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ADSORPTION CHARACTERISTICS OF DICHLORODIFLUOROMETHANE (FREON-12) OVER Pd-SUPPORTED ON SiO_2 AND AlF_3 MATRICES PREPARED BY SOL-GEL METHOD

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Abstract

0.5% Pd supported on SiO_2 and AlF_3 matrices were prepared by sol-gel method. The morphology, surface porosity (BET surface area, pore volume & pore diameter) and total surface acidity of these catalysts were investigated using scanning electron microscopy (SEM), N_2 adsorption isotherm and gas-phase pyridine adsorption, respectively. It was found that the BET specific surface area and total pore volume of 0.5% Pd/SiO_2 are larger than those of 0.5% Pd/AlF_3 whereas the total surface acidity was higher in the case of 0.5% Pd/AlF_3 catalyst. The gas-phase adsorption process of dichlorodifluoromethane (freon-12) over the prepared catalysts was investigated at 0, 31, 55 and 180 °C. The fraction of sites (θ) occupied by freon-12 at these conditions, were calculated from Langmuir adsorption isotherm. Thermodynamic analysis of freon-12 adsorption data at equilibrium (K_{ads}, ΔG_{ads}, ΔH_{ads} and ΔS_{ads}) indicates that the adsorption of freon-12 over 0.5% Pd/AlF_3 was more favorable than that on 0.5% Pd/SiO_2.

Key words: Freon-12, Adsorption thermodynamics, Sol-gel, Pd-supported on silica and aluminumfluoride, SEM.

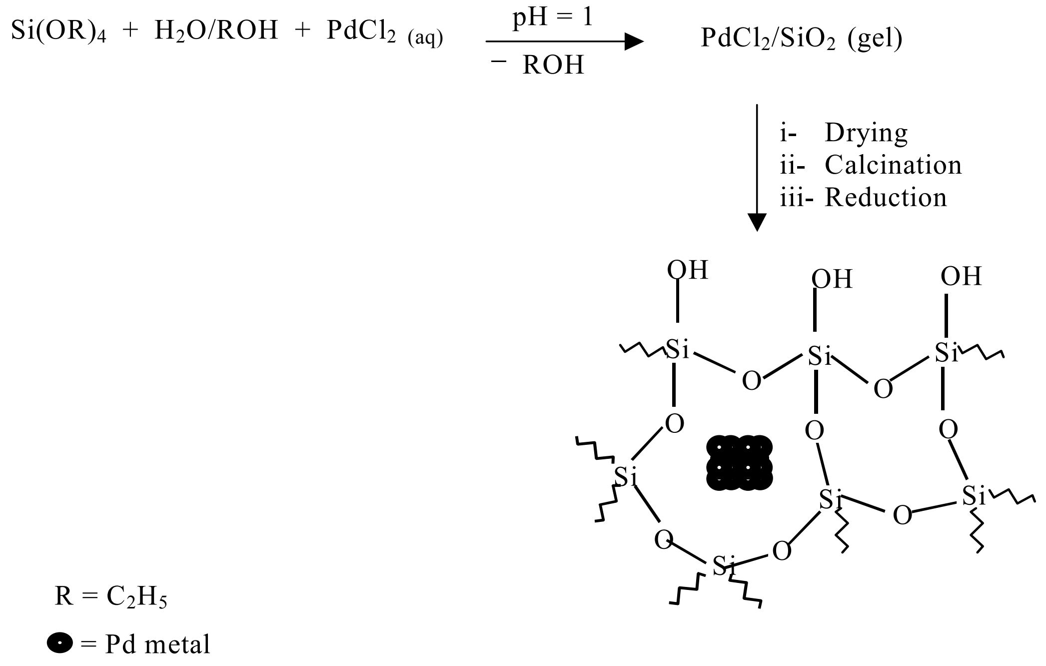
Introduction

Chlorofluorocarbons (CFCs) and other chlorinated organic compounds have been implicated in the depletion of ozone layer in the stratosphere.[1-16] This class of compounds is widely used in air-conditioning, dry cleaning, propellant in aerosol and other industries. Under atmospheric conditions, the C-Cl bond in these compounds homolytically dissociates to generate chlorine radical ($Cl^\bullet$), which consequently reacts with ozone causing its degradation. Under "Montreal Protocol" the production and use of CFCs are band. Current research efforts in this area have focused on the development of catalytic and non-catalytic processes to safely destroy or convert CFCs into environmentally acceptable hydrofluorocarbons (HFCs).[7-16] These processes include hydrolysis,[2,3] oxygenation[4-6] and hydrogenation[7-15] of C-Cl bond. The catalytic hydrogenation of CFCs over a variety of transition metals (Pt, Pd, Ag, Au, Cu, and other bimetallic alloys such as Pd-Au) supported on Al_2O_3, SiO_2, AlF_3, graphite and other matrices has received great deal of attention as a promising route for the catalytic conversion of CFCs into HFCs.[7-16] The performance of these heterogeneous catalysts was reported to be influenced by the surface properties of the support.[17] Although there are numerous reports on heterogeneous catalytic hydrogenation of CFCs, studies concerned with the adsorption behavior of CFCs on the catalyst surfaces are rare.[17] In this study, we have prepared 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3 catalysts by sol-gel method and examined their morphology, surface porosity and acidity, and investigated gas-phase adsorption of freon-12 at variable pressures and temperatures. The adsorption data in the low-pressure range of 0.02-0.30 atm (physisorption) was fitted to Langmuir adsorption-isotherm and the corresponding thermodynamic parameters (K_{ads}, ΔG_{ads}, ΔH_{ads}, ΔS_{ads}) for this process were calculated.

