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Catalytic Hydrodechlorination of Chlorocarbons. 2. Ternary Oxide Supports for Catalytic Conversions of 1,2-Dichlorobenzene[1]

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Ternary oxides of Ti-Zr-Al and Ti-Zr-Si were prepared by coating commercial Al_2O_3 and SiO_2 with a THF solution of $Ti(OPr^i)_4$ and $Zr(OPr^i)_4$ under controlled conditions. Nitrogen adsorption and X-ray powder diffraction indicate that the structure of the base supports, Al_2O_3 and SiO_2, were not significantly altered upon coating and that TiO_2 and ZrO_2 were quite uniformly spread on them. The acid resistance of alumina was found to be increased upon coating. Palladium supported catalysts, $Pd/TiZrAlO_x$, $Pd/TiZrSiO_x$, Pd/TiO_2, Pd/ZrO_2, Pd/SiO_2, and Pd/Al_2O_3 were prepared to evaluate the ternary oxides relative to the component single oxide supports. Palladium dispersion was determined using hydrogen chemisorption and the catalysts were evaluated for hydrodechlorination of 1,2-dichlorobenzene. The experimental runs were carried out in a microflow reactor system at atmospheric pressure, in the gas phase. The catalysts were oxidized and then reduced, prior to reaction. The kinetic studies showed that the ternary oxide-based catalyst, $Pd/TiZrAlO_x$ exhibited an improved stability and activity much higher than the arithmetic sum of the activities of the component single oxide based palladium catalysts. Comparison of the specific activities of the catalysts expressed as TOF, indicate that the observed differences in activity may be related to the chemical nature of the supports. The best catalyst had an initial specific activity of 16.6 s^{-1}. We observed that the pretreatment of the catalyst has a profound effect on its stability and activity. Also, the experimental results indicated that the major factors of the catalyst deactivation are agglomeration of palladium particles and HCl poisoning. Prospects for optimization of these catalysts are discussed in light of the results of this work.

INTRODUCTION

Aromatic chlorocarbons are among the most widespread and persistent toxic pollutants. Consequently, an improved process for their destruction would be of significance. Several methods have been developed for their destruction: incineration, reduction by transition metal activated alkali metal hydrides (1, 2), biodegradation using microbes (3–5), photocatalytic oxidation using semiconductor materials such as titania or perovskites irradiated with UV light (6–8), and catalytic hydrodechlorination. Among these processes, catalytic hydrodechlorination is one of the most effective because it excludes the formation of more toxic compounds such as dioxins, it is applicable to waste with any content of chlorine, the hydrocarbon produced can be recovered and recycled, and it is economical.

There is a large body of published work in the area of catalytic hydrodechlorination of chlorinated aromatics (9–18). These works can be broadly classified in two groups according to the catalytic system used. The first group involves catalysts such as Pd, Pt, or Rh supported usually on γ-alumina or carbon. Many researchers have investigated this class of catalysts. Dini *et al.* (9) have studied the gas-phase catalytic hydrodechlorination of chlorobenzene over Pd, Pt, and Rh supported on aromatic polyamid or alumina and found the polyamide-based catalysts to be highly selective. Only benzene was produced over the temperature range investigated on the Pt/polyamide catalyst. Kovenklioglu *et al.* (10) have described the liquid phase hydrodechlorination of various chlorinated hydrocarbons over Pd, Pt, Rh supported on carbon materials of different sources or supported on alumina. They nicely demonstrated the importance of the chemical nature of the support on the rate of conversion of the chlorinated hydrocarbon. Kinetic studies of hydrodechlorination with this first group of catalysts have been carried out by several researchers including LaPierre *et al.* (11). Coq *et al.* (12) elucidated the mechanism of the C-Cl hydrogenolysis using a simple molecule, chlorobenzene, in the gas phase with Pd/Al_2O_3 and Rh/Al_2O_3 catalysts of varying dispersions. They studied the influence of the by-product HCl, a point that was not addressed in previous studies, and the effect of the size of the metallic particle on the stability of the catalyst. The advantage with this first group of catalysts is that they are active at low temperature and pressure. However, they deactivate rapidly.

The search for more stable catalysts has led to a second group of catalysts which involves metals such as Ni, Mo, Co, Ni-Mo, or Co-Mo on γ-alumina or carbon (13–18). These

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catalysts display better performance when sulfided prior to reaction. Although they are more stable, high temperatures and high pressures are required to reach significant activity.

Our objective in the work reported here is to design catalysts which will show both high activity and stability under less energy intensive conditions. We chose to use palladium as the active metal because it has previously been reported to be the most active metallic catalyst for hydrodechlorination of organic chlorides (12, 19). Our work has focused on the design of a novel support that will impart stability to the final catalyst and is based on the fact that support composition can influence the bonding of the metal particles to the support. The support can also assist in the adsorption of the reactants, thereby accelerating the reaction (10). In this report we describe the synthesis and characterization of novel ternary oxide supports, $TiZrAlO_x$ and $TiZrSiO_x$, and their applications in catalytic hydrodechlorination of 1,2-dichlorobenzene.

Ternary oxides of Ti-Zr-Si have been synthesized for other applications (20) but our synthetic approach is different from those found in the literature and to the best of our knowledge, we are the first to report the use of these materials as supports in catalytic hydrodechlorination. The rationale for choosing these systems is founded in the fact that titania and zirconia have demonstrated interesting properties as catalyst supports in several reactions. For example, Katzer *et al.* (21) found relative activities of Rh/TiO_2 and Rh/SiO_2 to be 100/1 in the hydrogenation of CO. For the same reaction, Haller *et al.* (22) found relative activities of 100/6 for Rh/TiO_2 and Rh/SiO_2 systems. Murase (23), Kibbel (24), and Stevens *et al.* (25, 26) reported that incorporation of zirconia into alumina resulted in increased mechanical strength. Unfortunately, titania and zirconia display relatively low surface area and low porosity compared to alumina and silica (see Table 1). All of these are important properties in heterogeneous catalysis. Note that titania is not easy to pelletize or extrude in high surface area forms. The 150 m^2/g for the titania used in this work is an exceptionally high surface area form. The surface area of most commercial titania rarely exceeds 50 m^2/g.

