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Effects of SiO_2 on the catalytic properties of TiO_2 for the incineration of chloroform

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Abstract

The effects of the addition of silica to titania were examined via a comparison of TiO_2 and TiO_2/SiO_2. Various characterizing techniques such as XRD, FT-IR, and temperature-programmed ammonia desorption (TPAD) were utilized for this investigation. The activity of the catalysts for the incineration of chloroform was explored under atmospheric pressure through a continuous flow tubular reactor. The results revealed that the addition of silica enhanced the dispersion of titania and formed Ti–O–Si bonds. The activity of TiO_2 was increased about 60% with the incorporation of 43 wt.-% silica. The ignition temperature of chloroform on TiO_2 was not altered by SiO_2. However, the characteristics of the deactivation and the acidity of TiO_2 were modified by the incorporated silica.

1. Introduction

Chlorinated hydrocarbons are widely employed in industry as solvents and chemical intermediates. The majority of these hydrocarbons are carbon tetrachloride, chloroform, methylene chloride and trichloroethane. Chlorinated hydrocarbons are toxic and their release results in serious soil and underground water contamination problems. In addition, releasing these hydrocarbons to the atmosphere destroys the ozone layer and threatens human life with skin cancer by exposing mankind directly to UV radiation from the sun. Therefore, investigations into the disposal of chlorinated hydrocarbons are of great interest.

The desired treatment of the chlorinated hydrocarbons is to convert them to HCl and CO_2. The conversion can be achieved thermally at a temperature above 1200 K. This temperature is required to ensure a complete combustion without the formation of harmful byproducts such as dioxins. Costly supplementary fuel is demanded to maintain such a high temperature, especially for a waste gas stream of low organic concentration. Besides the fuel cost, significant amounts of nitrogen oxide and CO are emitted from the thermal process [1]. The emissions constitute additional disadvantages to the thermal process because nitrogen oxide causes acid rain and photochemical smog and CO is toxic.

Catalytic oxidation offers an effective and economic alternative to the thermal process. Catalytic oxidation is very effective in treating a waste stream of either low or high organic concentration. Catalytic oxidation can be performed at a temperature between 650–900 K. The operation costs and the emissions of NO_x and CO at this temperature are limited. Various advantages of catalytic oxidation have led to intensive research activities in this field.

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Earlier studies on the catalytic oxidation of chlorinated hydrocarbons have focused on the comparison of commercially available catalysts [2–6]. The research efforts in this field have led to several patents concerning catalyst formulation and reactor configuration [7–10]. Review papers [11,12] have indicated that Cr_2O_3 [13,14], and Co_3O_4 [4] are among the most active catalysts. Other catalysts such as MnO_2 [15], CuO [16,17], Co-Y [18], Pt [16,19], and TiO_2/SiO_2 [20] have also been shown to have significant activities. Comparing the activities of these catalysts has led to the conclusion that metals, in general, are less active than metal oxides. In addition, metals show less resistance to deactivation than metal oxides, mainly due to the strong interaction between the metal and the chlorine of the compounds.

Silica has been used to improve the activity of V_2O_5/TiO_2 in controlling power plant NO_x emissions [21]. The improvement is obtained via a reconfiguration of the pore structure by the silica. Incorporating silica to V_2O_5/TiO_2 results in the silica being coated with TiO_2 and the V_2O_5 being still supported on the TiO_2. As a consequence, the chemical nature of the V_2O_5/TiO_2 surface is retained and the pore structure of the catalyst is changed. Imamura et al. [20] have used TiO_2/SiO_2 to decompose 1,2,-dichloroethane and have discovered that the catalyst has much higher activity than many other acidic catalysts such as zeolite Y, mordenite, ZSM-5, etc. The catalyst can also retain a high activity for a long period of time. Similar results have been observed by Bose and Senkan [22]. The objective of this investigation is to explore the effects of silica on various catalytic properties of titania. The titania is used in the decomposition of chlorinated hydrocarbons.