Results and discussion

Sol-gel method was employed to prepare the studied Pd supported on SiO_2 and AlF_3 matrices (Scheme 1 and 2). This method was employed in the preparation of numerous supported catalysts and was shown to give stable heterogeneous catalysts with respect to deactivation, thermal resistance to sintering, large surface area and a high dispersion of catalytic metal within the support matrix.[18-22] In this process, $Si(OC_2H_5)_4$ undergoes hydrolysis and polycondensation in an aqueous ethanol solution containing $PdCl_2$ under acidic conditions (pH = 1.0) at 70-80 °C. These conditions lead to the formation of silica gel matrix in which $PdCl_2$ is uniformly dispersed (Scheme 1). Lopez and coworkers studied the interaction between $PdCl_2$ and the silanol groups (≡Si-OH) by UV-visible and IR spectroscopy and concluded that the interaction between Pd(II) and the silica matrix has an important effect on the specific area of the catalyst.[17] Subsequent calcination and reduction results in the formation of metallic Pd(0) clusters entrapped into the silica network.

The FT-IR spectrum of Pd-supported on SiO_2 was recorded in 4000-400 cm^{-1} range as KBr pellets. Generally, the silica surfaces are usually covered with silanol groups (≡SiOH) and adsorbed moisture. Characteristic strong and broad band centered at 3462 cm^{-1} region was observed, which is typical for the stretching frequency of the O-H bonds ($\nu_{O\text{-}H}$) in silanol groups and water. Furthermore, the peaks at 1082 cm^{-1}, 955 cm^{-1} and 800 cm^{-1} regions are assigned to $\nu_{Si\text{-}O\text{-}Si}$, (asym.), $\nu_{Si\text{-}OH}$ and $\nu_{Si\text{-}O\text{-}Si}$, (sym.), respectively.



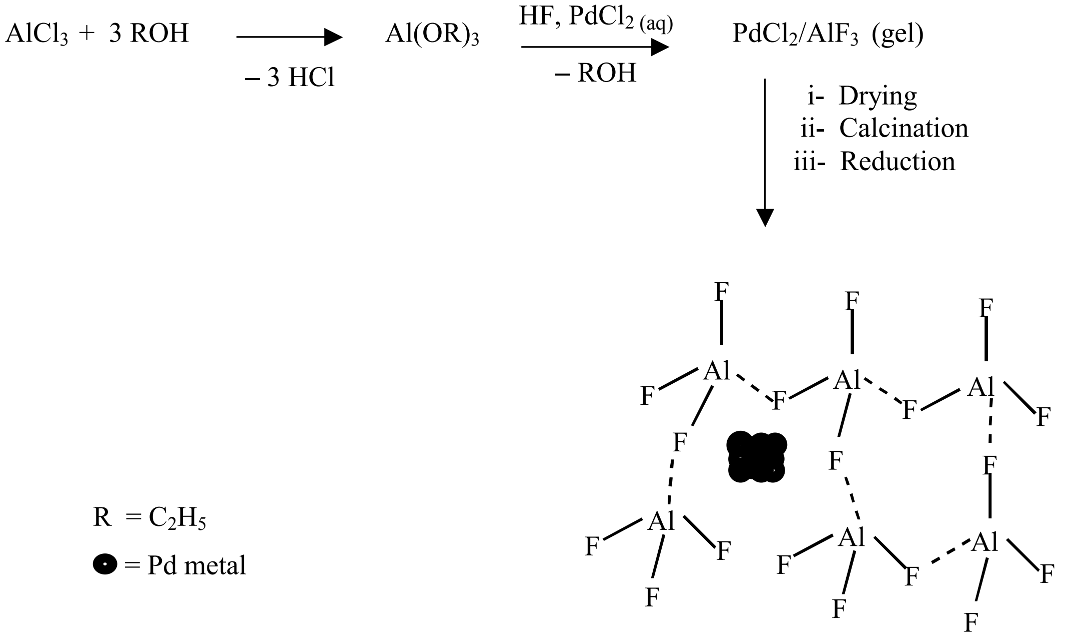
$$Si(OR)_4 + H_2O/ROH + PdCl_{2\,(aq)} \xrightarrow[-\ ROH]{pH\ =\ 1} PdCl_2/SiO_2\ (gel)$$

