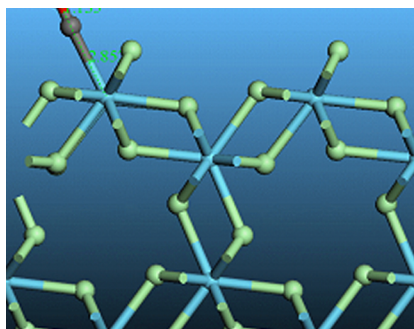


# ACTIVITY OF LANTHANUM-BASED CATALYSTS AT THE DOW CHEMICAL COMPANY



Understanding and interpreting chemical effects in surface reactions is pivotal to chemical catalysis. Materials Studio enables investigation and insight into new systems that is hard to obtain experimentally

## Module Used

- Materials Studio DMol<sup>3</sup>

## Industry sectors

- Catalysis
- Chemicals

## Organizations

- Dow Chemical Company
- University of Utrecht
- Technical University of Munich

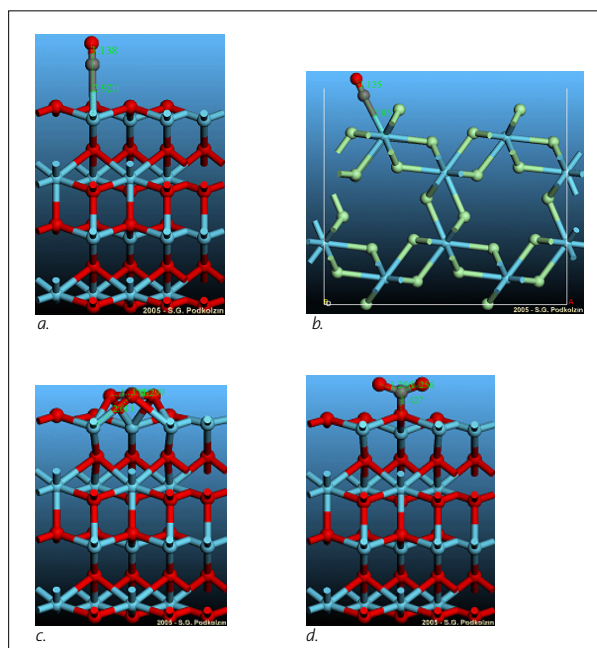
Scientists at the Dow Chemical Company in collaboration with the University of Utrecht in the Netherlands and the Technical University of Munich in Germany studied the properties and activity of the lanthanum-based catalysts: La<sub>2</sub>O<sub>3</sub>, LaOCl, LaCl<sub>3</sub>, and lanthanum phases with an intermediate extent of chlorination.

These materials are used as components in the formulation of commercial catalysts or studied as potential catalysts for such processes as oxidative methane coupling, oxidative dehydrogenation of ethane, oxidative chlorination of methane, decomposition of chloromethane and conversion of ethane and ethylene to vinyl chloride. The work illustrates how experimental and computational results complement each other; how computation can provide results that are inaccessible to experiment; and ultimately provides information on reaction mechanisms that can be used to design improved commercial catalysts.

Reporting in the scientific literature,<sup>1,2,3</sup> the researchers studied the decomposition of chloromethanes, such as CCl<sub>4</sub>, to carbon oxides over the lanthanum materials. This reaction can proceed non-catalytically

with a gradual conversion of La<sub>2</sub>O<sub>3</sub> to LaOCl and, eventually, to LaCl<sub>3</sub> through diffusion of oxygen atoms from the bulk into the surface together with the reverse diffusion of chlorine atoms. The reported results suggest that the reaction can be run catalytically, i.e., a catalytic cycle can be constructed if the surface of the lanthanum materials is dechlorinated with steam.