2. Experimental

2.1. Preparation

TiO_2/SiO_2 catalysts of various TiO_2 content were prepared by precipitation following the procedure described in Fig. 1. In the procedure, titanyl oxysulfate was first dissolved in a 0.1 M H_2SO_4 solution. Silica (aerosil, 200 m^2/g) was then added to the solution. The acidity of the solution was gradually adjusted with a 7 wt.-% aqueous ammonia until the pH of the solution reached 9.5. The precipitate was obtained from the pH adjustment. The precipitate was then thoroughly washed with deionized water until the pH of the effluent water became 7. The slurry from the washing step was then dried at 373 K for 16–24 h and calcined at 823 K for 6 h to produce TiO_2/SiO_2. The TiO_2/SiO_2 catalysts of various TiO_2 content were prepared by employing different quantities of titanyl oxysulfate. The prepared catalysts were denoted as TiO_2/SiO_2(x%) where x represented the weight percentage of the silica in the catalyst.

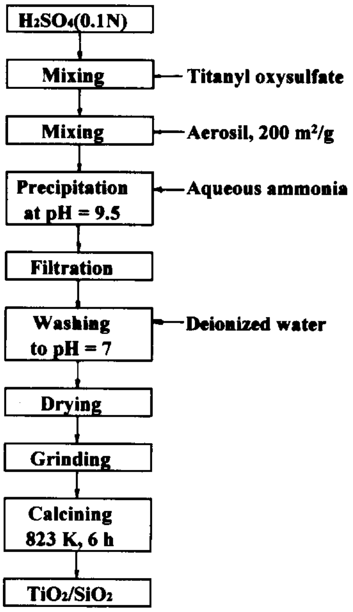

Fig. 1. Catalyst preparation procedure.

The TiO_2 of this investigation was also prepared by precipitation, following the same procedure as that for TiO_2/SiO_2. The titania was then ground mixed with silica (aerosil, 200 m^2/g) to produce a $TiO_2 + SiO_2$ catalyst. Ground mixing resulted in no change in the properties of the TiO_2. Therefore, a comparison between TiO_2/SiO_2 and $TiO_2 + SiO_2$ was equivalent to a comparison between TiO_2/SiO_2 and TiO_2.

2.2. X-ray diffraction (XRD)

A Philips X-ray diffractometer (model PW 1710) was used for the analysis. The light source was Cu Kα. The applied current and voltage were 30 mA and 40 kV, respectively. During the analysis, the sample was scanned from 8° to 110° with a speed of 0.05°/s.

2.3. Fourier transform infrared (FT-IR)

FT-IR (Digilab, FTS-40) with a resolution of 4 cm^{-1} in the absorption mode was used for the analysis. The sample for FT-IR analysis was prepared by drying the catalyst, mixing the catalyst with KBr in an agar mortar, and then pressing the mixture into a thin disk. The disk, weighing 20 mg and containing 1 wt.-% catalyst, was further dried at 423 K in an IR cell under 3×10^{-3} Torr vacuum for 0.5 h before being analyzed.

2.4. Temperature-programmed NH_3 desorption (TPAD)

The sample, weighing 40 mg, was placed in a U-shaped Pyrex tube. Quartz wool was packed on both sides of the sample so as to keep it from being carried away by the gas flowing through the sample. The experiment was initiated with an oxidation to activate the catalyst and to drive-off the moisture and the gases retained by the sample. The oxidation was performed at 673 K under an air flow for 3 h. The temperature was then lowered to 308 K under a nitrogen flow. NH_3 was introduced at this temperature for 1 h to allow the adsorption of ammonia to occur. Temperature-programmed desorption was conducted after the adsorption, with a temperature ramp of 10 K/min and a helium flow-rate of 10 ml/min. The desorption of NH_3 was continuously monitored by a thermal conductivity detector and was recorded by a recorder (Shimadzu R-122T).

2.5. Oxidation of chlorinated hydrocarbons

The schematic diagram of the reaction system is illustrated in Fig. 2. The reaction was carried out under atmospheric pressure in a 0.64-cm O.D., U-shaped Pyrex tube reactor. The catalyst bed constituted a mixture of 0.2 g catalyst and 0.5 g quartz sands (0.2–0.8 mm, Merck). The application of the quartz sands reduced the problems of gas channeling and temperature gradient in the catalyst bed. Quartz wool was employed on both sides of the catalyst bed to minimize the loss of catalyst by the gas flowing through the bed. A thermocouple was inserted in the bed to accurately measure the reaction temperature.