R = C_2H_5

● = Pd metal

Scheme 1

In the case of Pd supported on AlF_3 matrix, the $Al(OC_2H_5)_3$ is formed *in situ* by the reaction of anhydrous $AlCl_3$ with excess absolute ethanol (exothermic). The resulting $Al(OC_2H_5)_3$ reacts with concentrated HF in the presence of aqueous solution of $PdCl_2$ to form $PdCl_2/AlF_3$ gel, which upon drying, calcinations and reduction gives the desired 0.5% Pd/AlF_3 catalyst (Scheme 2). The FT-IR spectrum of 0.5% Pd/AlF_3 catalyst in KBr pellet displayed bands at 1106 and 940 cm^{-1}, which are attributed to asymmetric and symmetric stretching of the bridging fluoride. The porosity of the prepared 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3 catalysts was conveniently characterized from nitrogen adsorption isotherm at –196 °C. The specific surface area, total pore volume and pore diameter of these catalysts are summarized in Table 1. The specific surface areas were analyzed by single point BET method. The BET specific surface area of 0.5% Pd/SiO_2 (357 m^2/g) catalyst was higher than that of 0.5% Pd/AlF_3 (198 m^2/g). This surface area is typical for sol-gel prepared catalysts and is much higher than that of similar catalyst prepared by impregnation method.[17,18,22] The total pore volume of Pd supported on SiO_2 and AlF_3 samples were found to be 0.20 and 0.11 ml/g, respectively. However, the average pore diameters of these catalysts were comparable (2.2, 2.3 nm for the 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3, respectively). It is important to emphasize that the average pore diameters obtained for the studied catalysts are slightly larger than those ascribed to micropores in common classification of pores (micropores, d < 2 nm; mesopores, d ~ 2-50 nm; macropores > 50 nm).



Scheme 2

Table 1. BET specific surface area (SSA), pore volume, pore diameter and total surface acidity (TSA) of 0.5% Pd supported on SiO_2 and AlF_3 matrices.

Catalyst	SSA[a] (m^2/g)	Pore Volume[b] (mL/g)	Pore Diameter[c] (nm)	TSA[d] (µmole/g)
0.5% Pd/SiO_2	357	0.20	2.2	48.2
0.5% Pd/AlF_3	198	0.11	2.3	97.0

[a] Determined by single point BET method at $P/P_o \approx 0.35$. [b] The total pore volume was calculated from the total amount of nitrogen adsorbed, $V_{liquid} = P\ V_{ads}\ V_m/RT$ where V_m is the molar volume of liquid nitrogen adsorbed (34.7 mL/mol). [c] Average pore diameter was calculated assuming cylindrical pore geometry, $r_p = 2\ V_{liquid}/S$ where r_p is the pore radius and S is the specific surface area. [d] Evaluated from the total amounts of irreversibly adsorbed pyridine at 29 °C.

Surface Acidity of 0.5% Pd Supported on SiO_2 and AlF_3 Matrices

The surface acidity of the support plays an important role in determining the nature and extent of interactions between the substrates and the surface of the support. Pyridine (pKa = 5.25) has often been used to assess the total acidity of solid surfaces[23] The capacity of the surface to retain pyridine after evacuation at room temperature is indicative of the number of acid sites on the surface. The nature of pyridine interaction with the acids sites on the surface of the supports varies depending upon type of the surface acid. Brönsted acids, Lewis acid and other hydrogen-bonding sites interaction with pyridine are reported to form pyridinium ion, covalently bonded pyridine and hydrogen-bonded pyridine, respectively. The surface acidity of Pd supported on silica is mainly attributed to the Brönsted acid property of the silanol groups (≡Si-OH) and water adsorbed on the surface of silica matrix. However, the acidity of Pd supported on AlF_3 is due to the electron deficient AlF_3 support (Lewis acids) and adsorbed moisture. In this study, the total surface acidity of both catalysts, 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3 was determined from the gas-phase adsorption data of pyridine at 180 °C. At these conditions pyridine selectively interacts with Brönsted and Lewis acid sites. The pyridine adsorption data obtained serve as quantitative estimation of the total number of acid sites on the surface of these catalysts (Table 1). The pyridine adsorption data indicates that the surface of 0.5% Pd/AlF_3 is more acidic than that of 0.5% Pd/SiO_2. However, detailed information about the various types of acid sites on the surfaces of both catalysts could not be obtained from these adsorption data and requires performing variable temperature reflectance infrared spectroscopy.[23]

Surface Morphology of 0.5% Pd Supported on SiO_2 and AlF_3 Matrices

The morphology of the sol-gel prepared catalysts was examined by scanning electron microscopy (SEM). The SEM micrographs of these Pd –supported catalysts are depicted in Figure 1. The SEM micrograph of the fine texture of the Pd supported on SiO_2 shows that the surface structure of this catalyst is considerably different from that of Pd/AlF_3. The micrograph of 0.5% Pd/SiO_2 surfaces reveals that they are composed of aggregates of relatively regular in shape and curvature micro-spherical globules, whoseaverage diameter is about 0.5-2.5 μm (Figure 1A). However, it was difficult to draw conclusions regarding the coordination number of these globular particles. The morphology of 0.5% Pd/AlF_3 shows that it consists of loose aggregates of small globular particles with average diameter of 0.3-0.5 μm (Figure 1B). The main textural differences between the studied Pd/SiO_2 and Pd/AlF_3 catalysts can be explained based on extensive cross-linked network that silica can form compared to the weak framework of AlF_3. Two types of interstitial cavities are clearly observed in the surface structure of these catalysts. The first type is relatively large macropores, which is formed by compacting of gel particle aggregates. The second type is microporous in nature that is formed during the drying process.

