemical Characterization of the Catalysts

Elemental analysis of original pillared clay was carried out by X-ray fluorescence measurements on a PW 1600 spectrometer calibrated against 40 standard rock specimens and eight man-made mixtures.

The surface of the catalysts was analyzed by XPS on an LAS-3000 instrument (Riber) with an OPX-150 retarding-field hemispherical photoelectron analyzer. Spectra were recorded at an exciting X-ray energy of 1486.6 eV (AlK_α), an X-ray tube voltage of 12 kV, and an emission current of 20 mA. Binding energy was calibrated against the C1*s* line ($E_b = 285$ eV).

Phase analysis was carried out by X-ray powder diffraction on a DRON-3 diffractometer (graphite-monochromated CuK_α radiation, $\lambda(K_{\alpha 1}) = 1.54051$ Å).

Catalytic Activity Measurements

The activity of the catalysts in CO oxidation in the presence of hydrogen was measured in the temperature range 70–300°C in a quartz flow reactor 3 mm in diameter. The weight of a catalyst sample was 20 mg, and the flow rate of the gas mixture was 40 ml/min. The reaction mixture had the following composition (vol %): H_2, 98; CO, 1; O_2, 1. The reaction products were analyzed by GC using two columns, one packed with the molecular sieve 13 Å (NaX) and the other with Porapak QS, and thermal-conductivity detectors. Conversion was determined with an accuracy of ±0.2%.

RESULTS AND DISCUSSION

Figure 1 shows how CO conversion on specimens *3* and *4* varies with temperature. The highest CO conversion on specimen *3* is 62% and is attained at 250°C. As

Table 1. Concentrations of elements (at %) on the catalyst surfaces according to XPS data

Specimen	C	O	Zr	Si	Al	Pt	N
Montmorillonite	6.5	69	–	19.5	5.0	–	–
1	15.4	60.3	3.4	17.2	3.7	–	–
2	16.8	61.6	3.3	14.8	3.5	–	–
3	14.5	58.7	3.1	15.5	4.9	0.4	2.9
4	18.2	59.7	2.1	14.7	4.9	0.4	Qualitatively
5	13.1	68.7	1.1	16.8	–	0.3	–
6	20.9	56.0	1.5	16.6	5.0	Qualitatively	–
7	19.2	59.0	1.6	15.2	5.0	–	–
8	10.1	64.6	3.1	17.3	4.9	Qualitatively	–
9	14.1	56.7	3.4	20.6	5.2	–	–

Table 2. Photoelectron binding energies (eV) for Pt-containing pillared clays

Specimen	$O1s$	$Zr3d_{5/2}$	$Si2p$	$Al2p$	$Pt4f_{7/2}$	$N1s$	$E_b(Zr3d_{5/2})/E_b(Zr3p_{3/2})$
Montmorillonite	532.8	–	103.0 101.8	74.2	–	–	–
1	532.9	183.1	103.6 102.0	73.6	–	–	1.68
2	533.0	183.4	103.3 101.7	74.0	–	–	1.39
3	532.0	181.5	102.3	74.0	72.0	399.5	1.76
4	533.4	182.5	103.7	74.4	72.0	399.4	1.75
5	532.4	182.0	102.5 101.3	–	72.8	–	1.10
6	532.1	181.6	102.3 101.1	73.7	–	–	–
7	532.4	181.6	102.8 102.0	73.3	–	–	–
8	531.8	181.3	102.3	73.5	72.0	–	–
9	532.4	181.2	102.2 100.6	74.2	–	–	1.7

the reaction temperature is further raised, the conversion decreases. The CO conversion on specimen *4* is no higher than 3.5–4.5% throughout the temperature range examined (Fig. 1). This is explained by the fact that the Ca content of this pillared clay was increased by ion exchange. According to X-ray fluorescent analysis, the Ca content of specimens *3* and *4* is 0.036 and 0.102 at %, respectively.

XPS data characterizing the surface of pillared clay are presented in Table 1. Note that the carbon signal usually arising from the evaporation of hydrocarbons from rubber gaskets into vacuum allows the traces of hydrocarbons on the sample surface to be used for precise calibration of binding energy against the C1*s* line [20, 21]. As is clear from Table 1, ion exchange does not modify the clay surface (specimens *1, 2*) and neither does supported platinum (specimens *3, 4*).