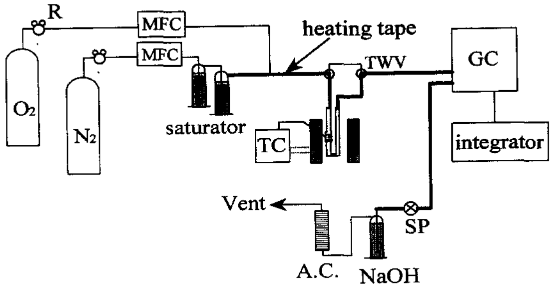

Fig. 2. A schematic diagram of catalytic incineration of chloroform. R: regulator; MFC: mass flow controller; TWV: three-way valve; TC: temperature controller; SP: sampling port; A.C.: activated carbon adsorption.

Catalyst activation was performed in situ before the reaction. The activation was conducted by oxidizing the catalyst with air at 673 K for 3 h. After the activation, the catalyst temperature was lowered to a desired reaction temperature and chloroform feeding started. The chloroform was carried to the reactor by a gas stream containing nitrogen and oxygen. The flow-rates of chloroform, nitrogen and oxygen were 1.8, 17.8 and 4.4 ml/min, respectively. The flow-rate of chloroform was determined by a carefully calibrated gas chromatograph while the flow-rates of nitrogen and oxygen were set by two mass flow controllers. The total flow-rate was maintained at 24 ml/min throughout the experiments. The space velocity for the reaction was calculated to be 7200 h^{-1} with this flow-rate. The reaction conditions for a typical run are illustrated in Table 1.

2.6. Analysis of reaction products

The oxidation of chloroform constitutes several reactions. The main reaction produces CO_2, HCl and Cl_2:

Table 1
Reaction conditions

Temperature (K)	523–673
Pressure (kPa)	100
Space velocity (h^{-1})	7200
Chloroform conc. (mol-%)	7.5
Oxygen conc. (mol-%)	18.3
Nitrogen conc. (mol-%)	74.2

$$CHCl_3 + O_2 = CO_2 + HCl + Cl_2 \tag{1}$$

The production of highly toxic and corrosive chlorine is not desired. Minimizing the generation of chlorine can be achieved by the use of H_2O to cause the Deacon reaction:

$$Cl_2 + H_2O = 2HCl + 1/2O_2 \tag{2}$$

With the presence of water, the desired overall reaction becomes:

$$CHCl_3 + 1/2O_2 + H_2O = CO_2 + 3HCl \tag{3}$$

Some side reactions may also be present. For example, an incomplete oxidation of chloroform produces CO:

$$CHCl_3 + 1/2O_2 = CO + HCl + Cl_2 \tag{4}$$

The CO may further react with Cl_2 to generate extremely toxic phosgene:

$$Cl_2 + CO = COCl_2 \tag{5}$$

The possible production of extremely toxic products requires the reaction to be handled with caution. The effluent gas must be treated before being released to the atmosphere. The effluent can, in general, be treated with a caustic solution to remove the acidic substances and then be passed through activated carbon to retain other chemical compounds by adsorption.

Multiple methods were utilized to analyze the reaction products, including the application of two gas chromatographs. The effluent gas from the reactor was sampled by an auto-sampling valve and was immediately analyzed by the first gas chromatograph (China Chromatography 8900). The chromatograph was equipped with a thermal conductivity detector (TCD). The column for the analysis was Porapak Q, 80/100 mesh, 2 m × 0.32 cm stainless steel. In the analysis, the column temperature was initially programmed at 363 K for 2 min, then raised to 463 K at 29 K/min, and finally at 463 K for 6 min. Chloroform, carbon dioxide, water, and phosgene were effectively separated in this column. The resolutions of nitrogen, oxygen and CO in this column were found to be inadequate.

