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Gold/cobalt oxide catalysts for oxidative destruction of dichloromethane

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Abstract

A series of catalysts consisting of small gold particles supported on cobalt oxide (Co_3O_4), were synthesized by co-precipitation and tested for their ability to oxidize dichloromethane (CH_2Cl_2). The addition of the small gold particles to the Co_3O_4 (which as the only catalyst has the highest activity for the oxidation of CH_2Cl_2 among the first row transition metal oxides) significantly improved the activity of the Co_3O_4. The rate constant at 300°C was increased by a factor of 25. The activity was essentially independent of the gold loading at gold loadings between 0.2 and 10.0 wt.-%. In addition to this, the Au/Co_3O_4 catalysts were also significantly more active than noble metal catalysts, and exhibited activities 10 times higher than Cr_2O_3/Al_2O_3, 70 times higher than 0.5% Pt/Al_2O_3, and 560 times higher than 0.5% Pd/Al_2O_3 at 300°C. The Au/Co_3O_4 catalysts selectively oxidized CH_2Cl_2 to CO_2 and HCl (which can readily be stripped from air by a basic solution), and were quite stable at 350°C in the presence of the oxidation products. In addition, water did not have an adverse effect on the catalytic activity. No detectable by-products (such as $CHCl_3$ or CCl_4) or partial oxidation products (CO, Cl_2, $COCl_2$ and HCHO) were observed at 350°C. The oxidation of CH_2Cl_2 was first order in CH_2Cl_2 concentration, with activation energies of ca. 20 kcal/mol.

Keywords: Chlorinated hydrocarbons; Oxidative destruction; Dichloromethane

1. Introduction

Chlorinated hydrocarbons (CHCs) are widely used in industry with about 15000 chlorinated compounds currently being used in commerce. Organic molecules containing chlorines however, pose both environmental and health risks. Some commonly used CHCs such as dichloromethane and chloroform have been shown to be mutagens and carcinogens whilst others are highly toxic. Emissions of CHCs are difficult to control because the allowable emissions are low and the compounds are thermally and chemically stable.

Catalytic oxidation is a low cost method for CHC destruction. The most active catalysts for the oxidation of hydrocarbons are noble metals supported on alumina, but a high reaction temperature is needed to increase the reaction rate and to overcome chloride poisoning [1]. At higher temperatures where rates are more favorable however, HCl attacks the alumina support. Support degradation by HCl at higher operating temperatures has been reduced by supporting the noble metals on TiO_2/V_2O_5. The most active CHC oxidation catalysts at lower temperatures have been oxides such as Co_3O_4 and

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Cr_2O_3/Al_2O_3. In a preliminary study, Aida and co-workers [2] reported that the oxidation of Freon-12 (CCl_2F_2) and methyl chloride (CH_3Cl) over oxides such as Co_3O_4, was enhanced by addition of gold particles to the cobalt oxide surface. This paper compares the oxidation of CH_2Cl_2 over Au/Co_3O_4, Co_3O_4, Cr_2O_3/Al_2O_3 and noble metal catalysts.

2. Experimental

The Au/Co_3O_4 catalysts were prepared by co-precipitation. A mixture of cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Aldrich, 99+%) and hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, Aldrich, A.C.S. Reagent) was dissolved in distilled water and the solution was heated to 60–70°C. A 2 M sodium carbonate (Na_2CO_3) solution was then added drop-wise to the stirred solution by a Sage single syringe infusion pump (model 341 B) until a pH of 8.5 was reached. The precipitate was then aged at 60–70°C for 1 h, washed with the distilled water, dried at 110°C, and calcined at 350°C for 8 h. The Cr_2O_3/Al_2O_3 catalyst was prepared by incipient wetness according to a US patent [3].

