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Selective formation of chloroethane by the hydrochlorination of ethene using zinc catalysts

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Abstract

A detailed study of the hydrochlorination of ethene and higher alkenes using $ZnCl_2/SiO_2$ and $ZnCl_2/Al_2O_3$ catalysts is described and discussed. Based on earlier observations that supported gold can be an active catalyst for both ethyne hydrochlorination and oxidation reactions, we initially investigated using supported gold as catalysts for the oxychlorination of ethene. However, we found that oxychlorination did not occur in the presence of oxygen and, furthermore, that the gold acted as a poison/inhibitor during the initial reaction period, with the underlying reaction being ethene hydrochlorination. Supported Zn^{2+} was found to be a very effective catalyst for this reaction. The hydrochlorination of higher alkenes occurred, with high selectivity to a range of relatively complex chlorinated hydrocarbon products at rates of ca. 10–13 $mol/(kg_{cat}\,h)$.

Keywords: Ethene hydrochlorination; Zinc catalysts

1. Introduction

Chlorinated hydrocarbons remain important solvents and intermediates even with the current trend toward removing solvents from chemical syntheses as one of the foundations of green chemistry. Among chlorinated hydrocarbons, chloroethane in particular remains one of the most important. Of course, a major application of chloroethane has been the manufacture of tetraethyl lead, an antiknock additive for gasoline with an average production of approximately 10 millions tons per year [1]. Currently, chloroethane in particular is used in cleaning and degreasing applications; however, its most important use is as a treatment agent for cellulose to manufacture ethylcellulose, with an annual production of some thousands of tons [1]. Chloroethane has been manufactured by the pyrolysis of ethanol and the chlorination of ethene, but both of these routes have now been superseded [2]. Although chloroethane can be synthesized as a byproduct from the production of vinyl chloride, today it is manufactured mainly by the hydrochlorination of ethane, performed in a slurry phase batch reactor at 130–250 °C and 1 bar, using $AlCl_3$ as a catalyst [3]. Indeed, $AlCl_3$ is the only catalyst that has been reported for this reaction to date. Industrially, this process is highly efficient; however, safety-related problems can be encountered due to the properties of $AlCl_3$. In fact, if traces of water are present, $AlCl_3$ can be readily hydrolyzed, which can be potentially explosive [4]. This potential problem has stimulated an interest in finding alternative catalysts that are able to carry out the reaction under safer conditions, while using smaller amounts of the active species. Indeed, the role of $AlCl_3$ is to act as a Lewis acid, but the amount required to carry out the reaction is close to stoichiometric [5]. To some extent, this is because the reaction pathway involves $AlCl_3$ abstracting Cl^-, and then H^+ reacts with the alkene double bond and $AlCl_4^-$ donates Cl^-, so for every HCl that reacts an $AlCl_3$ is required, however, because the rate is very slow, stoichiometric amounts of $AlCl_3$ are used, and the $AlCl_3$ is not a source of Cl in the absence of HCl. Against this background, we initiated a study to identify a heterogeneous catalyst that could be used as a replacement for $AlCl_3$.

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This paper describes the experimental work that forms the basis of the identification of ZnO and supported $ZnCl_2$ as very selective catalysts for the direct hydrochlorination of ethene to chloroethane.

2. Experimental

2.1. Catalyst preparation

The carbon-supported gold catalyst (1 wt% Au/C) was prepared using an incipient wetness impregnation technique and aqua regia as a solvent, as described previously [6].

2.1.1. Preparation of Au/MO_x via deposition precipitation

ZnO (Aldrich, 3.0 g) was stirred in distilled water (150 mL), and $HAuCl_4 \cdot xH_2O$ (Strem, 62 mg, assay 50.14% in 10 mL water) was added dropwise over 2 min, to produce a final Au loading of 1 wt%. The slurry was then heated to 80 °C, and the pH was adjusted by adding a saturated Na_2CO_3 solution, to reach a final value 9. After stirring for another 1 h and cooling, the slurry was filtered and washed in approximately 4 L of distilled water. The solid was then dried at 120 °C for 16 h. The same procedure was used for the preparation of Au/MgO, Au/La_2O_3, Au/Al_2O_3, and Au/CeO_2. All of these catalysts were used as dried materials; in addition, all of the materials were calcined in static air (400 °C, 4 h) but these calcined materials were found to be inactive as catalysts.