TABLE 1

BET Surface Area and Total Pore Volume for Various Supports and Catalysts

Sample	Total surface area (m^2/g)	Total pore volume (cc/g)
TiO_2	150	0.33
ZrO_2	90	0.30
Al_2O_3	265	0.78
SiO_2	225	1.42
$TiZrAlO_x$-ML (before activation)	268	na
$TiZrAlO_x$-DL (after activation)	231	na
$TiZrAlO_x$-ML (after activation)	254	0.63
$TiZrSiO_x$ (after activation)	236	1.22
Pd/Al_2O_3	257	na
$Pd/TiZrAlO_x$ (before reaction)	244	na
$Pd/TiZrAlO_x$ (after 70.5 hours on stream)	238	na

Note. na = not available.

Our approach is designed to take advantage of both the beneficial properties of titania or zirconia and the well-characterized high surface area and high porosity of commercial alumina and silica.

For catalytic evaluation, we used 1,2-dichlorobenzene (DCB) because it is among the most challenging aromatic chlorides to dechlorinate, it is present as a contaminant in many waste streams, and it is relatively safe for exploratory work. Our long-range research goal is to develop highly active, stable catalysts for use in the destruction of a wide range of environmentally persistent halocarbons including PCBs.

EXPERIMENTAL

Materials

Titania, zirconia, and alumina were all donated by Norton Chemical Company and silica was donated by PQ Corporation. Titanium(IV) isopropoxide (99.99+%) and zirconium(IV) isopropoxide isopropanol complex (99.9%), both purchased from Aldrich, were kept in a nitrogen-filled inert atmosphere until use. 1,2-Dichlorobenzene (DCB), 99% HPLC grade, also purchased from Aldrich, was used as received. THF, HPLC grade from Fisher, was dried over potassium by distillation. The gases, hydrogen (>99.8%) and helium (>99.99%) purchased from Air Products, were purified by in-line gas dryers and oxygen scavengers. Air was purified using in-line moisture scavengers.

Supports Preparation

The preparation of the ternary oxide supports involves reaction of the oxide precursors with the surface hydroxyl groups of the supporting oxide under controlled conditions in order to achieve homogeneous deposition. Before use, alumina or silica was dried to remove any physisorbed water, leaving the surface fully hydroxylated. In a typical experiment for the $TiZrAlO_x$ support, 3.5 g of alumina was weighed and transferred into a Schlenk flask. 1.53 mL of titanium isopropoxide and 2.02 g of zirconium isopropoxide, which corresponds to a 1 : 1 mole ratio and the amount required to react with all the surface hydroxyl groups (27–29), were dissolved in 12 mL of dry THF. While the alumina support was heated to 70–80°C, the alkoxide solution was also heated to boiling and kept under reflux for 1 h. Then, the alumina was impregnated with the hot alkoxides solution and heating was continued for 20 h. Following removal of excess solvent, along with small amounts of unreacted alkoxides, the remaining solid residue was washed with

THF and slowly hydrolyzed by passing water vapor in a nitrogen carrier for 24 h. The removed solution was saved for subsequent testing to determine the degree of reactivity of the alkoxides. At the end of the hydrolysis process, the material was calcined at 500°C for 24 h to yield the final support. This support, with a monolevel coating of alumina, will subsequently be identified as $TiZrAlO_x$-ML. A second level of coating was also carried out. The preparation procedure was the same as described above, except that the base support was $TiZrAlO_x$-ML instead of alumina. The resulting support, with a double level coating of alumina, will be identified as $TiZrAlO_x$-DL. For the preparation of $TiZrSiO_x$-ML support, a 0.66 mL portion of titanium isopropoxide and 0.86 g of zirconium isopropoxide in a 1 : 1 mole ratio, dissolved in 7.5 mL of THF, were used to impregnate 3 g of silica. The preparation followed the same general procedure as previously described.

Catalysts Preparation

All the catalysts reported in this work were prepared in the same manner by dipping impregnation and were all 2 wt% Pd on the given support. A 0.068 g sample of palladium(II) chloride precursor was dissolved in 4 mL distilled water acidified with HCl ($pH = 0.4 \pm 0.2$) and stirred overnight. A 2.0-g portion of the support was impregnated with this solution, allowed to stand for 24 h, then opened to air at room temperature for 2 days. After that it was further dried in an oven at 100°C overnight and stored in a desiccator until use in catalytic measurements.

Nitrogen Adsorption

The BET surface area was measured for all supports and catalysts. In some cases the pore size distributions were also determined. These measurements were carried out by adsorbing nitrogen at liquid nitrogen temperature using a Micromeritics ASAP 2000 instrument according to the manufacturer's procedures (30).

X-Ray Powder Diffraction

X-ray powder diffraction (XRD) of the bare supports and the ternary oxide supports were recorded to fingerprint the phases present. All the samples were first finely crushed with a mortar then dried at 100°C overnight before use. The diffraction patterns were recorded on a Siemens D5000 powder diffractometer. For the experiments, a copper sample holder supplied by the instrument manufacturer was used. The sample was dusted onto it then flattened and smoothed with a razor blade. The diffractograms were recorded using copper $K\alpha$ radiation and a wavelength of 1.5418 Å. The samples were scanned in the 2θ range of 10 to 80°. The diffractogram of the copper sample holder was also recorded for background subtraction as it gives a diffraction pattern.

Static Hydrogen Chemisorption Measurements

Metal dispersion of the fresh $Pd/TiZrAlO_x$-ML, fresh Pd/Al_2O_3, and used $Pd/TiZrAlO_x$-ML catalysts were determined by hydrogen chemisorption. Measurements were performed using a static volumetric stainless steel system equipped with a high vacuum turbo molecular pump which can give a dynamic vacuum of 10^{-7} torr. The backsorption method described by Benson *et al.* (31) was used. This technique has been demonstrated to be the most valuable tool to measure the dispersion of palladium catalysts (32). Measurements were done at 9–11 torr pressure range and at 25 and 27°C to avoid β-hydride formation. For the fresh catalysts, a 0.25-g sample was air oxidized at 400°C for 4 h in a tube furnace then transferred to a glass tube and inserted into the high vacuum manifold. The sample was evacuated, heated under helium to 350°C for a 1-h period, and then hydrogen reduced at that temperature for 4 h. After reduction the catalyst was evacuated for 16 h and chemisorption measurements were performed. The irreversibly bound amount of hydrogen was used to calculate the dispersion assuming 1 : 1 stoichiometry of H : Pd. For the used catalyst, the experimental procedure was the same as described except there was no oxidation and reduction step.

Determination of Cl^- Ion Adsorbed on Used Catalyst

A sample of the used catalyst was transferred into a beaker containing water and allowed to stand for 23 days then heated to 60–70°C overnight. The solvent was isolated by filtration afterwards to permit determination of the concentration of Cl^- ions. The experiment was carried out on a Dionex ion chromatographic system equipped with a AS9SC chromatography column. The total moles of Cl^- adsorbed per gram of catalyst was 8.65×10^{-4} and the total moles of Pd per gram of catalyst was 1.89×10^{-4}. This result strongly supports the suggestion that Cl^- was also adsorbed on the support.