For the screening experiments, 0.5 g of the catalyst (100–140 mesh) was placed on a quartz frit in a U-shaped, downflow reactor. Compressed air and CH_2Cl_2 gas were metered and mixed together prior to being introduced to the test cell using computer-controlled mass flow controllers. Part of the stream flowed through a water saturator and then merged with the main gas stream to obtain the desired relative humidity in the reactant gas. Water is important for the oxidation of CHCs since H_2O can inhibit the Deacon reaction ($HCl + O_2 \rightarrow Cl_2 + H_2O$) and provide the hydrogen needed for the formation of the desired product (HCl). The temperature of the catalyst bed was controlled by an electronic control-box interfaced with a computer program (Control-EG, Quinn–Curtis). A gas chromatograph (SRI-8610 GC) equipped with an electrolytic conductivity detector (ELCD), was used to detect chlorinated hydrocarbons (both reactants and by-products). The ELCD is specific for the analysis of halogenated compounds (chlorinated, brominated and iodated compounds), and has a sensitivity of 1 ppm. Draeger tubes were used to detect concentrations of HCl, Cl_2, $COCl_2$ and HCHO. A CO/CO_2 non-dispersive infrared (NDIR) analyzer (California Analytical) was used to monitor the formation of CO and CO_2.

3. Results and discussion

We tested the activity, stability, and selectivity of Au/Co_3O_4 catalysts for the oxidation of CH_2Cl_2. Several Au/Co_3O_4 catalysts with different Au loadings were prepared and evaluated to investigate the effect of Au addition on the activity of Co_3O_4. For comparison, other base and noble metal catalysts were evaluated under the same conditions. Kinetic analyses were conducted by using the activity test data to estimate the kinetic parameters (activation energy and pre-exponential factor) and the reaction orders.

3.1. Effect of Au loading

Fig. 1 shows that the addition of small Au particles to the Co_3O_4 greatly increased the

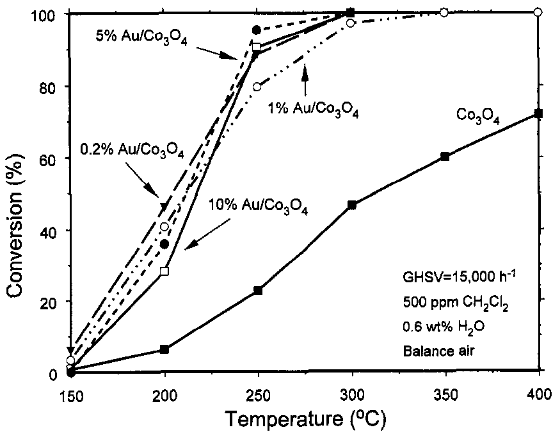

Fig. 1. Effect of gold loadings on the catalytic activity of Au/Co_3O_4 for the oxidation of dichloromethane.

activity of the catalyst, and that activity of the Au/Co_3O_4 catalysts is essentially independent of the amount of gold present. The reactant stream contained 500 ppm of CH_2Cl_2 and 0.6 wt.-% H_2O (40% relative humidity at room temperature) in air. The gas hourly space velocity (GHSV) was 15000 h^{-1}. As shown in Fig. 1, the addition of Au to Co_3O_4 significantly increased the activity of Co_3O_4 for CH_2Cl_2 oxidation, decreasing T_{50} (the temperature at which 50% conversion is obtained) from 310 to 210°C and increasing the rate constant by a factor of approximately 25 at 300°C. The activity of the Au/Co_3O_4 catalysts was independent of the Au loading over the range 0.2 to 10.0 wt.-%. Over all Au/Co_3O_4 catalysts we tested, CH_2Cl_2 started to convert at 150°C and complete conversion is seen at 350°C. At higher temperatures, CH_2Cl_2 was converted to CO_2 and HCl. At temperatures below 250°C however, CH_2Cl_2 tended to form chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4), which are more toxic than CH_2Cl_2. The formation of highly chlorinated compounds at lower temperatures is probably caused by the reaction of CH_2Cl_2 reactant with Cl adsorbed on the surface of Au/Co_3O_4 catalysts.

The role of Au in Au/Co_3O_4 catalysts for the CHC oxidation is still unclear. For low temperature oxidation of CO over Au supported on TiO_2, α-Fe_2O_3 and Co_3O_4, Haruta et al. [4] showed that gold was very active for this oxidation when it was highly dispersed on the oxidic supports. They indicated that small gold particles not only provided the sites for the reversible adsorption of CO, but also appreciably increased the amount of oxygen adsorbed on the support oxides. In a recent FTIR and isotopic study for CO oxidation over Au/ZnO, Boccuzzi et al. [5] indicated that both CO and O_2 were activated on Au sites. The oxygen adsorbed on gold was probably strongly basic, and it could easily oxidize CO to CO_2.