2.1.2. Preparation of Au/ZnO and Au/MgO via co-precipitation

$Zn(NO_3)_2 \cdot 6H_2O$ (Aldrich, 7.3 g) was dissolved in distilled water (150 mL), and $HAuCl_4 \cdot xH_2O$ (Strem 41 mg, assay 50.14%, in 10 mL water) was added dropwise over 2 min, to reach a final Au loading of 1 wt%. The solution was then heated to 80 °C, and saturated aqueous Na_2CO_3 was added until a pH of 9 was achieved. The mixture was then stirred for 3 h, and the resulting precipitate was filtered and dried for 16 h at 120 °C. The same procedure was used to prepare co-precipitated Au/MgO and Au/CeO_2 with $Mg(NO_3)_2 \cdot H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$. Both catalysts were calcined in static air (400 °C, 4 h).

2.1.3. Au/ZnO/SiO_2 via co-precipitation and deposition precipitation

ZnO/SiO_2 was prepared using a deposition–precipitation method. $Zn(NO_3)_2 \cdot 6H_2O$ (Aldrich, 14.6 g) was dissolved in a slurry containing 250 mL of distilled water and 4 g of SiO_2 (Aldrich). The amount of precursor was calculated to have a final ZnO/SiO_2 ratio of 1:1 (by weight). The slurry was then heated to 80 °C and maintained at this temperature for 5 h. The solid thus obtained was dried for 16 h at 120 °C and then calcined in static air (500 °C, 5 h) to give ZnO/SiO_2.

ZnO/SiO_2 (2 g) was stirred in 150 mL of distilled water, and 41 mg of $HAuCl_4 \cdot xH_2O$ (Strem, assay 50.14%, in 10 mL water) was added dropwise over 2 min, for a final Au loading of 1 wt%. The slurry was then heated to 80 °C, and saturated aqueous Na_2CO_3 solution was added until pH 9 was attained, after which the mixture was stirred for another 1 h. After cooling, the slurry was filtered and washed using approximately 4 L of distilled water. The solid was then dried at 120 °C for 16 h and calcined in static air (400 °C, 4 h) before use.

2.1.4. $ZnCl_2$/SiO_2 and $ZnCl_2$/Al_2O_3 via impregnation

$ZnCl_2$/SiO_2 with 15 wt% Zn was prepared by incipient wetness impregnation (BDH, $ZnCl_2$, 265 mg per gram of silica). The solution was added to the support (7 mL of solution per gram of silica), and the product thud obtained was dried (16 h, 80 °C). An identical procedure was used to prepare $ZnCl_2$/Al_2O_3.

2.1.5. Catalyst characterization using transmission electron microscopy and X-ray photoelectron spectroscopy

Samples were prepared for transmission electron microscopy (TEM) analysis by dispersing the catalyst powders in high-purity ethanol and allowing a drop of the suspension to dry on a lacey-carbon film supported on a 300-mesh Cu TEM grid. Bright-field (BF) imaging and selected-area ring diffraction patterns were acquired using a Jeol 2000FX TEM operating at 200 keV with a LaB_6 filament.

X-ray photoelectron spectra were recorded on a Kratos Axis Ultra DLD spectrometer using a monochromatized AlK_α X-ray source (100 W). Spectra were recorded at analyzer pass energies of either 160 eV (survey scans) or 40 eV (detailed scans). Binding energies are referenced to the C(1s) binding energy of adventitious carbon contamination, which is taken to be 284.7 eV.

2.2. Catalyst testing

Catalysts were tested for ethene hydrochlorination and oxyhydrochlorination in a fixed-bed glass microreactor operating just above atmospheric pressure as described previously for ethyne hydrochlorination. Ethene or higher alkenes (5 mL/min) and hydrogen chloride (5 mL/min) were fed though a mixing vessel/preheater (70 °C) through calibrated mass flow controllers to a heated glass reactor containing catalyst (200 mg), giving a total GHSV of 6400 h^{-1}. The pressure of the reactants (both HCl and C_2H_4) was in the range of 1.1–1.2 bar. The products were analyzed in two ways. First, the exit gas mixture was passed through a Dreschel bottle containing NaOH at known concentration for a predetermined time to measure the conversion of HCl. Alternatively, the gas stream was analyzed by gas chromatography (GC). A reaction temperature of 250 °C was chosen; blank tests using an empty reactor filled with quartz wool did not display any catalytic activity with the reactants under these flow conditions.

