COMMUNICATIONS

Low-Temperature Destruction of Chlorinated Hydrocarbons over Lanthanide Oxide Based Catalysts[**]

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Chlorinated hydrocarbons (CHCs) have widespread industrial applications as, for example, lubricants, cleaning solvents, heat-transfer fluids, and intermediates of pharmaceuticals, herbicides, and fungicides.[1] The increasing volume of CHCs released into the environment, together with the suspected toxicity and carcinogenic properties, have prompted researchers world-wide to find clean and effective routes for destroying CHCs. The method currently used most frequently is thermal incineration at temperatures higher than 1300°C, so as to avoid formation of dioxins and polychlorinated biphenyls (PCBs).[2] The high incineration temperatures and related costs forced researchers to look for other solutions. As a result, a number of methods have been developed for the degradation of CHCs. These include for example, sonolysis,[3] electrochemical dehalogenation,[4] microbial systems,[5] destructive adsorption,[6] and catalytic transformation over supported metals, noble metals, and transition metal oxides.[7–10]

Two main catalytic routes are reported in the literature. The first one is the (total) oxidation of CHCs at temperatures between 300 and 550°C over supported noble metal catalysts (for example, Pt, Pd, and Au).[7] The essential drawback of this method is the deactivation of the catalyst by the decomposition products, such as Cl_2 and HCl. This problem can be (partially) solved by using supported transition metal oxide catalysts (for example, V_2O_5 and Cr_2O_3),[8] although the formation of volatile metal oxychlorides can still be a problem. Another possibility to avoid catalyst deactivation is the use of steam.[9] A second catalytic route is hydrodechlorination, in which CHCs are transformed in the presence of hydrogen into alkanes and HCl. Commonly used catalysts are supported Ni, Pd, and Pt.[8, 10] Although this method has clear economic and environmental advantages, including the re-use of reaction products and the elimination of hazardous by-products (for example, Cl_2 and $COCl_2$), it is not very often used. The main reason is the very fast

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deactivation of the catalyst material as a result of chlorine poisoning and coke formation.

Here, we report on a new and stable catalyst material, which destroys different CHCs, such as CCl_4, in the presence of steam at temperatures between 250 and 350°C. This destruction process can be written as $CCl_4 + 2H_2O \rightarrow 4HCl + CO_2$, and no other products than HCl and CO_2 are found in the effluent gas and condensate. The reaction is also not equilibrium limited. The catalyst itself is based on the use of lanthanide oxides, such as La_2O_3, Nd_2O_3, Pr_2O_3, and Ce_2O_3, which are supported on a high surface area support, preferably Al_2O_3. Figure 1 illustrates the catalytic performance of
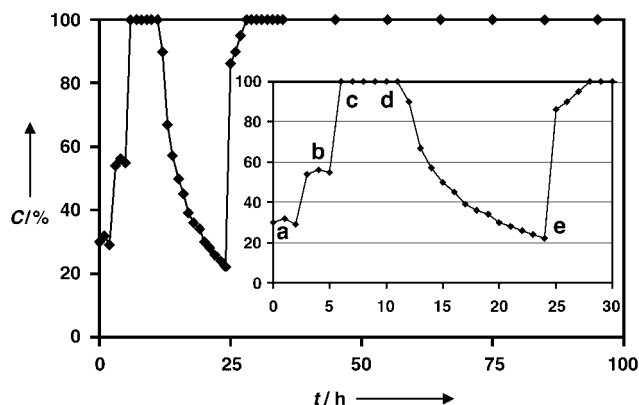

Figure 1. Catalytic conversion (C) of CCl_4 over 10 wt% La_2O_3/Al_2O_3 catalysts in the presence and absence of steam at various reaction temperatures (T) as a function of the reaction time (t; GHSV = 800 h^{-1} and inlet concentration of CCl_4 = 47000 ppm (v/v)): a) T = 250°C; b) T = 300°C; c) T = 350°C; d) T = 350°C; switching off the steam, and e) T = 350°C and switching on the steam.