Catalytic Measurements

Testing was carried out at atmospheric pressure in a flow reactor system which consists of gas and liquid delivery lines with flow control devices, a tubular fixed-bed reactor heated by an IR furnace, and an analysis work station. The DCB was fed into the reactor using an ISCO LC-5000 precision pump. The reactor tube temperature was maintained to within ±1°C of the set point as measured by a thermocouple directly inserted in the catalyst bed. The reactor effluent analysis was performed on an in-line HP 5890 gas chromatograph interfaced with a Dionex Advanced Computer Interface. The gas chromatograph was equipped with a thermoconductivity detector and a 1/8 in. OD × 0.085 in. ID × 6-ft long stainless steel column packed with 10% Carbowax 20M on Chromosorb WHP (120/140 mesh) from

Alltech. Further detail of the reactor system have been published (33).

As a general procedure, the catalyst was diluted with SiC of the same size (0.25 mm) in order to attain a more isothermal profile within the reactor. Then it was loaded in the reactor between quartz wool plugs, air oxidized at 400°C for 4 h, and hydrogen reduced for 4 h at 350°C prior to initiation of reactant feed. In one case the catalyst was only reduced to examine the influence of pretreatment on catalyst reactivity. This will be specified in the report of results. Preliminary tests were made under integral conditions to establish a rough estimate of the relative activity and stability of the catalysts. Following the integral mode experiments, kinetic studies were carried out under differential conditions to explore the specific activities. Prior to the detailed kinetic studies, several reactor characterization studies were undertaken to determine (a) the catalytic activity of the reactor walls, the thermocouple, and the SiC diluent and (b) the extent of mass transport limitations.

RESULTS

Blank Tests

To determine if the reactor, thermocouple, and the SiC diluent were active in the catalysis of dechlorination, dichlorobenzene and hydrogen were pumped through either the empty reactor with the thermocouple inserted or the reactor filled with SiC at various temperatures. The average DCB conversion was 0.75 mol% at 340°C with the empty reactor and 1.65 mol% at 300°C when the reactor was loaded with SiC. Although SiC shows more reactivity than the empty reactor, its contribution can be neglected at high chlorocarbon conversion. No catalytic activity was detected at 250°C when the reactor was filled with SiC. Therefore, the results reported at 250°C or below can be considered to be due solely to the catalyst.

Integral Test Results

In preliminary runs, about 0.4 g samples of catalysts were used to establish a rough estimate of the relative activity and stability of palladium supported on the ternary oxides compared to palladium supported on the single oxides. These runs were instrumental in our decision whether or not to pursue studies on the novel supports, Ti-Zr-Al or Ti-Zr-Si. At 200°C, at atmospheric pressure, hydrogen : DCB mole ratio of 10 : 1, a space time of 5 s, and space velocity of 5.64 NL/g cat · h (where NL represents the number of liters of reactants at STP), all catalysts gave 100% conversion initially. When the conversion fell below 100%, the test was stopped. The catalysts were evaluated by determination of how long they maintained 100% conversion. Four catalysts were used in these preliminary runs: Pd/Al_2O_3, Pd/TiO_2, $Pd/TiZrSiO_x$, and $Pd/TiZrAO_x$. They maintained 100% conversion for 24, 23, 183, and 390 h, respectively. Pd/Al_2O_3, $Pd/TiZrSiO_x$, and $Pd/TiZrAlO_x$ produced exclusively cychlohexane and benzene throughout the run, while for Pd/TiO_2, the major product was benzene and the amount decreased with time on stream with an appearance of chlorobenzene near the end of the reaction. Although data related to 100% conversion is of limited value, it gives a crude estimate of the relative activity and stability of the catalysts. To gain deeper insight into catalyst performance, kinetic studies were undertaken.

Kinetic Studies

The kinetic runs were carried out at 250°C, under differential conditions (2–21% conversion depending on the catalyst). Differential conditions prevail when the rate is assumed to be constant at any point within the reactor. This assumption is usually reasonable for shallow reactors, at low conversion, but as discussed by Levenspiel (34), this is not necessarily so, e.g., for slow reactions, where the reactor can be large, or for zero order kinetics, where the composition change can be large. The weight of catalysts used ranged from 4 to 7 mg for the ternary oxide-based catalysts, and 15 to 40 mg for the single oxide-based catalysts. The reaction products were benzene, chlorobenzene, and trace amounts of cyclohexane. For each catalyst, the selectivity to cyclohexane was 2% maximum at the beginning of the reaction and then quickly dropped to zero after about 2 h on stream. The rates were calculated using Eq. [1]

$$\text{Rate} = F_o \text{Conv}/W, \qquad [1]$$

where F_o is the entering molar flow rate of dichlorobenzene, Conv, its fractional conversion, and W is the catalyst weight. Before the kinetic studies, precautions were taken so that the collected rate data were exempt of heat and mass transport artifacts.

Heat and Mass Transport Processes

There are two important heat and mass transport phenomena that can influence the rate of the reaction in a fixed-bed reactor: interparticle and intraparticle transport processes. The most active catalyst, $Pd/TiZrAlO_x$-ML was selected to study the extent to which these transport phenomena affect the hydrodechlorination rate.

In all the experiments, the catalyst was diluted with SiC which has a very high thermal conductivity (37.2×10^{-3} cal/s · cm°C) to ensure that heat transfer was not an influential factor. Although the reaction is highly exothermic and the Pd loading quite high (2 wt%), the dilution (0.5/100 to 3/100 catalyst/SiC volume ratio) can be considered high enough to prevent a significant temperature gradient across the gas–solid interface. Nevertheless, we carried out calculations to determine the extent of temperature rise at the catalyst surface.

The temperature gradient across the gas film, ΔT_{film}, can be estimated by Eq. [2]

$$\Delta T_{\text{film}} = (V_p/A_p)r_{\text{obs}}(-\Delta H)/\text{h} = L^2 r_{\text{obs}}(-\Delta H)/\lambda, \quad [2]$$

where V_p is the volume of the catalyst pellet, A_p is its external area, r_{obs} is the observed rate per unit volume of catalyst, ΔH is the heat of reaction, λ is the heat conductivity of the DCB and hydrogen mixture, and h is the film heat transfer coefficient. In this expression $L = V_p/A_p$ and, as a conservative estimate, it is assumed that the film thickness is equal to L. At 250°C the temperature rise was found to be 0.90°, indicating that the reaction remained isothermal.