Oxychlorination of ethene was carried out under the same temperature and pressure conditions but with a reactant ratio C_2H_4:HCl:O_2 of 1:2:0.7. Air was used as the source of oxygen and reactant flows of C_2H_4, HCl, and air of 5, 10, and 17.5 mL/min, respectively, were used, giving a total GHSV of 20,800 h^{-1}. Higher alkene reaction products were collected in a chloroform trap at the outlet of the catalytic reactor and subsequently analyzed by ^{1}H-NMR using an Avance DPX-400 Spectrospin Bruker instrument operating at 400 MHz.

3. Results and discussion

3.1. Oxychlorination of ethene

Initial experiments were carried out using Au/C as the catalyst, because this has been found to be very effective for the hydrochlorination of ethyne [7–9]. At 180 °C or temperatures up to 250 °C, under our standard reaction conditions, this catalyst was inactive for ethane hydrochlorination; indeed, in a mixture of ethene and ethyne, only the ethyne was reactive. This preference for the reaction of carbon–carbon triple bonds over the reaction of carbon–carbon double bonds has been noted with supported Au catalysts for hydrogenation reactions [10]; this effect is thought to be due to the preferential adsorption of alkyne at the edges of the Au nanocrystals. In view of this, we anticipated that oxychlorination could be a viable approach, because supported Au catalysts have been found to be effective oxidation catalysts for alkenes [11–13]. We investigated the oxychlorination reaction at 180 and 250 °C but observed only negligible activity. We also investigated Au/TiO_2, which is known to be an effective catalyst in alkene epoxidation [11–13], but again we observed no reactivity. In view of this finding, we also investigated Au/MgO (3 wt%) and Au/ZnO (1 wt%), which are known to be efficient oxidation catalysts [14,15], along with a range of supported gold catalysts; the results are shown in Fig. 1. In all these cases, under the relatively short time scale of our experiments, the surface of the supports and the gold could be chlorided, arguing by analogy with gold catalysts for ethyne hydrochlorination where Au^{3+} is the active component [8]. In addition, the supports were found to be inactive for the oxychlorination of ethene. For both Au/ZnO and Au/MgO, the catalytic activity was observed to increase with reaction time for the catalyst obtained through deposition precipitation but not for the catalyst obtained through co-precipitation, which displays lower activity. In all cases, the only product observed was chloroethane (see supplementary data Fig. S1 for the data for the Au/ZnO/SiO_2 catalyst). Furthermore, negligible amounts of CO_2 and H_2O were observed in these experiments, and no CO was observed (within the limits of detection). We investigated the oxidation of ethene under the same reaction conditions and found only a negligible reaction.

3.2. Hydrochlorination of ethene

In view of the lack of oxidation activity observed with ethene and the observation that the only product observed was from hydrochlorination, not oxychlorination, we subsequently investigated the Au/ZnO catalyst obtained through deposition precipitation and Au/ZnO/SiO_2 catalysts, in the absence of O_2. The removal of oxygen from the reaction mixture led to enhanced activity (Fig. 2). Consequently, we investigated the ethene hydrochlorination reaction over Au/ZnO and, in particular, we carried out a systematic set of experiments to isolate and identify the effect of each reactant on activity, as follows:

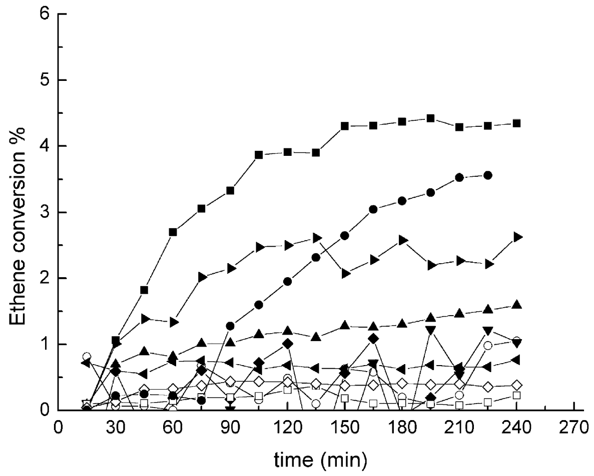

Fig. 1. Oxychlorination of ethene over Au/MO_x catalysts. (■) Au/ZnO DP, (◇) Au/ZnO CP, (◀) Au/ZnO CP clc, (●) Au/MgO DP, (▼) Au/MgO CP, (◆) Au/MgO CP clc, (▲) Au/La_2O_3 DP, (▶) Au/Al_2O_3 DP clc, (○) Au/CeO_2 DP, and (□) Au/CeO_2 CP clc. Where: DP = deposition precipitation; CP = coprecipitation; clc = calcined; all catalysts have a gold loading of 1% except Au/MgO (3%).