Adsorption of Freon-12 over 0.5% Pd Supported on SiO_2 and AlF_3 Matrices

The adsorption process of freon-12 over 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3 catalysts was investigated using a Pyrex vacuum line at 0, 31, 55 and 180 °C (Figure 4).

In both cases, exposure of the catalyst to freon-12 gas resulted in a rapid decrease in the pressure and attained equilibrium in about 60-90 sec. The adsorption data is presented in Table 2. Further evidence for the adsorption process of freon-12 on both catalysts was obtained by conducting individual adsorption experiments as shown in the experimental section and the adsorbed amounts were determined using standard GC technique. In these experiments the amounts of freon-12 retained by the catalysts were desorbed at about 350 °C, flushed with helium, then collected in the U-loop of the GC at liquid nitrogen temperature (-196 °C) and finally analyzed by GC. The quantities of desorbed freon-12 were estimated from the areas under the GC peak. The results obtained from GC measurements are in good agreement with those obtained from the adsorption measurements treating freon-12 as an ideal gas (Table 2).

The freon-12 adsorption isotherms (chemisorption) over a wide range of relative pressures (0.00-0.90 atm) at high temperature (180 °C) displayed a nonlinear behavior as shown in Figure 2. Close examinations of these isotherms indicate that the initial rises in the isotherm plots are not steep, which suggests that the tendency of both catalysts to bind freon-12 molecules is weak. However, over low-pressure range of 0.02-0.25 atm both isotherms gave rise to linear plots. The fraction of sites (θ) occupied by freon-12 at 0, 31 and 55 °C (physisorption) were calculated from linear form of the Langmuir Equation:

$$P_{eq}/\theta = (1+ K_{ads}P_{eq})/ K_{ads}$$

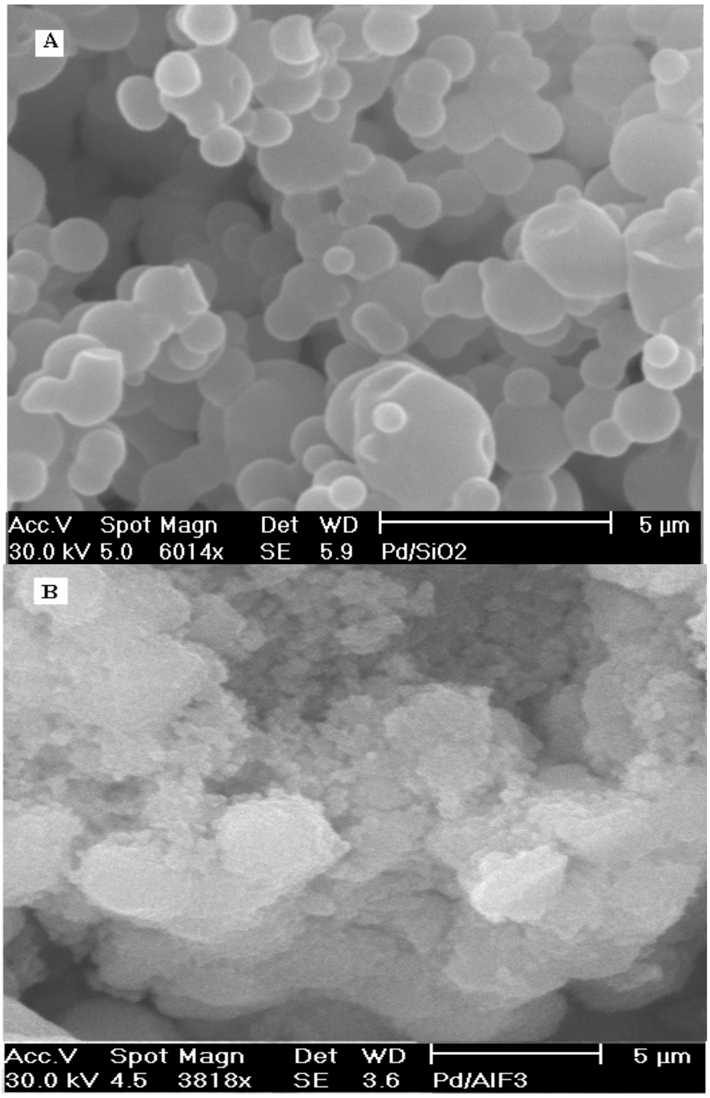


Figure 1. SEM micrograph of (A) 0.5% Pd/SiO_2 and (B) 0.5% Pd/AlF_3.

The maximum number of moles adsorbed per unit mass of catalysts (n_∞) and the adsorption equilibrium constants (K_{ads}) at each temperature were obtained from slopes and intercepts of the plots in Figure 3.