A second gas chromatograph was required to analyze nitrogen, oxygen, and CO. This chromatograph was equipped with a TCD and a molecular sieve 5A, 80/100 mesh, 2 m × 0.32 cm stainless steel column. The temperature of the column in this gas chromatograph was maintained at 308 K throughout the analysis. The sample for the second gas chromatograph was taken from the effluent with a syringe and was injected into the chromatograph.

HCl was analyzed by an electrode. Hydrogen chloride in the product stream was sampled by absorption using a 100 ml KNO_3 solution. The concentration of chlorine ion in the solution was determined after adding 5 ml of acetic acid as a buffer and increasing the solution volume to 250 ml by adding KNO_3 (aq).

Chlorine was analyzed by the JIS *o*-tolidine method, involving the usage of an *o*-tolidine solution to absorb the produced chlorine and 435 nm UV-VIS to determine the chlorine content in the solution.

3. Results and discussion

3.1. XRD

The X-ray diffraction data for various samples are shown in Fig. 3. Typical peaks of TiO_2 (anatase) are detected in both $TiO_2 + SiO_2$ catalysts. $TiO_2 + SiO_2$ (90%) contains only 10 wt.-% TiO_2. A different situation is observed for TiO_2/SiO_2 catalysts. TiO_2 peaks are not detected in these catalysts even for a catalyst containing as high as 57 wt.-% TiO_2 (TiO_2/SiO_2 (43%)). The effect of SiO_2 is obvious. The presence of SiO_2 in TiO_2/

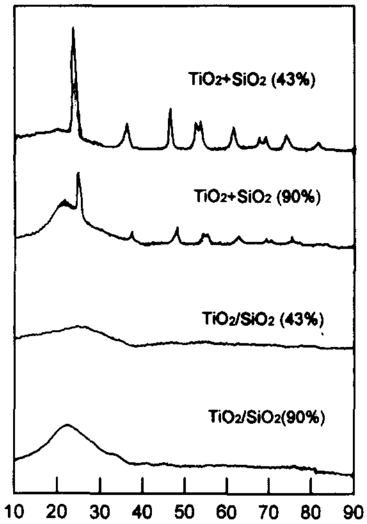

Fig. 3. XRD spectra.

SiO_2 obviously inhibits the growth of TiO_2 crystals and results in amorphous TiO_2.

3.2. *FT-IR*

Two common peaks, 800 and 1100 cm^{-1}, are found for all 3 samples (Fig. 4). These peaks are assigned to the symmetric (800 cm^{-1}) and the asymmetric (1100 cm^{-1}) Si–O–Si stretchings [23,24]. A unique peak, at 950 cm^{-1}, appears for TiO_2/SiO_2. This peak is assigned to a Ti–O–Si asymmetric stretching [25]. The appearance of a peak at 950 cm^{-1} in TiO_2/SiO_2 signifies the interaction between the TiO_2 and the SiO_2.

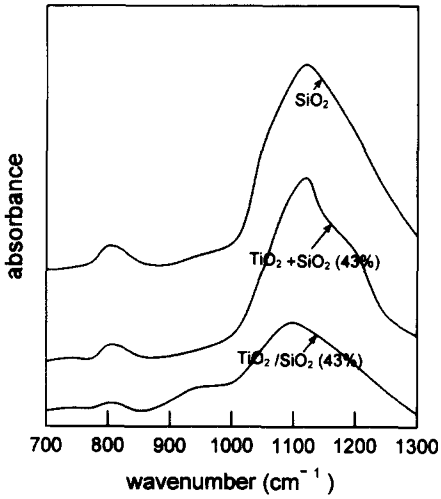

Fig. 4. FT-IR spectra.