a 10 wt% La_2O_3/Al_2O_3 catalyst for the destruction of 47000 ppm (v/v) CCl_4 between 250 and 350°C and the effects of changing the amount of steam in the CHC feed. It can be concluded that there is an increase in catalyst activity with increasing reaction temperature when steam was added to the CCl_4 feed. The catalyst material is able to convert 30% of the CCl_4 feed at 250°C (case a in Figure 1), this conversion rises to around 55% at 300°C (case b in Figure 1) and reaches a maximum of 100% at 350°C (case c in Figure 1). After 3 h of operation at 350°C (case d in Figure 1), the water source was switched off and the conversion gradually decreases with increasing time-on-stream. After 15 h of operation at 350°C only a conversion of 22% could be observed at 350°C. This result confirms the essential role of steam in the catalytic destruction of CCl_4, and the remaining activity must arise from the destructive adsorption of CCl_4 over supported La_2O_3.[11] The activity increased when steam was again added to the feed (case e in Figure 1), and a conversion of about 100% could be reached and maintained for more than 60 h of operation at 350°C. Since the gas streams of commercial plants—where the removal of CHCs is required—may contain oxygen we have also studied the influence of oxygen in the CCl_4 stream on the catalytic performances of the 10 wt% La_2O_3/Al_2O_3 catalyst. This was done by mixing He and O_2 in a ratio 95:5 and keeping all the other experimental conditions the same. It was found that the catalytic conversion of CCl_4 at

350 °C was lowered to a value of 60 %. Thus, a somewhat lower, but still stable and high catalytic activity could be obtained and retained with this catalyst.

Table 1 compares the destruction process of CCl_4 at 350 °C of some catalytic solids reported in the literature with our 10 wt % La_2O_3/Al_2O_3 catalyst and pure La_2O_3.[12–14] Although

Table 1. Comparison of the destruction capacities of different catalytic solids for the destruction of CCl_4 at 350 °C, together with the experimental conditions.

| Catalyst	Loading of CCl_4 [ppm]	GHSV [h^{-1}]	Destruction capacity [g $CCl_4 h^{-1} g^{-1}$ catalyst]	Ref.
$LaMnO_3$	500	6000	0.004	12
$LaCoO_3$	500	6000	0.016	12
Co-Y	1000	1367	0.009	13
Cr-Y	1000	1367	0.009	13
Cr_2O_3/Al_2O_3	1000	15000	0.036	14
Pt, Pd, or Rh/TiO_2	1000	15000	0.102	14
La_2O_3	47000	800	0.145	this work
La_2O_3/Al_2O_3	47000	800	0.289	this work

comparison is not easy because of the different experimental conditions used, the destruction capacity of the 10 wt % La_2O_3/Al_2O_3 is superior over the existing oxidation catalysts, and a stable destruction capacity of 0.289 g CCl_4 per hour per gram of catalyst could be reached for several days. Weiss et al. already reported the catalytic hydrolysis of CCl_4 to HCl and CO_2 in the presence of steam over unsupported MgO at 500 °C, but these authors observed a significantly lower catalytic activity than we do.[15] Actually, our own investigations indicate that alkaline and earth alkaline metal oxides (for example, MgO, CaO, SrO, and BaO) are not very active in comparison with lanthanide oxides (for example, La_2O_3, Nd_2O_3, Pr_2O_3, and Ce_2O_3) for the catalytic hydrolysis of CHCs.

To obtain more insight into the destruction mechanism of this catalyst material, several (in situ) characterization techniques were applied to study the physicochemical changes taking place in the catalytic solid, in particularly La_2O_3, as a function of the reaction time during the destruction of CCl_4 at 350 °C.[11] X-ray diffraction (XRD) studies revealed that lanthanum hydroxide was formed in the presence of steam at the reaction temperature. X-ray photoelectron spectroscopy (XPS) was then used to monitor the chlorination process of $La(OH)_3$ as a function of the reaction time. Chlorination was evident from an increase in the intensity of the Cl2p peak at around 198 eV in the spectrum, and a concomitant decrease in the intensity of the O1s peak at around 530 eV of the lanthanide hydroxide. The extent of chlorination increases with increasing reaction time, but reaches a maximum after about four hours. Thus, the subsurface of $La(OH)_3$ was partially transformed to a chlorinated lanthanide oxide during the catalytic reaction, but was not converted into $LaCl_3$. No substantial deposition of coke at the catalyst surface was evident by XPS during the destruction of CCl_4. The partial conversion of $La(OH)_3$ to LaOCl was confirmed by X-ray diffraction (XRD) studies, although additional diffraction peaks of a yet unknown compound were also detected. It was possible to confirm the formation of LaOCl in the catalytic reactor by using in situ Raman