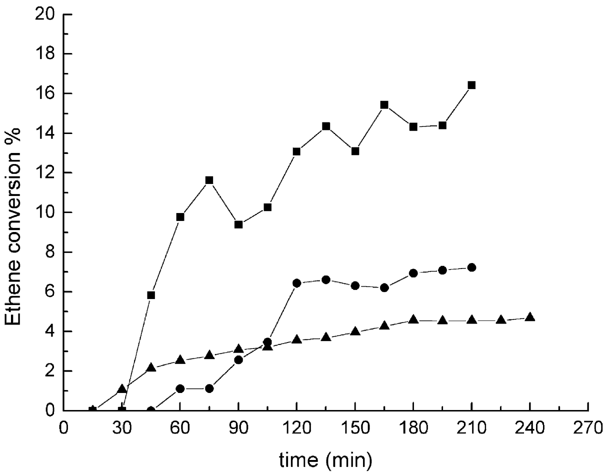

Fig. 2. Conversion trend for the (■) Au/ZnO/SiO_2 and (●) Au/ZnO DP catalyst for the hydrochlorination reaction of ethene; conversion trend of (▲) Au/ZnO DP catalyst in presence of oxygen.

- experiment A:
  C_2H_4/HCl (2 h) → He/HCl (2 h) → C_2H_4/HCl (2 h),
- experiment B:
  He/HCl (2 h) → C_2H_4/HCl (2 h) → He/HCl (2 h),
- experiment C:
  C_2H_4/HCl (2 h) → C_2H_4/He (2 h) → C_2H_4/HCl (2 h),
- experiment D:
  C_2H_4/He (2 h) → C_2H_4/HCl (2 h) → C_2H_4/He (2 h).

The results, shown in Fig. 3, exhibit the opposite trend to that observed for the same series of experiments carried out over Au/C for the hydrochlorination of ethyne [6]. The most significant observation concerns experiment C, in which the formation of chloroethane was improved after treatment with inert gas and ethene. In contrast, for ethyne hydrochlorination with Au/C [6], the increase in the yield of the hydrochlorination product was

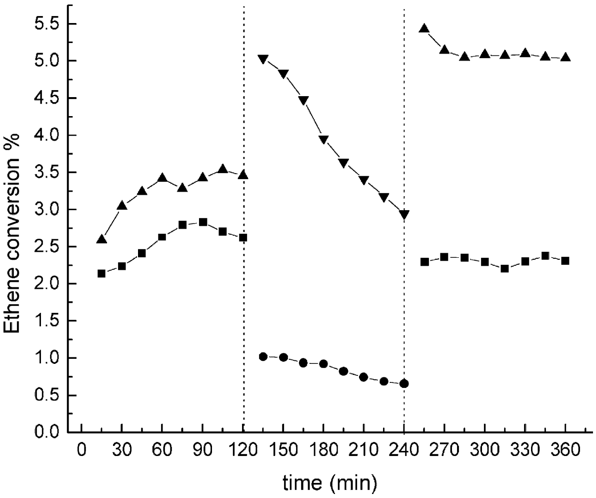

Fig. 3. Hydrochlorination of ethene over Au/ZnO DP: (■) experiment A: C_2H_4/HCl (2 h) → He/HCl (2 h) → C_2H_4/HCl (2 h); (●) experiment B: He/HCl (2 h) → C_2H_4/HCl (2 h) → He/HCl (2 h); (▲) experiment C: C_2H_4/HCl (2 h) → He/C_2H_4 (2 h) → C_2H_4/HCl (2 h); (▼) experiment D: He/C_2H_4 (2 h) → HCl/C_2H_4 (2 h) → He/C_2H_4 (2 h).