Because solids are much better thermal conductors than gases, the thermal conductivity of the gas is the controlling factor in the overall effective thermal conductivity. Therefore, the temperature gradient across the catalyst pellet can be neglected under these reaction conditions.

Mass transport processes were investigated by both theoretical calculations and by experiment. In the theoretical calculations, the criteria of negligible diffusion by Weisz and Prater (35) was used. According to them, for $\Phi \ll 0.1$ diffusion is not limiting. Our calculations gave a Φ value of 4.43×10^{-3}, suggesting that diffusional limitations can be ruled out.

Intraparticle processes were studied by varying the catalyst particle size and keeping all other operating parameters identical (Table 2). These results also confirm that there are no significant mass transport limitations under the reported reaction conditions.

Table 3 compares the rate of consumption of DCB for all the catalysts at 250°C. The last column contains the rates at steady state conversion. These rates represent averages of several measurements at steady state conversion after about 10 to 13 h on stream. The error ranges reported here and previously (Table 2) combine both systematic and random error. The systematic error, E_S, was obtained by propagating the error about the formula of the rate. The random error was calculated using statistical methods; a 95% confidence limit was considered. Our intention in this work is not a detailed kinetic study with just one catalyst but to compare the relative activity of palladium supported on ternary oxides of TiZrAlO_x or TiZrSiO_x and palladium supported on the corresponding single oxides.

TABLE 2

Results of Intraparticle Mass Transport Experiments at 250°C

Catalyst particle size	Space time (seconds)	Space velocity (NL/g cat · h)	Space velocity (h^{-1})	Rate × 10^3 (mol/g cat · min)
Conversion: 14-15 Mole%				
40/60 mesh	1.72	839	2097	12.7 ± 0.9
≪40/60 mesh	1.72	807	2097	13.3 ± 0.8

TABLE 3

Comparison of Steady State Rates at 250°C and H_2/DCB Mole Ratio of 8 : 1

Catalyst	GHSV (h^{-1})	Sp. T. (sec)	Sp. vel. (NL/ g cat · h)	Conversion (mole%)	10^3 × Rate at steady state (mol/ g cat · min)
Pd/TiZrAlO_x-ML	3222	1.12	1315	17	23.2 ± 3.0
Pd/TiZrAlO_x-DL	3222	1.12	1432	12	13.7 ± 0.7
Pd/TiZrSiO_x-ML	2685	1.34	707	16	9.4 ± 1.5
Pd/ZrO_2	2151	1.67	414	21	8.4 ± 2.9
Pd/Al_2O_3	2151	1.67	410	19	6.5 ± 3.3
Pd/TiO_2	2151	1.67	410	6	2.0 ± 0.1
Pd/SiO_2	2151	1.67	108	11	1.2 ± 0.3

Chemisorption Results

Two catalysts, Pd/Al_2O_3 and Pd/TiZrAlO_x were examined for hydrogen chemisorption and the results are shown in Table 4. The mean particle size, d_p, and surface area, S_{pd}, of Pd were calculated using Eqs. [3] (36) and [4] (37), respectively,

$$d_p(\text{nm}) = 112/D \quad (\%) \qquad [3]$$

$$S_{\text{pd}} = \upsilon^{-1} U N \sigma, \qquad [4]$$

where D represents the dispersion, υ is the stoichiometry of the chemisorption of hydrogen on palladium, U is the amount of gas consumed in moles per gram of catalyst, N is the Avogadro number, and σ is the area occupied by one surface palladium atom. The two catalysts have similar palladium dispersions. The activity expressed as turn over frequency (TOF), that is the number of dichlorobenzene converted per exposed palladium atom per second, were calculated from rates and the dispersion values. The initial TOFs were calculated using the number of exposed palladium atoms on the fresh catalysts and the rate after 30 min on stream. The TOF at steady state was calculated using the average rate at steady state conversion and the number of exposed palladium atoms on the used catalyst.

TABLE 4

Hydrogen Chemisorption Results

Catalyst	Dispersion (%)	d_p (Å)	Spd (m^2/g)	TOF (s^{-1})
Pd/TiZrAlO_x-ML (fresh Catalyst)	38	29.5	3.6	16.6^{i}
Pd/TiZrAlO_x-ML (used catalyst)	21	53.3		9.8^{ss}
Pd/Al_2O_3	34	32.9	3.2	5.6^{i}

Note. i = initial; ss = steady state.

Pore Size Distribution and Total Surface Area

As stated at the beginning, it was our desire to uniformly spread titania and zirconia on the supporting oxide, meanwhile maintaining high surface area and porosity. Comparison of the pore size distribution of the uncoated alumina or silica base supports against the coated ones indicates there is not a significant alteration in the pore structure. However, the pore structure of silica is altered more than that of alumina by the coating process. The average pore diameters of silica and alumina measured in our lab are 254 and 110 Å, respectively. Upon coating, the average pore diameter decreased to 207 and 99 Å, respectively. The alkoxides can react with hydroxyl groups located in pores large enough to accommodate them, whereas the hydroxyl groups located in small inaccessible pores will not participate in the reaction. This would explain the differences found in alumina and silica and also the trend observed. For alumina, the pore size distribution study indicates only a slight change in the pore structure upon coating, which occurs in the pore size range of about 50–150 Å and also in the range 275–575 Å. With silica, on the other hand, an increase in the contribution to the total pore volume of pores is observed in the size range 150 to 250 Å, whereas there is a decrease of the contribution from pores in the 300 to 825 Å range. Table 1 shows the BET surface area of most materials described in this work. In general, one would expect the introduction of a second oxide to fill a fraction of the pores of the supporting oxides, thereby decreasing the total surface area. This is what is seen with alumina but the opposite is observed with silica. Experimental error could account for the enhancement in surface area with silica. Also, the surface area of the coated alumina before and after activation do not differ significantly. This shows that during calcination the hydrolyzed precursor to the support did not undergo significant structural changes. The pore size distribution of the Pd/$TiZrAlO_x$ catalyst is basically the same as that of the corresponding support even though a strongly acidic medium and long contact time were used during its preparation. Because alumina is known to dissolve in an aqueous solution with $pH < 4$ (38, 39), this observation indicates that titania and zirconia deposition confers some acid resistance to alumina. Further tests were carried out by contacting alumina and $TiZrAlO_x$ separately with acidified water at pH 0.4 for 11 days to investigate the acid resistance. These results will be discussed later.