The obtained adsorption data indicates that the amounts of freon-12 retained on the surface of the catalysts increase with increasing relative pressure and decreasing temperature (Table 2). Although the BET specific surface area of Pd supported on SiO_2 matrix is larger than that of Pd supported on AlF_3, the adsorption data at low temperatures (physisorption) shows that the θ value for 0.5% Pd/AlF_3 is higher than that for 0.5% Pd/SiO_2. This observation suggests that the amount of freon-12 adsorbed does not depend only upon the BET surface area but also upon the nature of interaction between freon-12 and surface of the support. Moreover, the adsorbed amount correlates well with the surface acidity of the different supports (see surface acidity).

Table 2. Adsorption data for freon-12 over 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3 as a function of equilibrium pressure and temperature.[a-c]

T = 180 °C		T = 55 °C		T = 31 °C		T = 0 °C	
P_{eq}	μ mole/g	$P_{eq.}$	θ	$P_{eq.}$	θ	P	θ
Catalyst 0.5% Pd/SiO_2							
0.056	5.2	0.024	0.02	0.022	0.03	0.020	0.03
0.122	10.9	0.045	0.03	0.042	0.05	0.039	0.06
0.168	16.1(15.0)	0.090	0.05	0.085	0.10	0.075	0.13
0.234	22.2	0.172	0.10	0.162	0.17	0.148	0.19
0.290	26.4(24.5)	0.240	0.16	0.226	0.25	0.212	0.27
0.354	29.2	0.280	0.16	0.260	0.26	0.270	0.34
0.412	34.0	–	–	–	–	–	–
0.500	42.3	–	–	–	–	–	–
0.670	51.0	–	–	–	–	–	–
0.850	62.2	–	–	–	–	–	–
0.5% Pd/AlF_3							
0.055	7.5	0.024	0.04	0.022	0.07	0.020	0.09
0.112	14.2	0.046	0.07	0.042	0.12	0.038	0.15
0.166	21.7	0.092	0.13	0.087	0.19	0.080	0.25
0.224	28.4(27.1)	0.174	0.21	0.164	0.34	0.154	0.37
0.279	32.0	0.244	0.27	0.232	0.43	0.224	0.45
0.333	35.5	0.270	0.31	0.270	0.45	0.260	0.56
0.388	42.1(39.2)	–	–	–	–	–	–
0.510	56.1	–	–	–	–	–	–
0.670	69.0	–	–	–	–	–	–
0.880	82.0	–	–	–	–	–	–

[a] The adsorption data are the average of three experiments. Estimated error of measurements in P_{eq} = ± 0.003 atm, adsorbed amount = ± 0.4 μ mole/g and θ = ± 0.003. [b] $P_{eq.}$ = equilibrium pressure in atm (average of three experiments). The values in brackets are determined from GC analysis as described in the text. [c] θ = Fraction of the occupied sites ($\theta = n/n_\infty$) and n_∞ were calculated from 1/slope of Figure 3.

The corresponding thermodynamic parameters (K_{ads}, ΔG_{ads}, ΔH_{ads} and ΔS_{ads}) for the adsorption process of freon-12 over 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3 are summarized in Table 3. The Gibbs free energy ($\Delta G_{ads} = - RT \ln K_{ads}$) indicates that the adsorption process over 0.5% Pd/AlF_3 is spontaneous at the temperatures studied (0, 31 and 55 °C), whereas the adsorption over 0.5% Pd/SiO_2 is spontaneous at 0 and 31 °C but nonspontaneous at 55 °C. The enthalpies (ΔH_{ads}) for these adsorption processes were calculated from Van't Hoff plot (Ln K_{ads} vs. 1/T) and found to be -7.5 and –13.7 kJ/mol for 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3, respectively. Given the small values of ΔG_{ads}, and ΔH_{ads} one can conclude that the adsorption processes of freon-12 on both catalysts are favorable with weak interaction forces. The corresponding entropy changes (ΔS_{ads}) for the adsorption process on both surfaces are comparable.

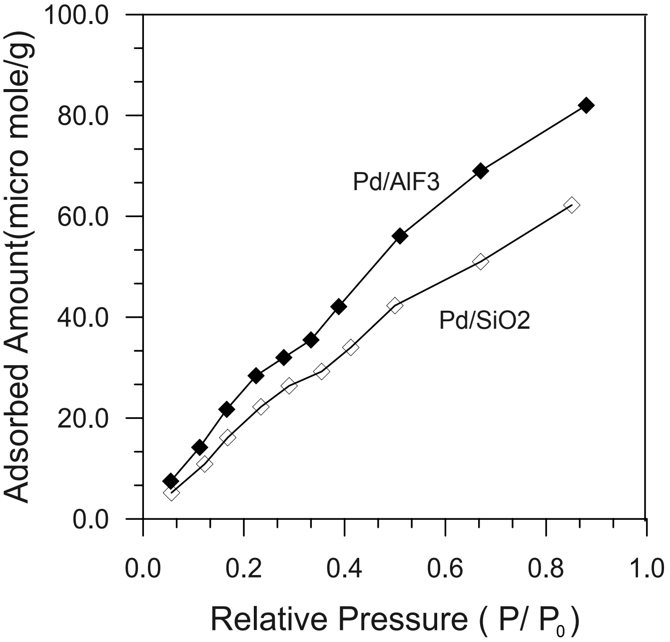


Figure 2. Adsorption isotherms of freon-12 over 0.5% Pd supported on SiO_2 and AlF_3 at 180 °C, see data in Table 2.