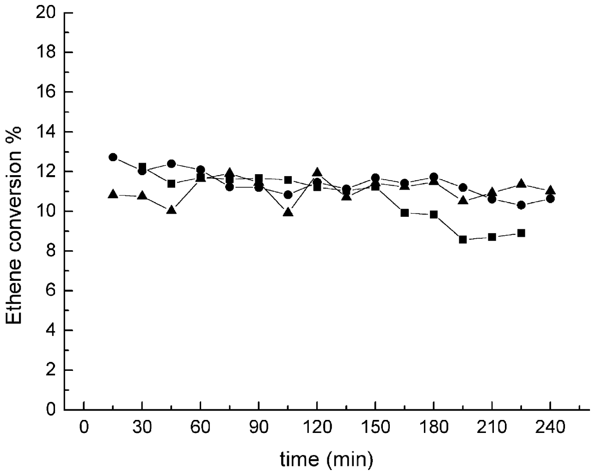

Fig. 4. Hydrochlorination of ethene over (■) ZnO/SiO_2, (●) $ZnCl_2/SiO_2$ and (▲) $ZnCl_2/Al_2O_3$ using the standard reaction conditions at 250 °C.

Table 1
Surface molar composition of the supported $ZnCl_2$ and ZnO catalysts estimated from the XPS data

	Molar ratios			
	Cl/Zn	Cl/(Si or Al)	Zn/(Si or Al)	C/(Si or Al)
$ZnCl_2/SiO_2$ fresh	1.38	0.25	0.18	0.54
$ZnCl_2/SiO_2$ used	1.24	0.23	0.18	0.40
$ZnCl_2/Al_2O_3$ fresh	1.55	0.39	0.25	0.40
$ZnCl_2/Al_2O_3$ used	1.66	0.42	0.26	0.44
ZnO/SiO_2 fresh	0.19	0.05	0.26	0.51
ZnO/SiO_2 used	2.28	3.78	1.66	4.70

observed only when the intermediate step involved treatment with inert gas and HCl (i.e., equivalent to experiment A in this set of experiments). In the present case, experiment A resulted in no significant changes in the yield of the hydrochlorination product. From experiment B (He/HCl → C_2H_4/HCl → He/HCl), a lower conversion to the hydrochlorination product was seen than when the HCl pretreatment step was excluded. This test is useful, because the trend for this catalyst was that conversion increased with time on stream (Fig. 2), and this experiment indicates that treatment with HCl alone was not the sole cause of this effect with this catalyst. The observation that the trends observed in ethene hydrochlorination were opposite to those observed with the Au/C catalyst for hydrochlorination of ethyne, suggested to us that the Au component was not an active species in this reaction. In fact, the bulk structure of all the materials was modified after the reaction, leading to formation of $ZnCl_2$ when Au/ZnO was used (see supplementary data Fig. S2, for the Au/ZnO catalyst obtained through deposition precipitation).

To investigate whether $ZnCl_2$ is the active species, samples of $ZnCl_2$ (nominal amount 15 wt% Zn) supported on SiO_2 and ZnO/SiO_2 (nominal ratio 1:1 wt%) were tested as catalysts for the hydrochlorination of ethene under the standard reaction conditions. The results, shown in Fig. 4, demonstrate that both catalysts exhibited high activity from the start of the reaction. This observation implies that Au acted as a poison in this reaction, because the corresponding Au catalysts were inactive at the start (Fig. 2). Furthermore, tests carried out using unsupported ZnO, $ZnCl_2$, and $Zn(OH)_2$ showed no activity. In view of this finding, we consider the active catalyst to be supported $ZnCl_2$. Because the catalyst is active at 250 °C, and the melting point of bulk $ZnCl_2$ is 290 °C, the formation of a supported, almost liquid-like layer may be responsible for this catalytic activity, emulating the nature of the current $AlCl_3$ slurry phase industrial process. This may help explain why the two materials, prepared using different methods, with significantly different zinc component loadings (32 and 9.1 Zn wt% for the for ZnO/SiO_2 and $ZnCl_2/SiO_2$, respectively) and surface areas (53 m^2/g and 104 m^2/g for ZnO/SiO_2 and $ZnCl_2/SiO_2$, respectively) gave similar catalytic performance; in addition, ZnO supported on SiO_2 is able to evolve to $ZnCl_2$ (see supplementary data Fig. S3). To further confirm that $ZnCl_2$ is an active species, $ZnCl_2/Al_2O_3$ (10.3 Zn wt%, 57 m^2/g) was prepared; it demonstrated the same activity (Fig. 4).

