ChemComm

The catalytic hydrolysis of CCl_4 to HCl and CO_2 over magnesium oxide

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Received (in Cambridge, UK) 29th November 1999, Accepted 1st February 2000

At temperatures > 400 °C, CCl_4 reacts with H_2O over a MgO catalyst to yield HCl and CO_2.

The destruction of carbon tetrachloride found in ground water and in effluent streams is typically carried out by using incineration[1] or catalytic oxidation.[2] We describe here the catalytic reaction of CCl_4 with H_2O to form CO_2 and HCl, which has not been previously reported except for a brief comment in the patent literature.[3] The kinetics of the corresponding uncatalyzed reaction in water was studied by Fells and Moelwyn-Hughes,[4] who observed a rather small second order rate constant (with respect to CCl_4) of $k = 1.21 \times 10^{-3}$ L mol^{-1} s^{-1} at 373 K for an initial CCl_4 concentration of 0.903 mmol L^{-1}. The rate was unaffected by proton, hydroxide or chloride ion concentration.

The use of an alkaline earth oxide catalyst is based on a non-catalytic cycle in which CCl_4 was first reacted with BaO to form $BaCl_2$.[5] The $BaCl_2$ was subsequently reacted with aqueous CO_3^{2-} to produce $BaCO_3$ and aqueous HCl. The $BaCO_3$ could be converted to BaO at elevated temperatures (600 °C), and the process could then be repeated. However when CCl_4 and H_2O were passed over BaO at 500°C, the catalytic reaction [eqn. (1)]

$$CCl_4 + 2H_2O \rightarrow 4HCl + CO_2 \quad \Delta G^{o}_{500\,°C} = -390\ \mathrm{kJ\ mol^{-1}} \qquad (1)$$

did not occur. Magnesium oxide, however, is an effective catalyst for this reaction, in part because magnesium chloride is not extensively formed, and, more importantly, magnesium carbonate decomposes at temperatures near 400 °C.

The catalyst was prepared by the decomposition of $Mg(OH)_2$ obtained by stirring a slurry of MgO (Fisher, light) and water at 80 °C for 24 h. The $Mg(OH)_2$ (20–40 mesh size) was decomposed at 400 °C in flowing O_2 (100 mL min^{-1}). The reaction of CCl_4 with H_2O was carried out in a plug flow reactor at a total flow rate of 80 mL min^{-1} with He as the diluent. Gas chromatography was used to analyze for CCl_4, CO_2 and H_2O, while HCl was trapped in water and subsequently titrated with $AgNO_3$ (aq). X-Ray photoelectron spectra (XPS) were acquired using a Perkin-Elmer (PHI) model 5500 spectrometer.

The conversions of CCl_4 and H_2O are shown in Fig. 1 for the reaction carried out at 500 °C over 0.58 g MgO with $P(CCl_4)$ = 2 Torr and $P(H_2O)$ = 4 Torr. Under these conditions, the initial conversion of 88% decreased to *ca.* 74% during the first hour, but thereafter the conversion remained nearly constant. After 24 h on stream, the conversion was 68%. The surface area of the catalyst decreased from 90 to 38 m^2 g^{-1}, with most of the decrease occurring during the first hour. At the same partial pressures of CCl_4 and H_2O, but with 1.72 g MgO at 525 °C, the conversion was > 99% (no remaining CCl_4 was detected) for 72 h. Thus, nearly complete removal of CCl_4 can be achieved over a long period.

Kinetic results were obtained under differential reaction conditions, which were achieved either by using a smaller amount of catalyst or by operating at lower temperatures. Over the temperature range 400–500 °C with 2 Torr CCl_4 and 4 Torr H_2O, the apparent activation energy was 85 kJ mol^{-1}. At the same initial pressures and at 450 °C, the specific activity was 0.167 μmol (g s)$^{-1}$ or 4.1 nmol (m^2 s)$^{-1}$ for a catalyst having a surface area of 38 m^2. The reaction orders with respect to CCl_4 and H_2O are given in Fig. 2. The reaction order with respect to H_2O at 400 °C was slightly dependent on the partial pressure of CCl_4 and increased to $n = 0.16$ at 6 Torr of CCl_4.

The amount of chloride in the sample after reaction was 4 wt%, which corresponds to a Cl/Mg ratio of 0.047. This value may be compared with a near-surface Cl/Mg ratio of 0.12 (as determined from XPS spectra), which was nearly the same for samples that had been on stream for 1 h at 500 °C or for 70 h at 525 °C. After steady state was attained, there was nearly a 100% chlorine balance between CCl_4 reacted and HCl formed.