The oxidation states of Zr, Al, Si, and O in the clays remain unchanged (Table 2). The nitrogen detected apparently belongs to cyano groups [20]. The electronic structure of platinum is difficult to study because of the overlap of the Al2*p* line ($E_b \approx 74$ eV for Al^{3+}) and the lines from Pt (ranging from $E_b = 71.3$ eV for Pt^0 to $E_b = 76.2$ eV for $Pt4f_{7/2}$ in *cis*-$Pt(NH_3)_2Cl_4$) [20]. From electron kinetic energy (E_{kin}) data, it is possible to judge the presence of some substance on the support. For example, $E_{kin} = 1300$ eV for $Zr3d_{5/2}$ and 1150 eV for $Zr3p_{3/2}$ E_{kin}, so $E_{kin}(3d_{5/2})/E_{kin}(3p_{3/2}) = 1.13$. This ratio will be larger for samples in which zirconium is covered with some layer than for samples whose surface is not coated. Note that this is apparently true only for zirconium-free coatings. Supported Pt changes this ratio from 1.68 (specimen *1*) to 1.76 (specimen *3*) or 1.75 (specimen *4*). Therefore, the zirconium oxide layer in
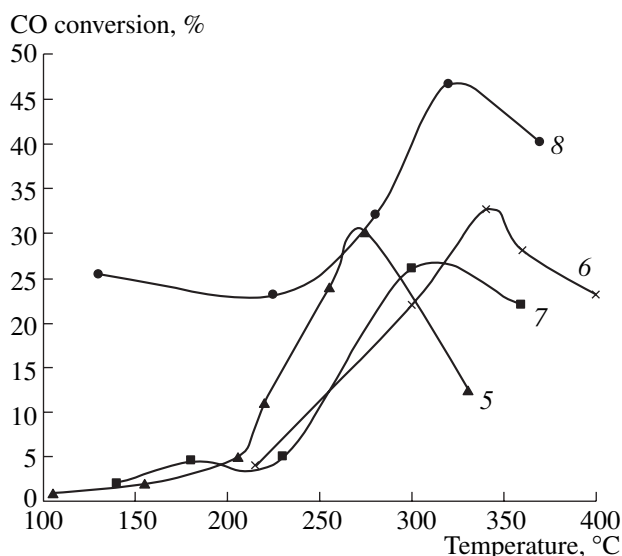
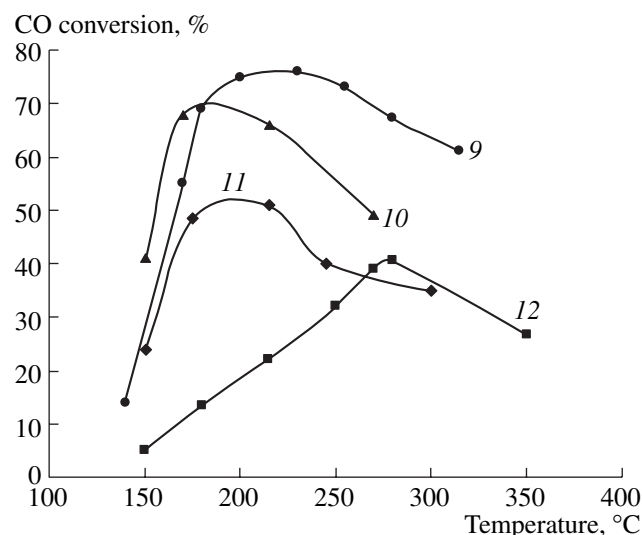**Fig. 2.** CO conversion over specimens *5–8*.

Fig. 3. CO conversion over specimens *9–12*.

specimens *3* and *4* is covered with a platinum-containing compound.

Platinum supported on pillared clay affects the electron work function of silicon and zirconium. While the work functions of Si2*p* electrons for the initial pillared clay are 103.6 and 102.0 eV, the same work functions for the specimen containing 0.4% Pt have smaller values of 102.2 and 100.6 eV, respectively. Likewise, the work function of Zr3$d_{5/2}$ electrons decreases from 183.1 to 181.2 eV. It is believed that platinum is present both on clay layers and on zirconium oxide. Increasing the calcium content of a clay decreases the number of protonic acid sites. In turn, as the number of acid sites decreases, the catalyst loses its activity. The dependence of catalytic activity on the acidity of the original clay has already been reported for the selective catalytic reduction of nitrogen oxide with ammonia [22]. The Fe-containing catalyst used in this process was supported on titanium dioxide–pillared clay prepared from natural bentonite and from bentonite pretreated with 1% sulfuric acid. This sulfuric acid treatment raised the activity of the catalyst by 33%. In our case, it is likely that ion exchange diminishes CO adsorption on pillared clay (makes the formation of H+– CO bonds less likely), thereby causing a decrease in catalytic activity.