XPS analyses of the fresh and used silica- and alumina-supported $ZnCl_2$ and silica-supported ZnO catalysts corroborate these conclusions. All of the samples showed the presence of Zn, Cl, O, C, and Si (Al) with no evidence of any contaminants. Quantification of the XPS data leads to the results given in Table 1. The supported $ZnCl_2$ materials show similar surface compositions, with the alumina-supported samples having somewhat higher Zn and Cl contents. The ZnO/SiO_2 sample shows very clear evidence for Cl uptake after reaction, leading to a Cl/Si atomic ratio 1.5–2 times greater than that for the supported $ZnCl_2$ catalysts. This may be due to enhanced wetting of the silica induced by chlorination of the ZnO. This sample also exhibits a significant increase in the C/Si ratio, indicating that the chlorination of the surface may involve more than a simple conversion of ZnO to $ZnCl_2$ as phase transitions of $ZnCl_2$.

We consider our observations significant, because there are no literature reports of the use of Zn^{2+} as a heterogeneous catalyst for hydrochlorination reactions. But these findings are consistent with the Lewis acid nature of Zn^{2+}, and hence we suggest that the supported zinc catalysts function as Lewis acid catalysts for the hydrochlorination reaction. Because the catalysts are operated at temperatures well below the boiling point of bulk zinc chloride (732 °C), we do not believe that the catalysts readily lose zinc chloride during use. Hydrolysis reaction is the main pathway by which the current $AlCl_3$ catalyst is deactivated; for this reason, $AlCl_3$ is used in stoichiometric amounts. We consider zinc chloride to be more stable toward hydrolysis, and consequently the catalysts are more stable. Although at present the longest run time that we have investigated is only 4 h, we have found no changes in the bulk structure of the catalysts (see supplementary data Figs. S4 and S5 for the $ZnCl_2/SiO_2$ and $ZnCl_2/Al_2O_3$ before and after reaction). This increased stability ensures that the supported zinc chloride materials can be used in catalytic rather than stoichiometric results.

Having established the nature of the $ZnCl_2$-like active species for the ethene hydrochlorination reaction, we carried out a set of experiments using the $ZnCl_2/SiO_2$ catalyst to identify the effect of each reactant on activity, as follows:

- experiment E:
  C_2H_4/HCl (2 h) → He/HCl (2 h) → C_2H_4/HCl (2 h),
- experiment F:
  He/HCl (2 h) → C_2H_4/HCl (2 h) → He/HCl (2 h),
- experiment G:
  C_2H_4/HCl (2 h) → C_2H_4/He (2 h) → C_2H_4/HCl (2 h),
- experiment H:
  C_2H_4/He (2 h) → C_2H_4/HCl (2 h) → C_2H_4/He (2 h).

The results, shown in Fig. 5, are very different from those when Au was present on the catalyst surface, confirming that Au had a negative effect for this reaction. But there are similarities to the trends observed for the Au/C catalyst for the hydrochlorination of ethyne [6]. Indeed, when Au/ZnO was used, the average conversion was 3–4%, whereas for $ZnCl_2/SiO_2$, it was 7–8%; however, these two catalysts exhibited opposing effects toward the different reactant treatments. For $ZnCl_2$, the active species was already present, whereas for Au/ZnO, the active species had to be created in situ by surface chloriding during the initial reaction period. This proposal is supported by the trend in conversion, which increased to a steady state for Au/ZnO, whereas for $ZnCl_2/SiO_2$, the activity started out high and remained steady throughout.

In a subsequent set of experiments, we investigated the hydrochlorination of higher alkenes over the $ZnCl_2/SiO_2$ catalyst. We first investigated propene (propene:HCl = 1:1 using 5 mL/min for each reactant, a relative inlet pressure of 1.1 bar, and a reaction temperature of 250 °C). Products were collected after the reactor in a chloroform trap and characterized by NMR spectroscopy. The conversion was observed to be 20%. Although the main product was the expected Markovnikov product 2-chloropropane, a significant amount of anti-Markovnikov product also was produced (see supplementary data Fig. S6), with a main product: secondary product ratio of ca. 5:1. Subsequent experiments involving feeding 1-chloropropane confirmed that isomerization occurred over the catalyst, which was the origin of the two chlorinated products (see supplementary data Fig. S7). To test whether the isomerization was a catalyzed or a thermal reaction, we further investigated the reaction over SiC and found it to be ineffective, indicating that the isomerization observed was due to a catalyzed process.