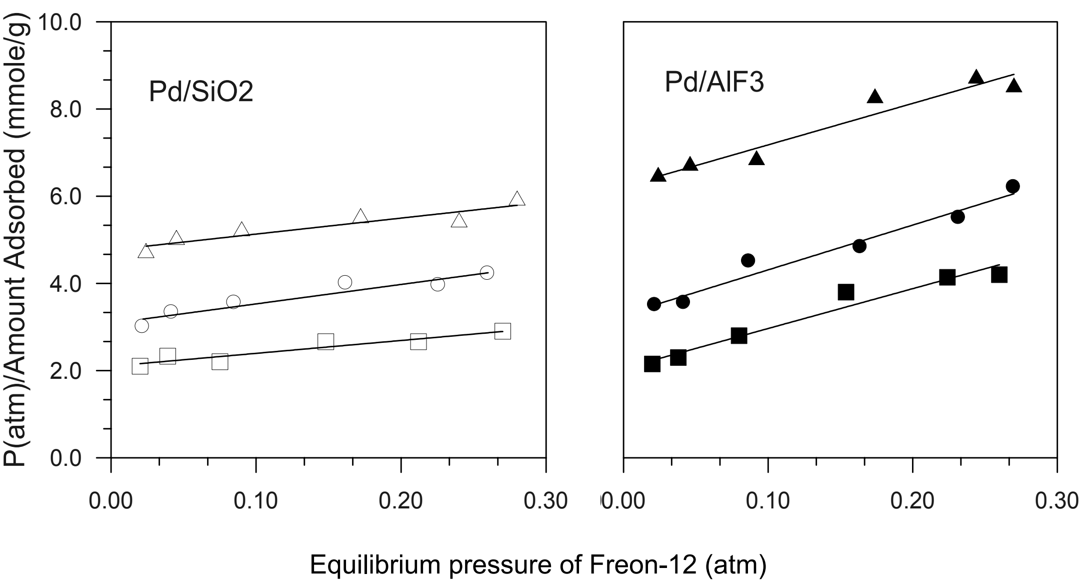


Figure 3. Linear form of Langmuir adsorption isotherm of freon-12 over 0.5% Pd supported on SiO_2 and AlF_3 (■ □ at T = 0 °C, ○● at T = 31 °C and ▲Δ at T = 55 °C), see data in Table 2.

Table 3. Langmuir adsorption equilibrium constant (K_{ad}), Gibbs free energy ($\Delta G_{ads.}$), enthalpy ($\Delta H_{ads.}$) and entropy (ΔS_{ads}) for the adsorption of freon-12 over 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3 at different temperatures.[a]

Catalyst	T °C	K_{ads} atm^{-1} [b]	ΔG_{ads} kJ/mol [c]	ΔH_{ads} kJ/mol [d]	ΔS_{ads} J/molK [d]
0.5% Pd/SiO_2	180	$1.23^e \pm 0.05$	- 0.71± 0.07	–	–
	55	0.77 ± 0.05	+ 0.71± 0.07	-7.5	-24.1
	31	1.36 ± 0.05	- 0.78± 0.07	–	–
	0	1.40 ± 0.05	- 0.76± 0.07	–	–
0.5% Pd/AlF_3	180	$1.33^e \pm 0.05$	-1.07± 0.07	–	–
	55	1.56 ± 0.05	-1.21± 0.07	-13.7	-37.3
	31	3.11 ± 0.05	-2.87± 0.07	–	–
	0	4.44 ± 0.05	-3.38± 0.07	–	–

[a] The values of $K_{ads,}$ ΔG_{ads}, ΔH_{ads} and ΔS_{ads} are the average of three experiments. [b] K_{ads} was calculated from Figure 3. [c] ΔG_{ads} = -RTln K_{ads}. [d] $\Delta H_{ads.}$ and ΔS_{ads} were calculated from Van't Hoff Plot, Ln K_{ads} vs. 1/T. [e] Chemisorption conditions, calculated from linear relation P/n vs. P at 180 °C. Adsorption data for Freon-12 on Pd/SiO_2 was as follows, $P_{eq.}$ (0.020, 0.056, 0.085 and 0.122 atm) and the corresponding adsorbed amounts on of 2.00, 5.20, 7.87 and 10.90 μ mol/g. The adsorption data for Freon-12 on Pd/AlF_3 was, $P_{eq.}$ (0.020, 0.055, 0.088 and 0.122 atm) and the corresponding adsorbed amounts were of 2.88, 7.50, 11.56 and 14.20 μ mol/g.