X-Ray Diffraction

The results of the X-ray diffraction experiments of the single and ternary oxide supports are briefly summarized in this section. The diffraction patterns indicated that the SiO_2 support used in this study is X-ray amorphous. A huge amorphous peak found on silica and centered at $2\theta = 23^\circ$ is also found in the $TiZrSiO_x$ ternary oxide diffraction pattern but with a much lower intensity. Likewise, the diffraction peaks found in Al_2O_3 are also found in $TiZrAlO_x$ but with a lower intensity. There is no diffraction pattern corresponding to that of free titania or zirconia in the spectra of the ternary oxides. Even though the absence of these features is not a guarantee for the absence of crystallites of titania or zirconia on the surface, it is at least an indication that there are no big crystallites.

DISCUSSION

The parameters that can affect the reaction rate are reported in Table 3. The space velocity expressed as liters of reactants at STP per gram of catalyst per hour (NL/g cat · h) gives an indication of the catalyst activity. The trend in activity is apparent from the data in Table 3. This comparison indicates the sequence, in order of decreasing activity, as Pd/$TiZrAlO_x$-ML > Pd/$TiZrAlO_x$-DL > Pd/$TiZrSiO_x$ > Pd/ZrO_2 > Pd/Al_2O_3 > Pd/TiO_2 > Pd/SiO_2. It is apparent from these data that the coating of alumina has a profound influence on the dechlorination activity of the final catalyst. As can be seen, the dechlorination rate of Pd/$TiZrAlO_x$-ML is almost twice that of Pd/$TiZrAlO_x$-DL. In an attempt to explain the drastic increase in activity with the $TiZrAlO_x$-ML based catalyst, the specific activities were determined for the uncoated and coated alumina-based catalysts (see Table 4). As indicated, the initial TOF of Pd/$TiZrAlO_x$-ML is about three times that of Pd/Al_2O_3, suggesting that the enhanced activity of Pd/$TiZrAlO_x$-ML cannot be explained only by consideration of a higher population of palladium atoms on the surface. The differences in dispersion would only account for a small portion of the overall range in activity. The observed differences in activity may be related to differences in the interactions of palladium with the support and/or to the adsorption properties of the support. Kovenklioglu *et al.* (10) have studied the role of the support in catalytic hydrodechlorination. They showed that the rate of dechlorination increased with the capability of the support to adsorb the chorinated hydrocarbons. They also demonstrated that the adsorption capacity depends on the chemical nature of the support. Their experimental data suggested two possible mechanisms: (1) migration of the reactant hydrocarbon on the support to the palladium where it reacts with adsorbed hydrogen; (2) reaction on the support with hydrogen that spills over to the support after dissociatively adsorbing on palladium. Their studies also indicated that the adsorption on the support contributed to the reaction significantly more than direct adsorption on palladium. By analogy to these studies, it is possible that the $TiZrAlO_x$ supports assist in the activation of the chlorinated hydrocarbon and/or modifies the electronic properties of palladium and thereby its adsorption properties. We established that pure $TiZrAlO_x$ does not display any catalytic activity by observing the reaction with just the support loaded in the reactor.

The rate of dechlorination alone is not sufficient to fully characterize the catalysts because two catalysts can have the same rate of dechlorination but produce different amounts of benzene or chlorobenzene. This research was undertaken with the main objective to find catalysts for the detoxification of toxic chlorocarbons. The toxicity of chlorocarbons is mainly due to the presence of the chlorine atom in the molecule (17). Therefore, the complete removal of all the chlorine atoms and the resulting production of hydrocarbons is an index of the efficiency of the catalysts. In this section, we will discuss the hydrocarbon selectivity of the various catalysts studied. The hydrocarbon selectivity here refers to the selectivity to produce cyclohexane and benzene. The selectivity of chlorobenzene, the other product of the reaction, when not stated, is equal to 100 − (hydrocarbon selectivity). Figure 1a compares the hydrocarbon selectivities for the single oxide-based catalysts with time on stream and Fig. 1b compares the DCB conversion with time. The data used to plot Figs. 1a and 1b were from the same experiments. The purpose of these figures is to highlight the hydrocarbon selectivity profile with time on stream, as the conversion also changes. The plots were drawn on the same scale to facilitate comparison. The hydrocarbon selectivity decreases with time on stream as the conversion decreases. Although Pd/ZrO_2 and Pd/Al_2O_3 have comparable activity within experimental error (see Table 3), they display very distinct hydrocarbon selectivity. While the hydrocarbon selectivity remained high on the alumina based catalyst (Fig. 1a), the conversion dropped quickly with time (Fig. 1b). Under the specified reaction conditions, the titania-based catalyst has the lowest hydrocarbon selectivity (see Fig. 1a), despite the high conversion achieved (see Fig. 1b). Pd/TiO_2 produced primarily chlorobenzene throughout the run.

Pd/Al_2O_3, which has the highest hydrocarbon selectivity among the single oxide-based catalysts, is compared with the ternary oxide-based catalysts in Figs. 2a and 2b.

Figure 3 compares the hydrocarbon selectivity of the various catalysts at a fixed conversion (at 33–36% conversion). Pd/TiZrAlO$_x$-ML and Pd/Al_2O_3 not only exhibit the highest hydrocarbon selectivity among all the catalysts tested, they also maintain appreciable hydrocarbon selectivity throughout an entire experiment. The cyclohexane selectivity under the reaction conditions specified is negligible, compared to the amount of benzene. Therefore, the hydrocarbon selectivity, that is the selectivity to benzene, may be used as an indication of the hydrogenolysis activity of the catalyst. Even though the silica-based catalyst initially displays high hydrocarbon selectivity, this falls quickly with time on stream. Comparison of the hydrocarbon selectivity of coated silica-based catalysts with the corresponding single-oxide-based catalysts (Fig. 3) indicates that the introduction of TiO_2 imparts a negative effect on the hydrocarbon selectivity as indicated by the very low hydrocarbon selectivity of Pd/TiZrSiO$_x$. Overall, the hydrocarbon selectivity decreased with time on stream for each catalyst, with the exception of Pd/TiO_2, which displays the lowest hydrocarbon selectivity. It is known that group VIII metals supported on TiO_2 can give rise to strong metal–support interaction (SMSI) (40), following H_2 reduction at 500°C or above. The SMSI decreases hydrogen chemisorption by the metal.