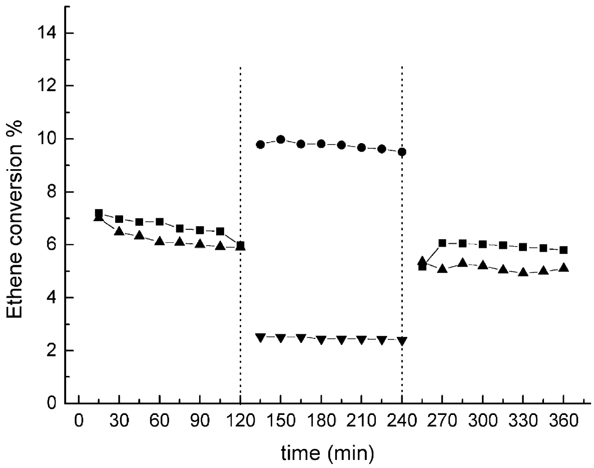

Fig. 5. Hydrochlorination of ethene using $ZnCl_2/SiO_2$ as catalyst: (■) experiment E: C_2H_4/HCl (2 h) → He/HCl (2 h) → C_2H_4/HCl (2 h); (●) experiment F: He/HCl (2 h) → C_2H_4/HCl (2 h) → He/HCl (2 h); (▲) experiment G: C_2H_4/HCl (2 h) → He/C_2H_4 (2 h) → C_2H_4/HCl (2 h); (▼) experiment H: He/C_2H_4 (2 h) → HCl/C_2H_4 (2 h) → He/C_2H_4 (2 h).

Subsequently, we reacted 2-methylpropene over $ZnCl_2/SiO_2$ using the same reaction conditions. A 15% conversion level was observed, with the major product being 2-chloro-2-methylpropane, as determined by NMR analysis, along with traces of 1-chloro-2-methylpropane (see supplementary data Fig. S8). When isoprene was used as the substrate, two well-defined chlorinated products were obtained: 2-methyl-4-chloro-2-butene and 2-methyl-2-chloro-3-butene (see supplementary data Fig. S9); conversions were 7–8%. This is a significant result, because there are no previous reports on the use of $ZnCl_2$ to synthesize these chlorinated products, and, furthermore, they can be generated without forming other byproducts using the $ZnCl_2/SiO_2$ catalyst. Thus, we can conclude that hydrochlorination reactions of alkenes using supported Zn^{2+} catalysts are selective. This finding is clear when the reaction products from higher alkenes are considered, but even for ethane, we do not observe other potential products, such as ethene oligomers and dichloroethane.

The discovery of supported Zn^{2+} as an effective alkene hydrochlorination catalyst is not overly surprising, because the present industrial production uses Al^{3+}, and both of these cations can act as Lewis acid catalysts. Consequently, we suggest that the reaction mechanism may be similar in both cases, probably involving the alkene adsorbing on the cation and HCl forming a complex before being added to the carbon–carbon double bond. However, it should be noted that other cations that we have investigated also could act as Lewis acid catalysts but were found to be inactive. Indeed, until our observation that Zn^{2+} is an active catalyst, only $AlCl_3$ had been used; moreover, Zn^{2+} is considerably more active.

To date, we have not attempted to optimize the preparation of the supported $ZnCl_2$ catalysts. Even so, rates of product formation of ca. 10–13 mol/(kg_{cat} h) were observed, although