Specimens *5–8* are less active than specimen *3*. The highest CO conversion on specimens *5–8* is 27–47% at 275–340°C (Fig. 2). According to XPS data, specimens *5–8* contain less surface platinum than specimen *3*, although all of these specimens received the same amount of chloroplatinic acid. It is possible that, in the synthesis of specimens *5–7*, the reaction between the Pt–amine complex and zirconyl chloride was incomplete and some of the complex was hydrolyzed, remained in the solution, and was then separated from the precipitate. Furthermore, the amine introduced exerted an effect on the formation of pillared clay so

that the zirconium and, accordingly, platinum contents of the clay were reduced. Adding excess ammonia to the pillared clay impregnated with chloroplatinic acid (specimen *8*) yields the complex $Pt(NH_3)_2Cl_4$ via the reaction $H_2PtCl_6 + 4NH_3 \Rightarrow Pt(NH_3)_2Cl_4 + 2NH_4Cl$. This complex decomposes upon calcination, leaving its platinum on the surface of the pillared clay. As is clear from Table 2, platinum in specimen *8* is in the same oxidation state as platinum in specimens *3* and *4*. However, according to XPS data, specimen *8* contains less surface platinum than specimen *3* or *4* (Table 1), although all of them were treated with the same amount of chloroplatinic acid. Possibly, the thermal decomposition of the complex yields large platinum particles that are hardly detectable by XPS and show a low activity in CO oxidation.

Of specimens *9–12*, which contain 0.4, 0.3, 0.2, and 0.1 at % Pt, respectively, the first is the most active in CO oxidation (Fig. 3). The conversion of CO on this catalyst is as high as 75% around 200°C. The CO conversion decreases with decreasing Pt content of the catalyst: for 0.3, 0.2, and 0.1 at % Pt, the highest CO conversion is 68% at 170°C, 51% at 215°C, and 40% at 280°C, respectively. Of the specimens containing 0.4% Pt, specimen *12* is the most active. It was obtained by impregnating pillared clay with chloroplatinic acid followed by hydrogen reduction.

In a series of studies by Son et al. [4–6], it was demonstrated that catalysts containing 4–5% supported platinum afford a higher CO conversion than the catalysts reported here. For example, at 200°C and $CO : O_2 = 1 : 2$, CO conversion on the 5% Pt/Al_2O_3 catalyst is 90% [4, 5]. Later [6], the operational stability of this catalyst was found to be insufficient: its catalytic activity decreased almost twice within 2 h. For the 1% Pt/Al_2O_3 catalyst, CO conversion is as high as 98–100% at 275°C, the gas flow rate is 100 ml/min, and the

catalyst weight is 0.02 g. However, it was reported in a later publication [2] that, at the same gas flow rate and a much larger catalyst weight of 1.5 g, CO conversion does not exceed 40%. Therefore, lengthening the contact time dramatically decreases the activity of the catalyst.

Besides alumina, activated carbon [7] and the carbon material Sibunit [8] have been used for supporting platinum. The activity of catalysts on these supports depends on the way the support was pretreated. The best performance is observed for activated carbon treated with hydrochloric acid and oxidized in air: the highest CO conversion is 80% at $CO : O_2 = 1 : 1$. In some cases, Pt-containing catalysts are modified with iron oxide [2] or tin oxide [7] for a higher CO conversion.

The conversion of CO on Pt-containing catalysts as a function of temperature is reported to pass through a maximum [4, 23]. The decrease in conversion at high temperatures is due to the decreasing selectivity of the process. Raising the temperature enhances hydrogen oxidation on platinum. Furthermore, CO adsorption on the Pt-containing catalyst decreases above $\approx 210°C$ [24].

Thus, the data available on the catalytic activity of alumina-supported platinum are discrepant: there is no consensus as to the dependence of the activity and operational stability of the catalysts on the percentage of supported platinum. The above results demonstrate that platinum catalysts supported on pillared clay prepared from acid montmorillonite (Montmorillonite K 10) are rather active in CO oxidation. Note that the activity of these catalysts does not decrease over an operation time of 8 h.

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