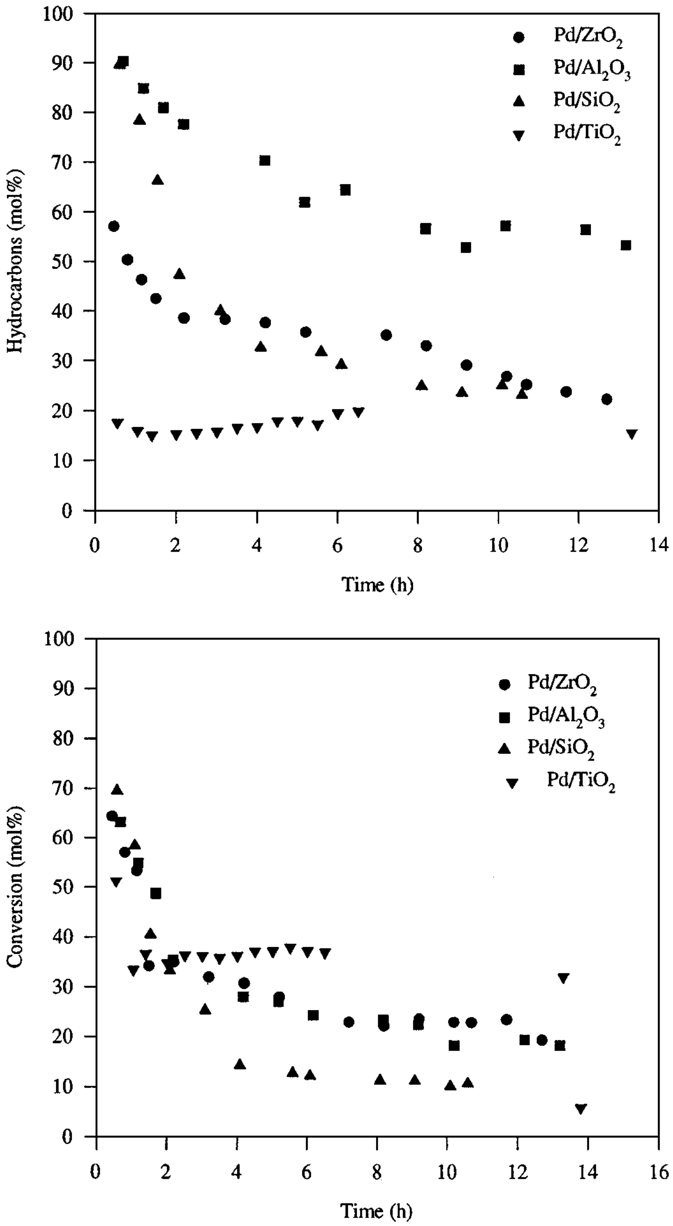

FIG. 1. For the single oxides-based catalysts with time on stream at 250°C, H_2 : DCB mole ratio of 8 : 1, GHSV of 2151-3222 h^{-1}: (a) comparison of hydrocarbon selectivity (hydrocarbon selectivity = selectivity to benzene + cyclohexane); (b) comparison of conversion with time.

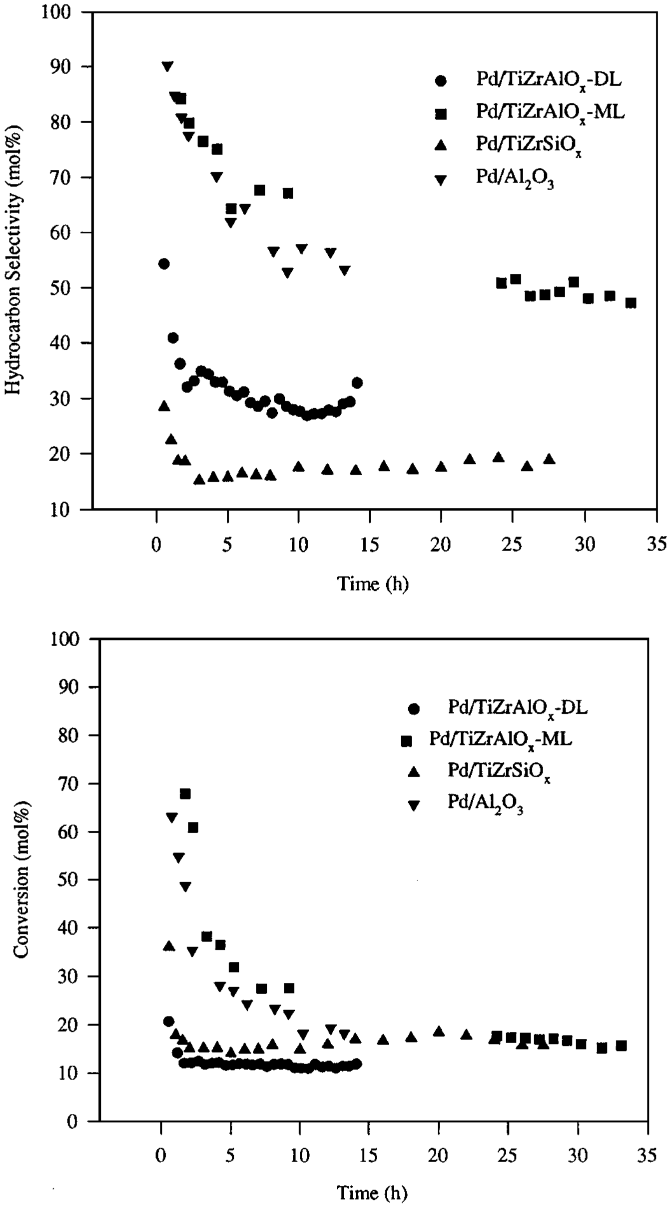

FIG. 2. For ternary oxide and alumina-based catalysts at 250°C, H_2: DCB mole ratio of 8 : 1, GHSV of 2151-3222 h^{-1}: (a) comparison of hydrocarbon selectivity with time (hydrocarbon selectivity = selectivity to benzene + cyclohexane); (b) comparison of conversion with time on stream.