Conclusions

The surface characteristics (morphology, acidity, porosity) of the sol-gel prepared 0.5% Pd-supported on SiO_2 and AlF_3 are different. The thermodynamic parameters obtained for the gas-phase adsorption processes of freon-12 on 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3 suggest that adsorption is generally spontaneous and weak in nature and was more favorable over 0.5% Pd/AlF3 than that on Pd/SiO2. In the temperature range studied, the fraction of sites (θ) of 0.5% Pd/AlF_3 surface occupied by freon-12 is higher than that of 0.5% Pd/SiO_2, and found to be in agreement with the total number of acidic sites on their surfaces but not with the BET surface area.

Experimental

All solvents and chemicals used were reagent grade and used as received. Hydrogen, helium and nitrogen (99%) were purchased from International Industrial and Medical Liquid-Gas Co. $PdCl_2$ (99%, Janssen Chemica), anhydrous $AlCl_3$ (99%, Merck) and tetraethoxysilane (99%, Janssen Chemica) and HF (40%v/v, Reidal de-Haen) were used without further purification. The purity of CF_2Cl_2 (freon-12, Mafron, dried over molecular sieve 5Å) was checked by gas chromatography [Chrompack Packard, model 437A connected with FID detector using 5% Fluorocol, 60/80 carbopack B column, 10 ft∗1/8 inch (Supelco)]. The temperature of the injector, oven and detector were maintained at 160, 45 and 200 °C, respectively. The data was collected on a SP Thermoseparation Electronic Integrator. FT-IR spectra were recorded on a Nicolet impact 410-FT-IR spectrometer. The surface morphology of these catalysts was investigated on a Philips scanning electron microscope (W-SEM, TMP, model XL-30) at 30 kV. The samples were crushed to a very fine powder (grain size = 60-100 μm), washed with ethanol and vacuum dried at 70-80 °C. They were sputter coated with gold (BALTEC, Model SCD005). The surface porosity (BET specific surface area, the total pore volume and the pore diameter) of the calcined catalysts was determined from nitrogen adsorption isotherms at liquid nitrogen temperature (–196 °C).

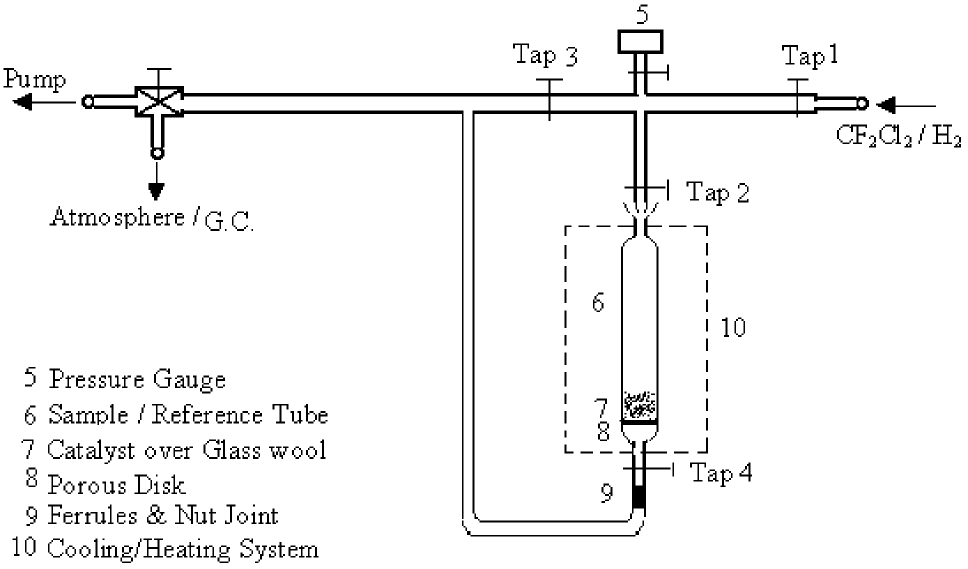


Figure 4. Schematic drawing of the Pyrex vacuum line used in this investigation.

Sol-Gel Preparation of 0.5% Pd Supported on SiO_2 and AlF_3 Matrices

0.5% Pd/SiO_2: $PdCl_2$ (0.1252 g, 0.7061 mmol) was dissolved in 20 ml distilled water. Equal volume of absolute ethanol (Baker Analyzed) was then added. The pH of the resulting solution was adjusted to 1.0 by addition of HCl. To this mixture tetraethoxysilane (52.08 g, 250 mmol) was added. The solution was magnetically stirred and then heated to reflux for about 4-5 hours until gel formation was complete. The solvent was then evaporated over a boiling water bath. The gel was allowed to stand overnight in air and then oven dried for several hours at about 100 °C. The isolated solid ($PdCl_2$ supported on silica) was crushed, milled with a hand mortar and then subjected to calcinations and reduction. The powder was loaded in the Pyrex cell connected to the vacuum line as shown Figure 4, heated for one hour in flowing air at 200 °C and then flushed with helium for 10 minutes. The Pd(II) was reduced to metallic Pd under dynamic hydrogen flow (30 ml/min, 4 hours, 450 °C). The obtained catalyst (0.5% Pd-supported on silica) was cooled to room temperature and stored in a desiccator. It was activated before use by heating in a hydrogen atmosphere for one hour at 450 °C and cooled to room temperature by passing helium. FT-IR (KBr) ν 3462, 1082, 955 cm^{-1}. Single point BET specific surface area: 357 m^2/g.