spectroscopy. This compound is characterized by vibrational frequencies at 125, 188, 215, 335, and 440 cm^{-1}. Finally, in situ infrared spectroscopy revealed the presence of CO_2 (2348 cm^{-1}), HCl (2884 cm^{-1}), and traces of $COCl_2$ (1827 cm^{-1}) evolving from the catalyst surface. No CO (2170 cm^{-1}) or products originating from dichlorocarbene (CCl_2), such as C_2Cl_4 (920 cm^{-1}), could be detected by vibrational spectroscopy during the reaction.

A plausible catalytic cycle can be proposed for this destruction process on the basis of the results (Scheme 1). In a first step, CCl_4 reacts with the partially hydrated La_2O_3 and a dichlorocarbene-like intermediate is formed at the catalyst surface. This reaction intermediate is very reactive and is therefore difficult to observe. A consequence of this first reaction step is the formation of a partially chlorinated catalyst. The adsorbed dichlorocarbene intermediate could in principle react with steam according to the equation: $CCl_2 + H_2O \rightarrow 2 HCl + CO$. However, since no CO was observed, this reaction should be minor. Most probably CCl_2 reacts with an oxygen atom of the lanthanide oxide to make phosgene, which is then released from the catalyst surface and relatively easy hydrolyzed with steam into HCl and CO_2. In a final step, steam regenerates the partially chlorinated La_2O_3, and HCl is formed. Thus, the presence of steam is essential for the hydrolysis of the reaction intermediate phosgene as well as for the in situ regeneration of the catalyst material.

In summary, we have developed novel and stable catalyst systems based on supported lanthanide oxides for the hydrolysis of CHCs into CO_2 and HCl at relatively low temperatures in the presence of steam. The active phase consists of a lanthanide oxide chloride, and $COCl_2$ is a reaction intermediate involved in this catalytic hydrolysis process. Further studies will be directed towards the destruction of chlorinated aromatic compounds and mixtures of aliphatic and aromatic CHCs under relevant industrial conditions.
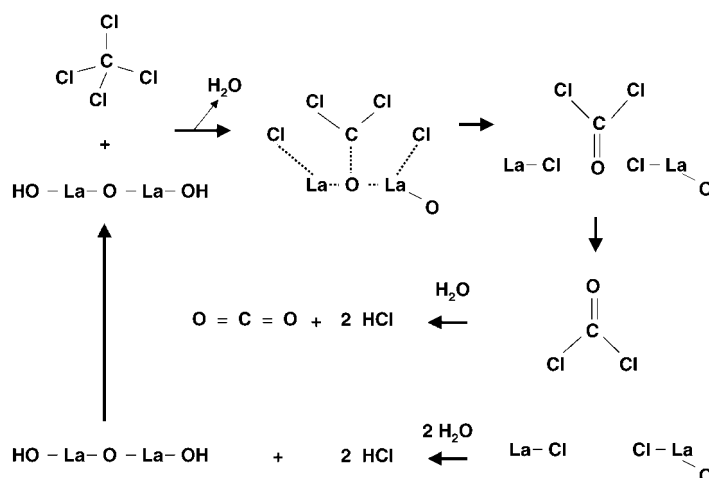
Scheme 1. Reaction cycle for the conversion of CCl_4 in the presence of steam over La_2O_3/Al_2O_3 catalysts.