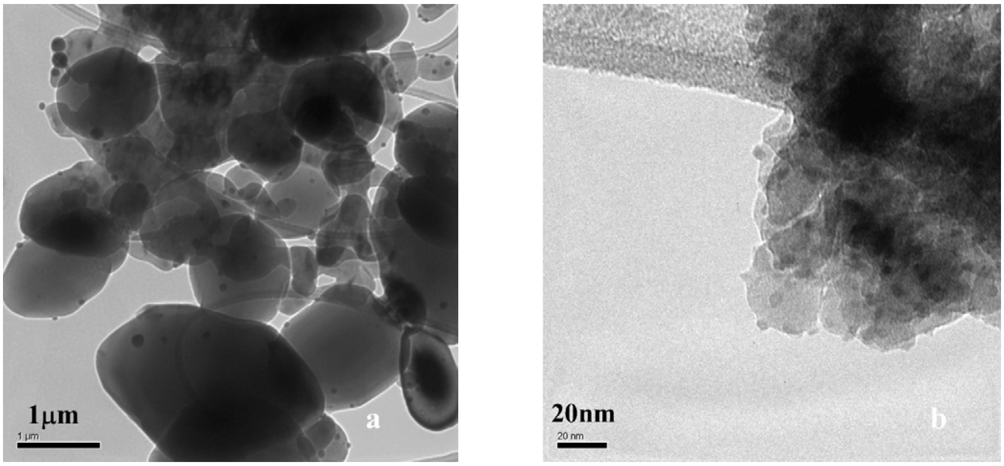

Fig. 6. Bright field electron micrographs of the (a) Au/ZnO and (b) ZnO/SiO_2 catalysts.

the conversions per pass that we achieved were relatively low (ca. 10–20%). We believe that this performance can be improved considerably. Our observation that supported $ZnCl_2$ acts as a very selective heterogeneous catalyst for hydrochlorination reactions is perhaps unique in the chemistry of zinc catalysts, because there have been no previous disclosures concerning the use of Zn^{2+} for this reaction. There are numerous examples of Zn^{2+} acting as a homogeneous catalyst for reactions with carbon–carbon double bonds [16–18], but examples of supported Zn^{2+} acting as a heterogeneous catalyst are less common. There is a recent report that $ZnCl_2/Al_2O_3$ can act as a Lewis acid catalyst for the O-methylation of catechol [19]; and more notably there are a number of studies concerning the use of zinc for the oxychlorination of ethene to form vinyl chloride [20,21] and the oxychlorination of ethane to vinyl chloride [22].

We further investigated two findings. First, we attempted to determine why bulk ZnO was inactive as opposed to supported ZnO, which was very active. This finding was somewhat surprising, because it could be expected that the surface of bulk and supported ZnO would both rapidly react with HCl, thereby creating the active catalyst. In particular, our results demonstrate that supported ZnO and supported $ZnCl_2$ are equally effective as catalysts and are effective without any induction period. Second, we wished to elucidate the way in which Au was acting as an inhibitor or poison during the initial phase of the reaction. To resolve these issues, we used transmission electron microscopy (TEM) to characterize some of the catalysts explored in this study. Electron microscopy of unsupported, calcined ZnO (Fig. 6a) showed that it was composed of relatively large crystals of zincite (ca. 0.1–3.0 µm) whereas the supported catalysts (Fig. 6b) contained much smaller (2–5 nm) ZnO crystallites supported on ca. 50-nm amorphous silica particles. Thus, the increased activity of the supported ZnO relative to its bulk counterpart can be correlated with a significant increase in the specific surface area of the ZnO species. The decreased particle size also means that the fraction of the total surface area represented by nonbasal plane ZnO surfaces in the crystallites is much higher, and these may be either catalytically more reactive or more easily converted to $ZnCl_2$.

Whereas discrete Au crystallites of ca. 20–100 nm diameter are readily visible on the bulk ZnO particles (Fig. 6a), proper characterization of the Au species in the supported ZnO/SiO_2 catalyst from bright field imaging is not possible due to the anticipated similarity in size between the nanoscale ZnO particles and those of the deposited Au. STEM analyses based on high-angle annular dark-field imaging and XEDS spectrum imaging to further investigate the Au dispersion on the complex ZnO/SiO_2 support are ongoing; we will report the results in a future paper. Thus, even though our catalytic results strongly imply that the Au is acting to block the active sites on the $ZnCl_2/SiO_2$ catalysts, the precise microstructural details of how this actually occurs have yet to be elucidated.

4. Conclusion

We have shown that supported Zn^{2+} acts as a very selective heterogeneous catalyst for the hydrochlorination of ethene and higher alkenes. In the case of ethene hydrochlorination, chloroethane is the exclusive product. Higher alkenes demonstrate similar reactivities to ethene and also give relatively few by-products. With the current nonoptimized catalysts, synthesis rates of ca. 10–13 $\text{mol}/(\text{kg}_{\text{cat}}\,\text{h})$ have been achieved; we anticipate that these rates can be improved through appropriate catalyst design.

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Supporting material

The online version of this article contains additional supporting material.

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