0.5% Pd/AlF_3: Anhydrous $AlCl_3$ (13.33 g, 100 mmol) was suspended in excess amount of absolute ethanol (30 ml) under nitrogen. The resulting alcoholic solution of $Al(OEt)_3$ was mixed with a magnetically stirred solution containing 16 ml of HF (40% v/v) and aqueous $PdCl_2$ (0.0700 g, 0.395 mmol dissolved in 10 ml of distilled water). The reaction mixture was then warmed at 70-80 °C for 4-5 hours during which ethanol evaporates forming a thick gel. The resulting gel was further dried over a boiling water bath for several hours to yield a white solid. The obtained solid (Pd(II) supported on AlF_3) was crushed, milled, calcined and reduced as described earlier to finally yield 0.5% Pd/AlF_3. FT-IR (KBr) ν 3360, 1106, 940 cm^{-1}. Single point BET specific surface area: 198 m^2/g.

Total Surface Acidity of the prepared 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3 catalysts

The catalyst (0.10 g) were introduced in the reactor, heated in hydrogen atmosphere (60 minutes) to 200 °C then brought under vacuum (1 x 10^{-6} atm) for about 30 minutes to remove physisorbed moisture and eventually cooled to room temperature. Liquid pyridine (5 μL) was introduced into the evacuated reactor by injection with microsyringe as a result of which the surface of the catalyst became saturated with pyridine base at equilibrium. The reactor was evacuated (1 x 10^{-6} atm, 15 minutes, room temperature) to remove excess pyridine and the pressure is recorded. The temperature was quickly raised and maintained at 180-200 °C. At this stage the pyridine molecules attached to acid sites on the catalyst surface were liberated and the pressure is recorded. The amount of liberated pyridine in this step can be calculated using gas law

(PV = nRT). Reference values were obtained using the same procedure in the absence of the catalyst.

Adsorption of freon-12 over 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3 catalysts

The adsorption process of freon-12 over 0.5% Pd/SiO_2 and 0.5% Pd/AlF_3 catalysts was studied at different temperatures (0, 31, 55 and 180 °C) using a Pyrex vacuum line (volume = 12.7 mL) connected to a double stage rotary pump and the pressure was recorded using a digital pressure gauge (DVR2, Vacuubrand) with accuracy of ± 0.5×10^{-6} atm Before each adsorption measurement, the system was checked for leaks, loaded with the desired catalyst (0.20 g) and activated by heating in hydrogen atmosphere (60 minutes, 200 °C) then evacuated and cooled to room temperature (29 °C, 1.0×10^{-6} atm). The desired temperature was fixed and a small amount of freon-12 was introduced into the upper part of the vacuum line through tap1 (taps 2, 3 and 4 are closed) and the initial pressure (P_i) was recorded. When tap1 was closed and tap2 opened, a drop in the pressure was observed. The final equilibrium pressure (P_f) was recorded after 10 minutes of establishing the equilibrium. After each adsorption experiment the catalyst was cleaned by purging with hydrogen (25 mL/min, 200 °C, 15 minutes) followed by degassing (1×10^{-6} atm, 60 minutes, room temperature). The discharged gases were analyzed by gas chromatography (GC) and satisfactory cleaning was obtained when freon-12 was not detectable.

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Povzetek

Po sol-gel postopku smo pripravili katalizatorja 0.5% Pd/SiO_2 in 0.5% Pd/AlF_3. Preučevali smo morfologijo, razvitost površine in poroznost (specifično površino po BET, prostornino por in premer por) ter kislost površine na teh vzorcih. V ta namen smo uporabili metode rastrne elektronske mikroskopije (SEM) ter volumetrični metodi adsorpcije dušika in piridina iz plinske faze. Ugotovili smo, da sta specifična površina po BET in celoten volumen por v 0.5% Pd/SiO_2 večja kot v 0.5% Pd/AlF_3, medtem ko je celotna površinska kislost višja v 0.5% Pd/AlF_3. Preučevali smo process adsorpcije diklorodifluorometana (freona-12) pri 0, 31, 55 in 180 ^{0}C na obeh vzorcih katalizatorjev. Izračunali smo delež zasedenosti površine (θ) s freonom-12 z uporabo Langmuirjevega modela za adsorpcijsko izotermo. Termodinamska analiza podatkov o ravnotežni adsorpciji freona-12 (dolčitev K_{ads}, ΔG_{ads}, ΔH_{ads} in ΔS_{ads}) kaže, da je adsorpcija na 0.5% Pd/AlF_3 ugodnejša kot na 0.5% Pd/SiO_2.