3.3. *Temperature-programmed NH_3 desorption (TPAD)*

The TPAD results of TiO_2/SiO_2 and TiO_2 are illustrated in Fig. 5. There are two peaks for TiO_2, at 470 K and 810 K, showing TiO_2 has two different acids. The peak of the weak acid of TiO_2 (475 K peak) is significantly smaller than that of TiO_2/SiO_2, demonstrating a marked increase in the number of the weak acid site upon the incorporation of SiO_2. The peak of the strong acid of TiO_2 (810 K peak) is about the same height as that of TiO_2/SiO_2 (shown as a shoulder), illustrating that the addition of SiO_2 cannot change the number of the strong acid site of TiO_2. In addition to the varied effects on different acids, the incorporation of silica creates new acid sites (720 K) with a strength in between the two acids of TiO_2.

3.4. *Chloroform oxidation*

The molar flow-rates of various compounds in the feed and in the effluent for a typical run are shown in Table 2. Hydrogen chloride is discovered as the only chlorine containing compound produced from the reaction. Chlorine is not detected in the effluent. This is a desired situation

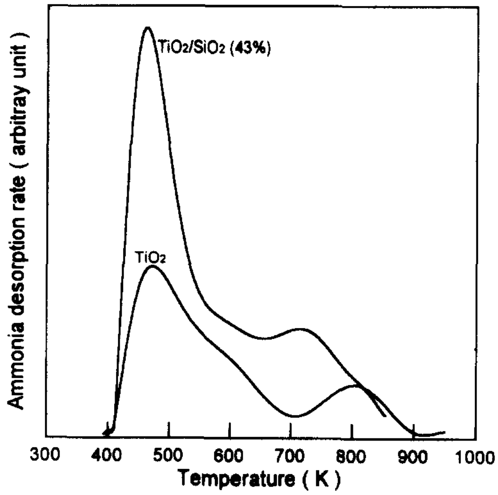

Fig. 5. Temperature-programmed ammonia desorption.

Table 2
Molar flow-rates of a typical run[a]

Compound	Molar flow-rate (μmol/min)	
	Feed	Effluent
$CHCl_3$	61.8	49.5
CO	0.0	3.0
CO_2	0.0	7.2
HCl	0.0	17.9
Cl_2	0.0	0.0

[a] Reaction conditions: $T=673$ K; $P=100$ kPa; space velocity = 7200 h^{-1}; catalyst = TiO_2+SiO_2; feed composition = 7.5 mol-% $CHCl_3$ in air.

Table 3
Material balances of a typical run[a]

Element	Molar flow-rate (μmol/min)		
	Feed	Effluent	Error[b] (%)
C	61.8	59.7	−3.4
Cl	185.4	166.4	−10.2

[a] Calculated from the data in Table 2.
[b] Error = [(effluent − feed)/feed] × 100%.

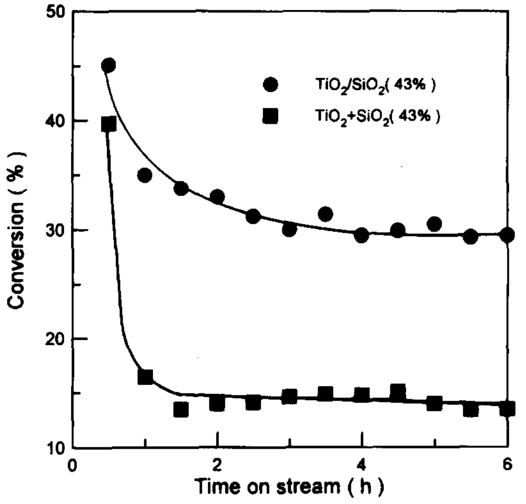

Fig. 6. Catalyst deactivation, reaction temperature: 673 K; space velocity: 7200 h^{-1}.

since chlorine is more toxic and corrosive than hydrogen chloride. The absence of extremely toxic phosgene in the products is another remarkable result using this catalyst. The material balances of carbon and chlorine atoms are illustrated in Table 3. The balance on the carbon atom can be closed to within −3.4%. Chlorine atom balance can be closed to within −10.2%. The inaccuracies inherent in the analytical procedures for chlorine and hydrogen chloride measurements limit the closure of the material balance on the chlorine atom.