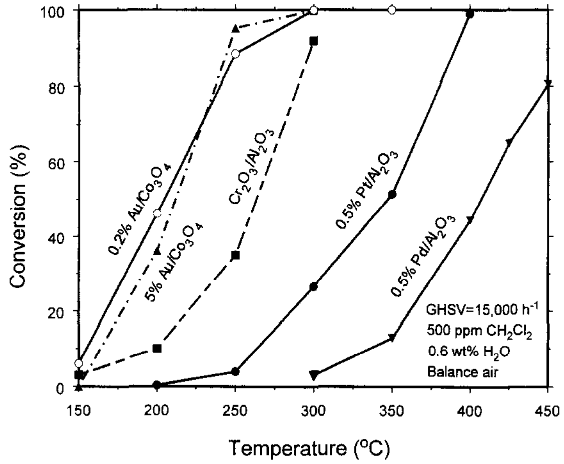

Fig. 2. Comparison of CH_2Cl_2 oxidation over Au/Co_3O_4 catalysts and selected CHC oxidation catalysts.

3.2. Comparison of Au/Co_3O_4 with conventional CHC oxidation catalysts

We compared the activities of our Au/Co_3O_4 (0.2% and 5%) catalysts with a Cr_2O_3/Al_2O_3 catalyst prepared at TDA; for many years, Cr_2O_3/Al_2O_3 catalysts were the only commercially available CHC oxidation catalysts. In addition to this, we tested two standard noble metal catalysts (0.5% Pd/Al_2O_3 and 0.5% Pt/Al_2O_3). The results (Fig. 2) showed that the activity of the Au/Co_3O_4 catalysts was significantly higher than that of other catalysts. T_{50} for Au/Co_3O_4 is 50°C lower than that for Cr_2O_3/Al_2O_3, 135°C lower than 0.5% Pt/Al_2O_3 and 195°C lower than 0.5% Pd/Al_2O_3. The difference is particularly evident when the Au/Co_3O_4 catalysts are compared with the noble metal catalysts, and is presumably a function of the well-known effect of chlorine poisoning of platinum group catalysts at lower temperatures.

3.3. Stability of the Au/Co_3O_4 catalyst

Since most current catalysts suffer from Cl-poisoning, it is important to test the stability of our Au/Co_3O_4 catalysts. Isothermal oxidation experiments were carried out at 350°C over 5% Au/Co_3O_4, 0.5% Pt/Al_2O_3 and 0.5% Pd/Al_2O_3 catalysts. To keep the conversion of

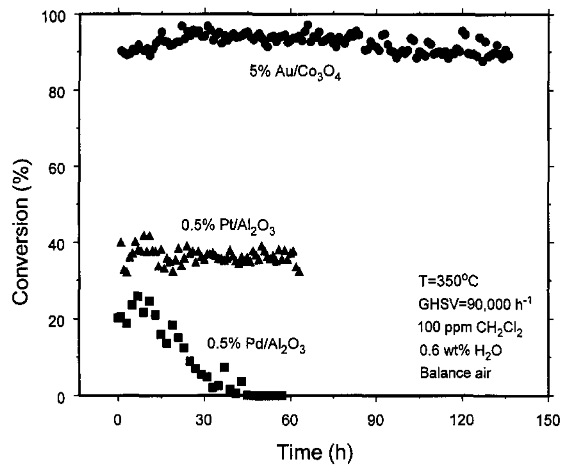

Fig. 3. Long-term stability tests for the oxidation of CH_2Cl_2 over Au/Co_3O_4, Pt/Al_2O_3 and Pd/Al_2O_3 catalysts at 350°C.