Hydrodechlorination reaction studies have shown that the rate determining step over palladium catalysts involves chemisorbed chloroorganic compounds and dissociatively chemisorbed hydrogen (12). It follows that a low population of adsorbed hydrogen will result in low hydrocarbon selectivity. Even though our catalysts were reduced at 350°C, we suspect some degree of metal–support interaction. Belzunegui *et al.* (41) have shown by NMR characterization that two consecutive processes are responsible in a progressive establishment of SMSI in a Rh/TiO$_2$ catalyst. According to these studies, the first process occurs in the reduction temperature range 100–400°C. In this temperature range, incorporation of hydride species into the metal–support interface produces a significant decrease in hydrogen adsorption by the metal, which can be recuperated by outgassing of the sample at 500°C. The strength of the interaction of TiO$_2$ and ZrO$_2$ with SiO$_2$ is weaker than with Al$_2$O$_3$, as suggested by the fact that there is a larger alteration of catalytic activity and hydrocarbon selectivity with the latter. One would expect a lower hydrocarbon selectivity for Pd/TiZrAlO$_x$ and Pd/TiZrSiO$_x$, since the surface is primarily titania and zirconia. Such is not the case with Pd/TiZrAlO$_x$, which indicates that the interaction of titania with palladium can be optimized by changing its chemical environment. The hydrogenolysis activity of these catalysts follow the sequence Pd/TiZrAlO$_x$-ML $\sim$ Pd/Al$_2$O$_3$ $>$ Pd/SiO$_2$ $>$ Pd/ZrO$_2$ $>$ Pd/TiZrAlO$_x$-DL $>$ Pd/TiZrSiO$_x$ $>$ Pd/TiO$_2$.

Table 5 displays the performance of the best previously reported catalysts and the best catalyst of this work. The two catalysts of this work marked with the superscript ss in the rate column, have their rates presented as the averages of those measured at steady state conversion. The last one, with superscript i, the initial rate, was obtained by linear regression of the rate versus time data and extrapolating it to time zero. Because the catalysts in this table have different surface areas, the rates per unit area were also computed for comparison. For those catalysts whose surface areas were not reported, the surface area of the support was used when available. These details are specified in the footnotes.

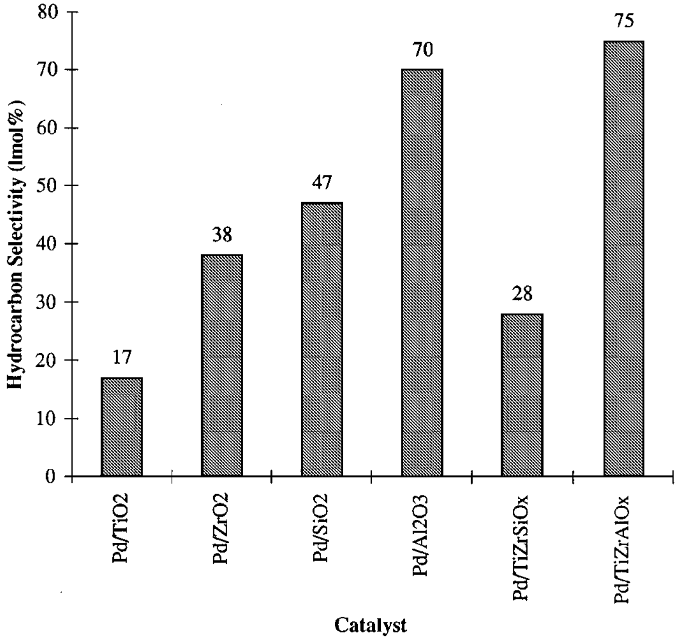

FIG. 3. Hydrocarbon selectivity at 33–36% conversion at 250°C, H_2:DCB mole ratio of 8:1, GHSV of 2151-3222 h^{-1} (hydrocarbon selectivity = selectivity to benzene + cyclohexane).

TABLE 5

Comparison of the Best Catalysts Described in the Literature for the Hydrodechlorination of 1,2-Dichlorobenzene

Catalyst	T (°C)	P (atm)	Dilution	H_2 : DCB (mole)	Rate × 10^4 (mol/g · min)	Rate × 10^4 (mol/m^2 · min)	Ref.
$NiMo/Al_2O_3$	300	107	1-5 wt% DCB in n-hexadecane	1 : 1	1.8	12.0	(14)
$NiMo/Al_2O_3$	300	20	3.3 wt% DCB in decane	535 : 1.5	12.7	na	(15)
NiMo/C	300	10	3 mol% DCB in n-decane	268.5 : 1	≤6	5.5[a]	(17)
5 wt% Pd/C	30	4	0.13M in ethanol		120[b]	126	(12)
2 wt% - $Pd/TiZrAlO_x$-ML	250	1	no dilution	6 : 1	126[ss]	518 ± 1	c
				8 : 1	221[ss]	904 ± 3	c
				8 : 1	484[i]	198 × 10^1	c

Note. na, neither support or catalyst surface area was reported; a, surface area of support, 1100 m^2/g was used for calculation; b, average rate of DCB consumption for the first hour; c, this work; ss, the steady state rate of consumption of DCB; i, initial rate of consumption of DCB.

Catalyst Deactivation

The activities as a function of time on stream for the most active and stable single oxide-based catalysts, Pd/Al_2O_3, Pd/ZrO_2, and the ternary oxide-based catalysts, $Pd/TiZrAlO_x$-ML, $Pd/TiZrAlO_x$-DL are compared in Fig. 4. In previous studies with palladium metal catalysts, the catalysts were reported to lose their activity with time on stream (12). In this work, the catalysts also lose their activity with time with the exception of $Pd/TiZrAlO_x$-DL which practically retains the same activity. Comparing the performance of the $Pd/TiZrAlO_x$-ML and $Pd/TiZrAlO_x$-DL catalysts suggests that the increased level of coating increased the catalyst stability while decreasing its dechlorination power. The behavior of $Pd/TiZrAlO_x$-ML is also remarkable. Even though it deactivates fast for the first 2 h, it comes to a steady state, as indicated in Fig. 4, with a rate which is very high, compared to the initial rates of other palladium catalysts found in previously reported studies (see Table 5). By contrast, the single oxide-based catalysts continue to deactivate. It should be pointed out that when the single oxide-based catalysts were tested under the same weight hourly space velocity used here for the $Pd/TiZrAlO_x$, they did not show measurable activity. The high activities of the ternary oxide-based catalysts masked their true deactivation profiles during the integral test measurements. The adsorption of Pd on the support may not be strong enough, leading to fast agglomeration of the metal particles, resulting in a reduction in exposed active sites. Consequently, this probably explains the deactivation profile observed in Figs. 4 and 5.