Spectroscopic measurements were used for evaluating the surface composition at various stages of the reaction and also for characterizing acid and base surface sites using multiple probe molecules, including CO and CO<sub>2</sub>. The scientists used Materials Studio's density functional theory (DFT) code DMol<sup>3</sup> to evaluate the modes of adsorption for CO and CO<sub>2</sub> on the different surfaces (some representative examples are shown in Figure 1). Theoretical frequencies for optimized CO, CO<sub>2</sub> and OH surface



**Figure 1.** Binding modes of CO on La<sub>2</sub>O<sub>3</sub> and LaCl<sub>3</sub> (a & b) and CO<sub>2</sub> on La<sub>2</sub>O<sub>3</sub> (c & d)

structures were used to elucidate experimental infrared spectra. Experimental and theoretical evidence was consolidated and interpreted in terms of the relative strength of acid and base surface sites; surface Lewis acidity and basicity were assessed in terms of the vibrational frequency for adsorbed CO, energy of the lowest unoccupied molecular orbital, and proton affinity.

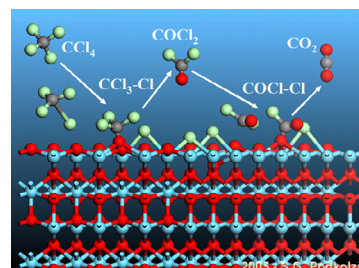
The characterization of surface sites allowed the researchers to identify possible catalytically active sites. Additional calculations with DMol<sup>3</sup> were used to explore the reaction mechanism. The calculations suggest that CCl<sub>4</sub> can react with the catalytic surface by initially splitting off one of its Cl atoms and forming a CCl<sub>3</sub> fragment, which is predicted to bind to the surface through a terminal lattice oxygen atom. The CCl<sub>3</sub> fragment can subsequently donate another Cl atom to the surface and abstract the bonding lattice oxygen atom, forming a COCl<sub>2</sub> intermediate.

1.  $O^{2-}(\text{surf}) + CCl_4 \rightarrow CCl_3O(\text{surf}) + Cl(\text{surf})$
2.  $CCl_3O(\text{surf}) \rightarrow COCl_2 + Cl(\text{surf})$

The calculations suggest that this intermediate rapidly decomposes in a similar sequence of steps by exchanging 2 Cl

atoms for one O lattice atom and forming the final CO<sub>2</sub> product. The formation of the predicted COCl<sub>2</sub> intermediate was confirmed experimentally. The overall process is shown in Figure 2.

An analysis of the computational results indicates that catalytic activity is dependent on the strength of an acid-base pair of sites, which are required for activating a chloromethane, and also on the geometrical arrangement of this pair, since stabilization of the intermediate is required after the initial activation. The relative activities of different lanthanum phases were evaluated with temperature-programmed reaction monitored with infrared measurements and also with theoretical models using DMol<sup>3</sup>. The higher activity of LaOCl sites compared to that of La<sub>2</sub>O<sub>3</sub> sites predicted computationally was confirmed experimentally. Furthermore, computational models were used to evaluate the activity of a partially dechlorinated LaCl<sub>3</sub>, a surface that is difficult to synthesize and test experimentally. The activity of the LaCl<sub>3</sub> model was predicted to be intermediate between the activities of LaOCl and La<sub>2</sub>O<sub>3</sub>.



**Figure 2.** Mechanism of CCl<sub>4</sub> to CO<sub>2</sub> conversion on the La<sub>2</sub>O<sub>3</sub> surface

The information on the catalyst characterization and reaction mechanism can be used to optimize process conditions, such as temperature, pressure and feed composition, and also to provide directional input for synthesis of better catalysts.

To learn more about Materials Studio by Accelrys, go to [accelrys.com/materials-studio](http://accelrys.com/materials-studio)

## REFERENCES

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4. Van der Avert, P.; Podkolzin, S. G.; Manoilova, O.; De Winne, H.; Weckhuysen, B. M., Chem. Eur. J. **2004**, 10, 1637.
5. S. G. Podkolzin, O.V. Manoilova, and B. M. Weckhuysen, J. Phys. Chem. B, **2005**, 109, 11634-1164.