CH_2Cl_2 below 100% at 350°C, a higher gas hourly space velocity (90000 h^{-1}) was used. The concentration of CH_2Cl_2 was 100 ppm. As shown in Fig. 3, the 5% Au/Co_3O_4 catalyst was quite stable with higher conversions (95%) of CH_2Cl_2 for the entire duration of the test (130 h). The 0.5% Pt/Al_2O_3 catalyst was also stable for about 70 h, but the activity was lower than that of Au/Co_3O_4. The 0.5% Pd/Al_2O_3 catalyst had both lower stability and lower activity and the conversion of CH_2Cl_2 dropped from 25% to zero over a period of 50 h of operation.

3.4. Product distribution

During the long-term isothermal experiment on CH_2Cl_2 oxidation over a 5% Au/Co_3O_4 catalyst, the reaction products were analyzed after 25, 45, 100 and 130 h of operation. With an inlet concentration of 100 ppm CH_2Cl_2, the expected outlet concentration of HCl is 200 ppm if the CH_2Cl_2 is completely converted to HCl and CO_2. As shown in Table 1, a very good chlorine mass balance was obtained and the only products were HCl and CO_2 (HCl is the desirable reaction product because it is easily removed from the gas stream by a basic solvent). No other chlorinated hydrocarbons (CH_3Cl, $CHCl_3$ or CCl_4) except for the reactant (CH_2Cl_2) were detected by GC–ELCD. We did not observe the formation of Cl_2, $COCl_2$ or HCHO (Draeger tube analyses), or of CO (CO-NDIR analysis).

Table 1
CH_2Cl_2 oxidation on 5% Au/Co_3O_4 at 350°C with 0.6 wt.-% H_2O in air and GHSV of 90000 h^{-1}

Time (h)	CH_2Cl_2 in (ppm)	HCl out (ppm)	HCl expected (ppm)
25	100	180 ± 18	190
45	100	170 ± 17	190
100	100	170 ± 17	180
130	100	170 ± 17	180

Note: No detectable Cl_2, $COCl_2$, HCHO by Draeger tubes analyses.
No detectable CO by CO-NDIR analyses.

3.5. Kinetic analysis

To determine the kinetic parameters (i.e. activation energy, pre-exponential factor and reaction order) for the catalytic oxidation of the CHCs, either differential or integral experimental methods can be used. For the differential method, the reaction rate can be measured if the conversion of the key reactant is less than 10%. By changing the reaction temperature at the constant reactant concentration and measuring the conversion, the activation energy can be estimated by plotting $\ln(r)$ versus $1/T$, where r is the reaction rate and T is the reaction temperature. If the reaction temperature is kept constant and the concentration is changed, the reaction order can also be evaluated. To determine the reaction conditions under which the conversion of reactant is less than 10%, we measured the conversion while changing the space velocity. In these experiments, 500 ppm of CH_2Cl_2 in air with a relative humidity of 40% was passed through the 5% Au/Co_3O_4 catalyst bed maintained at 300°C. The experimental results showed that the conversion of CH_2Cl_2 decreased linearly with the space velocity. One observation from these experiments is that the 5% Au/Co_3O_4 catalyst exhibits very high activity at 300°C for CH_2Cl_2 oxidation. At the highest space velocity tested (165 000 h^{-1}), the conversion of CH_2Cl_2 still exceeded 50%. To avoid the possibility of the feed gas stream channeling through the catalyst bed, we did not evaluate space velocities higher than 165 000 h^{-1}.

Since our catalyst (5% Au/Co_3O_4) was very active, conversion of less than 10% was difficult to obtain under these experimental conditions. Instead, the integral method was used to determine the kinetic parameters. The data obtained in the screening experiments as presented in Fig. 2, were fitted into the Arrhenius equation and the activation energies and reaction order were calculated. For the oxidation of CH_2Cl_2 to CO_2 and HCl in the presence of H_2O, we make the assumption that the order for oxygen is zero since the concentration of O_2 (20%) is significantly higher than the concentration of CH_2Cl_2 (which is in the order of 10–1000 ppm). The activity was also independent of water partial pressure at H_2O concentrations ranging from 0.3% to 1.5%. For all the catalysts tested, the conversion vs. temperature plot was well described by a first order reaction in CH_2Cl_2, and the data were therefore fitted to obtain the activation energy and pre-exponential factors.