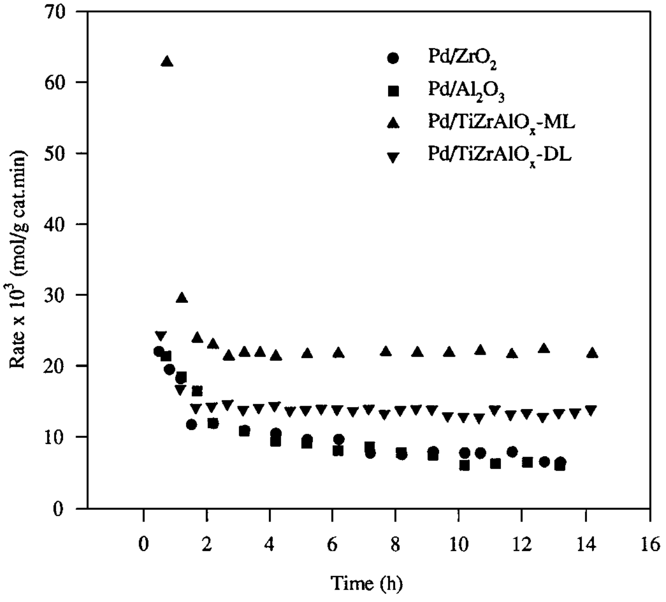

FIG. 4. Comparison of rates with time for the most active and stable catalysts at 250°C H_2 : DCB mole ratio of 8 : 1, GHSV of 2151-3222 h^{-1}.

The palladium surface area of the $Pd/TiZrAlO_x$-ML catalyst before reaction and after 70.5 h on stream is reported in Table 4. As can be seen, there is a significant increase in the metal particle diameter, suggesting that agglomeration of palladium atoms is an important factor in the catalyst deactivation. In addition, the initial TOF (fresh catalyst) is much higher than the TOF at steady state conversion (used catalyst). This points to another pathway of deactivation which is more likely through poisoning of the active sites by HCl adsorption as demonstrated by the studies of Coq *et al.* (12). In order to determine if HCl poisoning was significant, the used catalyst was washed to liberate the adsorbed chloride. This solution was analyzed for chloride by ion gas chromatography. The amount of adsorbed Cl^- was greater than the total adsorption capacity of the active palladium in the sample, suggesting that Cl^- not only adsorbed on the metal, but it also adsorbed on the support.

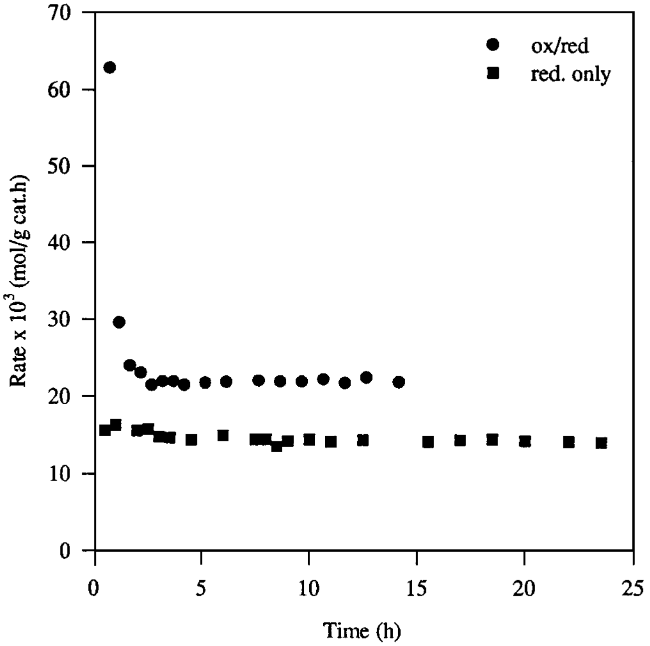

FIG. 5. Influence of pretreatment on the performance of Pd/ $TiZrAlO_x$ catalyst at 250°C, H_2 : DCB mole ratio of 8 : 1, GHSV of 3222 h^{-1}.

Figure 5 reveals a striking result of catalyst pretreatment. In this figure, the activity versus time on stream is compared for the same catalyst pretreated under different conditions. In one case the catalyst was oxidized, followed by a reduction (catalyst A), and in the other, it was only reduced as previously without prior oxidation (catalyst B). The latter does not show any deactivation for at least 24 h under differential conditions, although it displays a lower activity than the former. The deactivation rate of catalyst A is not constant as indicated by Fig. 5.

Test for Acid Resistance

We have not been successful in quantifying the degree of acidic dissolution of coated and uncoated alumina but we have made several observations. When uncoated alumina was contacted with acidified water, bubbles were observed, suggesting a possible reaction. The solution became more and more cloudy while the solution with the coated alumina remained crystal clear throughout the 11 days with no bubbling. When the solutions were filtered, there was a powdered deposit at the bottom of the beaker containing the alumina while there was no visible breakdown to powder for the coated alumina. These observations give a qualitative estimate to the relative acid resistance, but experiments measuring the concentration of Al^{3+} released during dissolution would be helpful in establishing the extent of dissolution for both oxides. It is not surprising that the acid attack on alumina was suppressed. Santacessaria *et al.* (45) have shown that the alumina surface is hydrated to $Al(OH)_3$ in the presence of an acidic solution and Schwarz *et al.* (46) reported that the hydrated alumina surface is directly responsible for the release of Al^{3+} ions as given by the following dissociation reaction:

$$Al(OH)_3(s) \rightleftarrows Al^{3+} + 3OH^-. \qquad [6]$$

Therefore, because the surface-active sites of alumina have been modified upon coating, it is to be anticipated that its behavior in acidic solution would be altered.

Prospects for Better Catalysts

From the results of this study it appears that more stable catalysts can be developed by:

(a) variation of Ti : Zr mole ratio. Coating of Al_2O_3 by TiO_2 and ZrO_2 changes the binding of palladium due to new M-O bonds and the local environment of TiO_2 and ZrO_2. We have found that the titania-based catalyst was the most stable and that the silica-based catalyst which was the most unstable acquired some stability upon incorporation of titania. Increasing the relative amount of titania may increase the strength of metal–support interactions, thereby preventing the metal particles from agglomerating. There may be an optimum Ti : Zr mole ratio different than the Ti : Zr 1 : 1 mole ratio used in this work;

(b) optimization of palladium dispersion through careful selection and control of the catalyst preparation parameters;

(c) investigation of pretreatment conditions that will yield the maximum population of the stable active species.

CONCLUSIONS

The results of this work suggest that a uniform coating of alumina and silica can be achieved by controlled reactions with isopropoxides of titanium and zirconium. The catalytic performance of palladium supported on the ternary oxide of Ti-Zr-Al in the hydrodechlorination of 1,2-dichlorobenzene exceeded that of the corresponding single oxide-based catalysts. The enhanced activity may be ascribed to interaction between the support and the metal or to adsorption of reactants on the support. Further optimization of the catalyst performance may be possible through variation of the support composition, the preparation method, and pretreatment of the catalyst. The increased acid resistance of the coated alumina, compared to uncoated alumina makes it a good support candidate for liquid phase applications in which the reaction medium is strongly acidic.

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