The results are consistent with the mechanism described in Scheme 1, which is adapted from an earlier one that was proposed by Hooker and Klabunde[6] for the destructive adsorption of CCl_4. Although phosgene is a potential intermediate, none was detected in the gas phase by IR spectroscopy. The rate limiting step is believed to be the dissociative adsorption of CCl_4, although this is inhibited by the presence of chloride ions on the surface, which is consistent with the fact

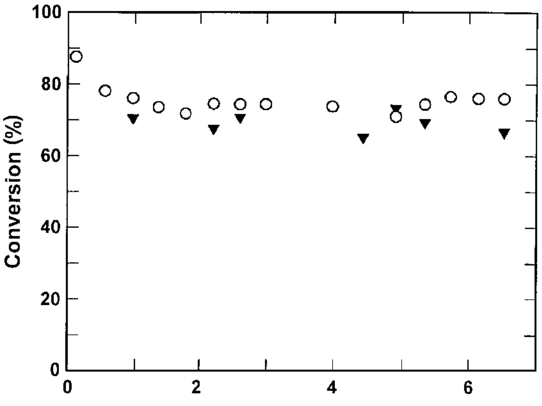


Fig. 1 Conversion of CCl_4 (○) and H_2O (▼) over 0.58 g MgO at 500 °C with $P(CCl_4)$ = 2 Torr and $P(H_2O)$ = 4 Torr.

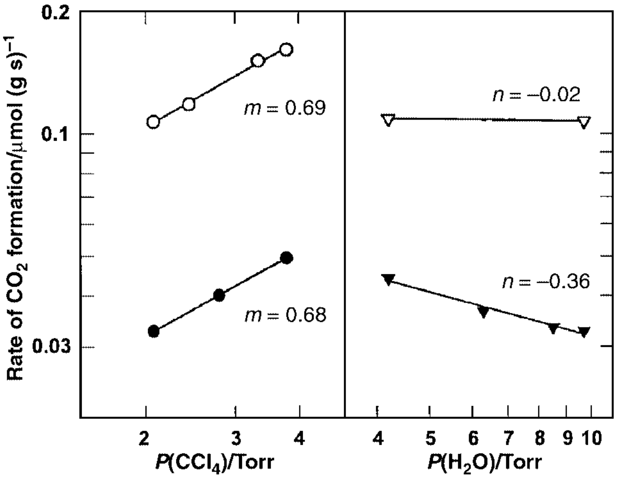
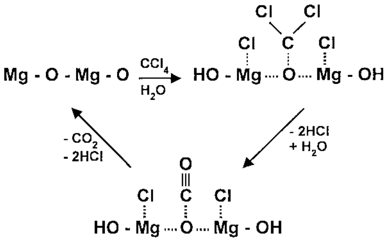


Fig. 2 Effect of CCl_4 and H_2O partial pressures on the rate of CO_2 formation over 0.40 g MgO: variation in CCl_4 pressure at 400 °C (●) and at 450 °C (○) with $P(H_2O)$ = 9.7 Torr; variation in H_2O pressure at 400 ° C (▼) and at 450 °C (▽) with $P(CCl_4)$ = 2.1 Torr.

DOI: 10.1039/a909552g



Scheme 1

that the reaction order with respect to CCl_4 is less than unity. The dissociative adsorption of H_2O to form hydroxide ions is very rapid at the reaction temperatures used. One might expect that the formation of carbonate ions, derived from CO_2, would inhibit the reaction, but this is not the case since the addition of CO_2 to the feed, in a 30-fold excess of that produced during the reaction, did not influence the reaction rate. The presence of chloride ions may decrease the basicity of the surface[7] and thereby minimize the formation of surface carbonates on MgO (see below).

The results described to this point were obtained using Fisher MgO (Ca < 1%, Fe < 0.05%); however, one experiment was carried out with Puratronic MgO (99.998%), and at comparable conditions the activity was the same, indicating that impurities such as iron do not play a role. By contrast, CaO and, as noted above, BaO were not active as catalysts. Both of these oxides are more effective than MgO for the activation of CCl_4 to form the metal chloride at 425 °C,[5] therefore, the first step in the reaction mechanism would readily occur. Moreover, the replacement of Cl^- ions by CO_3^{2-} ions on $BaO/BaCl_2$ can even take place at 25 °C, albeit slowly. It appears that the formation of stable carbonates on CaO and BaO inhibits the catalytic reaction over the temperature range employed in this study. At a pressure of 2 Torr CO_2, the decomposition temperatures of $MgCO_3$, $CaCO_3$ and $BaCO_3$ are 430, 600 and 970 °C, respectively.[8]

In summary, it has been found that MgO is a catalyst that promotes the reaction of CCl_4 with H_2O to yield CO_2 and HCl. For environmental purposes, the HCl could be easily removed from an effluent stream.

Notes and references

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Communication a909552g