When first-order was assumed, a linear correlation was obtained between $\ln\left(\frac{-\ln(1-x)}{t}\right)$ and $1/T$ for all catalysts (5% Au/Co_3O_4, Co_3O_4, Cr_2O_3/Al_2O_3, 0.5% Pt/Al_2O_3 and 0.5% Pd/Al_2O_3), as shown in Fig. 4, where t is the contact time between the reactant and the catalyst, x is the conversion of CH_2Cl_2 and T is the reaction temperature (neither zero-order nor second-order assumptions yielded a straight line fit). To further examine if the reaction order is first in CH_2Cl_2, the concentration of CH_2Cl_2 was changed from 50, 100, 250 and 500 to 1000 ppm, and the conversions of CH_2Cl_2 were measured during the oxidation reaction over 5% Au/Co_3O_4 at 300°C. The CH_2Cl_2 conversion was essentially independent of CH_2Cl_2 concentration (as would be expected for a first order reaction), with a slight inhibition at the highest concentrations.

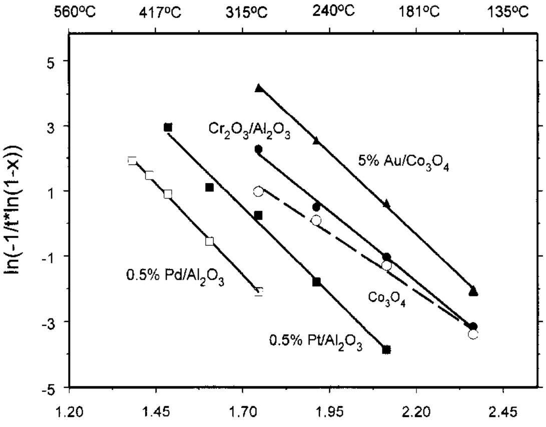

Fig. 4. Plot of $\ln\left(\frac{-\ln(1-x)}{t}\right)$ against $1/T$ assuming first order kinetics for CH_2Cl_2 oxidation.

The activation energy was estimated to be 20 kcal/mol for CH_2Cl_2 oxidation over 5% Au/Co_3O_4. Similar activation energies were obtained for the other catalysts (Co_3O_4, Cr_2O_3/Al_2O_3, 0.5% Pt/Al_2O_3 and 0.5% Pd/Al_2O_3). The CH_2Cl_2 oxidation rates were calculated at a range of reaction temperatures for various catalysts by using activation energies and pre-exponential factors. The results showed that 5% Au/Co_3O_4 was 10 times more active than Cr_2O_3/Al_2O_3, 25 times more active than Co_3O_4, 70 times more active than 0.5% Pt/Al_2O_3 and 560 times more active than 0.5% Pd/Al_2O_3 for CH_2Cl_2 oxidation at 300°C.

4. Conclusions

For the oxidation of low concentrations of CH_2Cl_2 (50 to 1000 ppm), we reached the following conclusions:

· The addition of Au significantly improved the activity of Co_3O_4, increasing the rate by a factor of roughly 25.

- The activity of the Au/Co_3O_4 catalysts is essentially independent of the Au loading over the range 0.2 to 10.0 wt.-% Au.
- The Au/Co_3O_4 catalysts were more active than other catalysts; the reaction rate over 5% Au/Co_3O_4 was 10 times higher than over Cr_2O_3/Al_2O_3, 70 times higher than over 0.5% Pt/Al_2O_3 and 560 times higher than over 0.5% Pd/Al_2O_3 at 300°C.
- The Au/Co_3O_4 catalysts were stable in the presence of CH_2Cl_2 and the reaction product (HCl).
- The Au/Co_3O_4 catalysts selectively converted CH_2Cl_2 to CO_2 and HCl. No detectable by-products (other CHCs) or partial oxidation products (Cl_2, $COCl_2$, HCHO or CO) were formed at 350°C.
- The oxidation of CH_2Cl_2 was first-order in CH_2Cl_2 and zero-order in O_2 or H_2O. The activation energy was estimated to be about 20 kcal/mol for CH_2Cl_2 oxidation over 5% Au/Co_3O_4.

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