COMMUNICATIONS

Experimental Section

The lanthanide oxide based catalysts were prepared by the incipient wetness impregnation technique with aqueous solutions of, for example, lanthanum acetate (Aldrich, > 99.9 %) with Al_2O_3 (Condea, surface area of 220 m g^{-1}) as support. La_2O_3 (99.99 %) was purchased from Alfa Aesar. The catalyst material was dried at 100 °C for 1 h, followed by granulation. The size fraction of 0.25–0.50 mm was loaded into the catalytic reactor. Catalytic tests were performed in a fixed-bed reactor at atmospheric pressure. The reactor consisted of a quartz tube, which was loaded successively with quartz wool, quartz pearls, quartz wool, catalyst (1 g), quartz wool, quartz pearls, and quartz wool. Before the reaction started, the catalyst was calcined for 8 h in O_2 at 450 °C. During reaction, the feed consisted of a He flow, which was led through a saturator filled with CCl_4 (VEL, p.a.) and maintained at 0 °C in an icebath to preserve the same vapor pressure of CCl_4. All the tubes were made of Vitton, and the total He flow was set at 0.480 L h^{-1}. This resulted in a CCl_4 loading of 47 000 ppm (v/v). The gaseous hourly space velocity (GHSV) was 800 h^{-1} (contact time of 4.5 s). The gas flows were controlled with Bronkhorst mass flow controllers, while H_2O was added to the reactor at a rate of 1.2 mL h^{-1} by a Methrom dosimeter and evaporated at the inlet of the reactor. The reaction temperature was controlled using a K-type thermocouple placed in the reactor. The condensate was trapped after the reactor in an impinger at room temperature and analyzed by GC-MS. The remaining gases were guided to a gas chromatograph (HP 4890D with a FID detector and methanator) and analyzed on a packed Hayesep Q CP column (80–100 mesh, 3 m length). X-ray diffraction patterns of the solids were measured with a Siemens D5000 Matic instrument, while Raman spectra were recorded with a Holoprobe Kaiser Optical spectrometer equipped with a holographic notch filter and CCD camera. XPS measurements were done with a VG MT 500 spectrometer. FTIR spectra were measured using a Nicolet 730 spectrometer.

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Selective Isomerization of a Terminal Olefin Catalyzed by a Ruthenium Complex: The Synthesis of Indoles through Ring-Closing Metathesis**

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Isomerization of olefins may proceed under acidic, basic, or photochemical conditions to give a mixture of olefins that depends on their thermodynamic stability. Recent advances in transition-metal chemistry (Fe, Pd, Rh, Pt, Ni, Ir, Ru, Co, and Cr) have enabled milder conditions for olefin isomerization to be used to realize selective and synthetically useful transformations, such as the deprotection of an allyl group on nitrogen and oxygen functionalities.[1] Recently, a few reports have appeared concerning this olefin isomerization using ruthenium–carbene catalysts, such as the Grubbs catalyst.[1m–o] This isomerization reaction is limited to substrates which contain an oxygen or a nitrogen substituent in the olefinic side chain. In addition, the reaction competes with metathesis.[2]

During the course of our investigation of the synthesis of nitrogen-containing heterocycles by using ring-closing metathesis (RCM),[3] we found a novel method for synthesizing substituted quinolines by RCM, which included a metathesis reaction of a silyl-protected enol ether with an alkene.[3f] These results prompted us to investigate cross metathesis to prepare a silyl enol ether. However, unexpectedly, we found selective isomerization of the terminal olefin to the corresponding internal olefin, which made a novel indole-ring synthesis possible by RCM. Herein, we report a novel and selective isomerization of a terminal olefin by combining a ruthenium–carbene catalyst with vinyloxytrimethylsilane, and its application to the synthesis of an indole ring from 2-(*N*-allyl-*N*-tosylamino)styrene by RCM.

When **1** was heated in CH_2Cl_2 at 50 °C with 2 molar equivalents of silyl enol ether (**2a**) in the presence of the Grubbs catalyst (**A**, 5 mol %),[4] we unexpectedly found that the terminal double bond of **1** isomerized to the internal double bond to give **3** in 60 % yield, 40 % of **1** was recovered (Table 1, entry 1, full experimental details are given in the supporting information). The exclusive formation of **3** was

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