TiO_2/SiO_2 and TiO_2+SiO_2 deactivate differently (Fig. 6). TiO_2+SiO_2 quickly loses most of its initial activity and reaches a steady state while TiO_2/SiO_2 decreases at a much slower rate. The time required for TiO_2/SiO_2 to reach a steady state is longer than that for TiO_2+SiO_2. A greater fraction of the initial activity can be preserved on TiO_2/SiO_2 after the deactivation.

The effect of temperature on the conversion of chloroform is illustrated in Fig. 7. The conversion increases with temperature at an accelerated rate. The ignition temperatures for both catalysts occurs at about 673 K. In additional to the approximate same ignition temperature, the conversion vs. temperature for the two catalysts are parallel to each other. These observations indicate that TiO_2/SiO_2 and TiO_2+SiO_2, despite their differences detected by other characterization techniques, have the same incineration properties.

The effect of silica content on the reaction rate is demonstrated in Fig. 8. The rate increases with the content until the catalyst contains 43 wt.-%

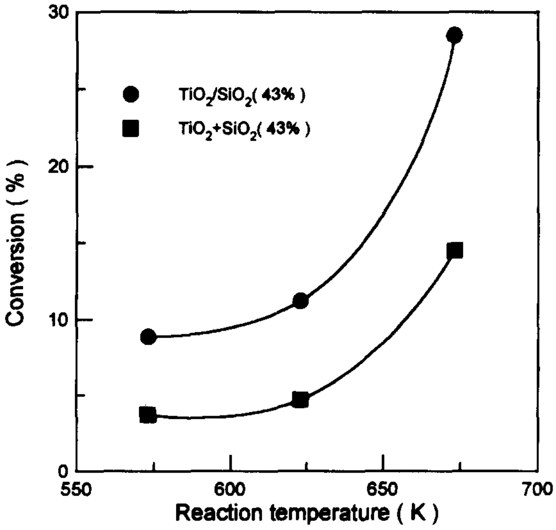

Fig. 7. Ignition temperature of chloroform, time-on-stream: 6 h; space velocity: 7200 h^{-1}.

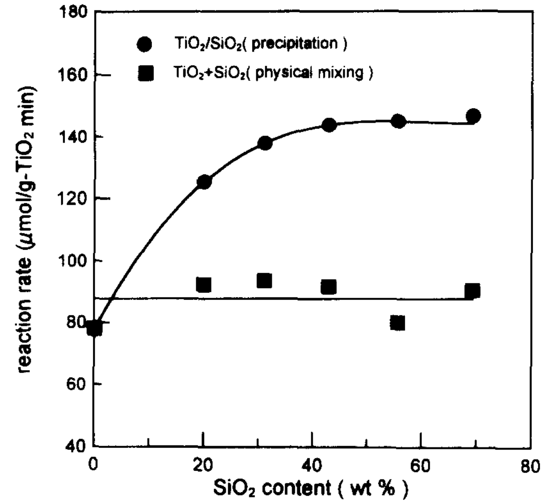

Fig. 8. Effect of silica content on the reaction rate, reaction temperature: 673 K; reaction pressure: 100 kPa; feed composition: 7.5 mol-% $CHCl_3$ in air.

silica. At this content the rate is about 60% higher than that of the TiO_2 without silica. A further increase in the content cannot result in a further increase in the rate. This observation clearly illustrates that a maximum dispersion of the TiO_2 is obtained with 43 wt.-% silica. The rate of $TiO_2 + SiO_2$ is independent of the content of silica and is not surprising as the physical mixing should not result in a TiO_2 dispersion change.

4. Conclusion

Adding silica to titania can increase the dispersion of titania and form Ti–O–Si bonds between the two oxides. The addition can significantly enhance the number of the weak acid site of the titania. The number of the strong acid site of the titania is not changed with the addition. In addition to the varied effects on different acids, the incorporation of silica to titania creates new acid sites with a strength in between the two acids of titania. The severe initial deactivation of TiO_2 in the incineration of chloroform can be modified with silica. Adding silica does not alter the ignition temperature but can enhance the activity of titania. The maximum enhancement is about 60% which occurs with a silica content of 43 wt.-%. A further increase in the content does not result in a titania of greater activity.

Acknowledgements

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