

Decomposition of Chlorinated Hydrocarbons using Metal Oxides supported on Carbonaceous Adsorbents

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A series of catalysts comprised of high-valent transition metal oxides supported in porous, carbonaceous adsorbents oxidize methylene chloride completely to CO, CO₂ and HCl at 250 °C and 1 atm; results with CD₂Cl₂ indicate that C–H bond dissociation is involved in the rate determining step of the reaction.

The contamination of the environment with chlorinated organic pollutants is of major ecological importance, as illustrated by recent restrictions passed by the Environmental Protection Agency.¹ The responsibility for remedying this problem will rest upon chemical manufacturers and processors, requiring them to limit the emission of these materials and restore ecosystems damaged already by contamination. The present technology for disposal of chlorinated organics involves combustion at extremely high temperatures (>1000 K) in order to obtain complete oxidation of the pollutant.^{2,3} The large energy input and expensive materials required for thermal combustion makes it impractical for large-scale use. Therefore, the development of catalytic combustion systems utilizing less extreme conditions is of considerable importance.

We have previously shown that metal species supported on carbonaceous supports are effective catalysts for the oxidative dehydrogenation of ethylbenzene to styrene,⁴ conversion of methanol to formaldehyde plus methyl formate⁵ and Fisher-Tropsch synthesis of hydrocarbons.⁶ This paper deals with the catalytic decomposition of chlorinated hydrocarbons over transition metal oxides supported on porous carbonaceous materials.⁷

Decomposition of chlorinated hydrocarbons can proceed *via* a deep oxidation, *i.e.* total combustion, pathway⁸ that results in CO₂ and HCl as the final products as opposed to partial oxidation, which leads to products such as phosgene or formaldehyde. It has been reported that deep oxidation involves both acidity and redox activity,⁹ so acidic metal oxides were investigated as catalytic agents in this work.

The support materials used in this study are Ambersorb® carbonaceous adsorbents 572 and 563. These materials (obtained from Rohm and Haas Co.) are prepared by the patented pyrolysis of highly sulfonated, macroporous divinylbenzene–polystyrene polymers in order to obtain very porous solids with exceptional adsorption ability for organic molecules. This adsorption ability, along with exceptionally high surface areas make these materials very well suited for application in heterogeneous catalysis.^{10,11}

Catalysts are prepared by impregnation of the carbon with an aqueous solution of CrO₃, KMnO₄, SO₃ and NH₄VO₃ to incipient wetness and the water is subsequently removed under vacuum. Metal chlorides in aqueous solution were used for iron and antimony. These were converted to hydroxides with NH₄OH and NaOH. Cobalt was added as an aqueous solution of Co(NO₃)₂. TiCl₄ is added in CH₂Cl₂ solution and hydrolysed with wet air. Water is removed and the oxides are generated by heating to 250 °C. All catalysts used in this study are 14% metal oxide by mass, with the exception of KMnO₄–Ce(NO₃)₃–Ambersorb 572 which has 2% each of KMnO₄ and Ce(NO₃)₃.

Table 1 presents the activities for various catalysts used in the deep oxidation of methylene chloride at 250 °C. Notice that the untreated supports show comparable activity to the supported metal oxide catalysts under these conditions; this may be due to residual metals incorporated during the synthesis of the support or acid sites arising from sulfonation of the copolymer before pyrolysis. Both of these cases allow for potentially active acid sites to be present in the supports.

Of all the oxides utilized in the study, chromium(vi) oxide

afforded the best results: essentially complete destruction of methylene chloride at 60 000 ppm in air (1 ml min⁻¹) in one pass over 2.0 g of the catalyst (*ca.* 2.5 cm bed height) at 250 °C. No methylene chloride is detected in the effluent gas stream; the GC detector sensitivity sets the maximum possible [CH₂Cl₂] in the effluent at 100 ppm. Two other catalysts which are close in activity are TiO₂–Ambersorb 572 and a mixed oxide KMnO₄–Ce(NO₃)₃ catalyst. These latter two catalysts have not yet been optimized with respect to metal oxide content level, flow rate or temperature. Conversion similar to the chromium catalysts could be obtained once these parameters are optimized. All of the most active catalysts appear to possess common characteristics of redox activity, acid sites and good metal dispersion. Amphoteric metal chloride, treated supports which are hydrolysed with an excess of alkali to obtain the final basic oxide forms of the catalysts, result in especially poor conversions for this reaction. This observation is consistent with the acidity requirement for the catalysts. Table 2 shows that treatment of unmodified carbon samples with base results in decreased activity with respect to the untreated material; there is even a sensitivity to base strength with KOH reducing catalytic activity to a larger extent than NH₃.

The final entry in Table 1 gives the results for an experiment where the catalytic agent consists of a two component mixture of a layer of untreated Ambersorb 563 over a layer of pure CrO₃. The conversion level of 48% for the separated

Table 1 Activity of catalysts in the deep oxidation of methylene chloride^{a,b}

Catalyst	Conversion (%)
CrO ₃ –Ambersorb 563	99.9 (± 0.1)
CrO ₃ –Ambersorb 572	99.9 (± 0.1)
TiO ₂ –Ambersorb 572	93 (± 1)
KMnO ₄ –Ce(NO ₃) ₃ –Ambersorb 572	95 (± 1)
Sb ₂ O ₅ –Ambersorb 572 ^c	52 (± 3)
V ₂ O ₅ –Ambersorb 572	82 (± 3)
H ₂ SO ₄ –Ambersorb 572	83 (± 3)
Co oxide–Ambersorb 572	75 (± 4)
Fe oxide–Ambersorb 572 ^c	65 (± 4)
Ambersorb 572	78 (± 3)
Ambersorb 563	69 (± 3)
Ambersorb 563, CrO ₃ ^d	48 (± 3)

^a 250 °C, 1 ml min⁻¹ air, 2.0 g catalyst, [CH₂Cl₂] = 60 000 ppm, reaction time = 72 h. ^b Conversions based on GC analysis and HCl product quantification. ^c Metal chloride-impregnated carbon support treated with base to obtain final catalyst oxide form. ^d Two layers.

Table 2 Effect of base treatment of Ambersorb 563 in deep oxidation of methylene chloride

Base	Amount added	Conversion (%)
None	—	69 (± 3)
NH ₃	8.29 × 10 ⁻² moles	52 (± 4)
KOH	8.82 × 10 ⁻³ moles	32 (± 4)

components is evidence that the CrO₃-Amborsorb 563 catalyst activity is not that due to a summation of metal and support activities but rather possesses stable catalytic sites not present in the heterogeneous mixture. Indeed, pure CrO₃, which has a melting point of 197°C, is not stable under the reaction conditions as observed by reduced Cr compounds collecting in the post-catalyst cool zone and mobility of the molten CrO₃ through the reactor during the blank reaction. No chromium containing species have been observed in the post-catalyst stream with the prepared catalyst even after 150 h of reaction.

The deep oxidation mechanism is not well understood. The dual dependence on acidity and oxidation ability appears to indicate a complex, multi-step scheme for the reaction. In an effort to understand one aspect of the mechanism, the isotopic substitution of deuterium for hydrogen was investigated in the methylene chloride system. The design of the experiment was such that the only change in using CD₂Cl₂ vs. CH₂Cl₂ was swapping of the reservoirs; the catalyst sample (Amborsorb 563) was not altered during the experiment. This procedure maintains consistency in experimental variables such as flow rate, bed height (*i.e.* residence time) and catalyst packing. In this experiment, a smaller bed height was employed than in Table 1. Conversion obtained for CD₂Cl₂ was 35% (± 2) as opposed to 49% (± 2) for CH₂Cl₂. This isotope effect ($k_H/k_D = 1.4$) is large enough to imply that the C-H bond cleavage is directly involved in the rate determining step. Further investigation of the reaction mechanism and catalyst charac-

terization is presently under way along with the examination of other chlorinated organic reactants.

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