

Methyl Chloride Production from Methane over Lanthanum-Based Catalysts

Simon G. Podkolzin,[†] Eric E. Stangland,[†] Mark E. Jones,[†] Elvira Peringer,[‡] and Johannes A. Lercher^{*‡}

Contribution from The Dow Chemical Company, Core Research and Development, Midland, Michigan 48674, and Department of Chemistry, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Received September 26, 2006; E-mail: Johannes.Lercher@ch.tum.de

Abstract: The mechanism of selective production of methyl chloride by a reaction of methane, hydrogen chloride, and oxygen over lanthanum-based catalysts was studied. The results suggest that methane activation proceeds through oxidation–reduction reactions on the surface of catalysts with an irreducible metal–lanthanum, which is significantly different from known mechanisms for oxidative chlorination. Activity and spectroscopic measurements show that lanthanum oxychloride (LaOCl), lanthanum trichloride (LaCl₃), and lanthanum phases with an intermediate extent of chlorination are all active for this reaction. The catalyst is stable with no noticeable deactivation after three weeks of testing. Kinetic measurements suggest that methane activation proceeds on the surface of the catalyst. Flow and pulse experiments indicate that the presence of hydrogen chloride is not required for activity, and its role appears to be limited to maintaining the extent of catalyst chlorination. In contrast, the presence of gas-phase oxygen is essential for catalytic activity. Density-functional theory calculations suggest that oxygen can activate surface chlorine species by adsorbing dissociatively and forming OCl surface species, which can serve as an active site for methane activation. The proposed mechanism, thus, involves changing of the formal oxidation state of surface chlorine from –1 to +1 without any changes in the oxidation state of the underlying metal.

1. Introduction

Methane is not widely used as a feedstock by the chemical industry because selective activation of the C–H bond presents a formidable challenge.^{1–3} The need to utilize methane efficiently as an alternative chemical feedstock is becoming more urgent due to diminishing proven reserves and increasing consumption of crude oil. Here, we report on a new catalytic chemistry for selective production of methyl chloride by a reaction of methane, hydrogen chloride, and oxygen. Our results suggest that methane activation proceeds through oxidation–reduction reactions on the surface of a catalyst that has, surprisingly, only an irreducible metal lanthanum. Methyl chloride can be converted to olefins with known catalysts,^{4,5} and the hydrogen chloride formed during olefin production can be recycled for reaction with methane. In this way, methane can be converted to olefins via a methyl chloride intermediate with no net consumption of hydrogen chloride.⁶ Lanthanum-

based catalysts can similarly be used to selectively activate other alkanes: for example, ethane can be directly converted to vinyl chloride.⁷

Natural gas is an abundant resource that can be used as fuel or chemical feedstock, yet 30–60% of its reserves are classified as stranded, meaning that such gas cannot be used locally and cannot be efficiently transported to market due to a lack of infrastructure.^{8,9} When stranded gas is produced in the course of crude oil production, it is usually burned at the well or vented as a means of disposal. In recent years, approximately 150 billion m³ of natural gas have been flared or vented worldwide annually,¹⁰ which is equivalent to about 5% of the global annual natural gas consumption¹¹ or about 25% of the consumption in the United States.¹⁰ The environmental aspect of this issue is being addressed by the introduction of a voluntary standard on flaring and venting reduction adopted in 2004 under the auspices of the World Bank.¹² Methane is a major component of natural gas, and development of practical technologies for methane utilization at remote locations is a critical component for the success of these efforts.

[†] The Dow Chemical Company.

[‡] Technische Universität München.

(1) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507.
(2) Periana, R. A.; Mironov, O.; Taube, D.; Bhalla, G.; Jones, C. J. *Science* **2003**, *301*, 814.
(3) Lunsford, J. H. *Catal. Today* **2000**, *63*, 165.
(4) Sun, Y.; Campbell, S. M.; Lunsford, J. H.; Lewis, G. E.; Palke, D.; Tau, L. M. *J. Catal.* **1993**, *143*, 32.
(5) Taylor, C. E. *Stud. Surf. Sci. Catal.* **2000**, *130D*, 3633.
(6) Podkolzin, S. G.; Stangland, E. E.; Schweizer, A. E.; Jones, M. E. International Patent Application WO 2006118935 A2, 2006.

(7) Jones, M. E.; Olken, M. M.; Hickman, D. A. U.S. Patent 6909024 B1, 2005.

(8) Thackeray, F.; Leckie, G. *Pet. Econ.* **2002**, *69*, 10.

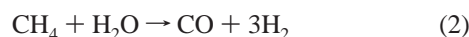
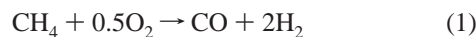
(9) Romanow, S. *Hydrocarbon Process.* **2001**, *80*, 11.

(10) Reducing the Gas Burning. *World Bank Weekly Update*, June 26, 2006.

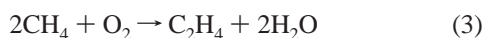
(11) *BP Statistical Review of World Energy*; British Petroleum Co.: London, 2006.

(12) *A Voluntary Standard for Global Gas Flaring and Venting Reduction*; The World Bank: Washington, DC, 2004.

Production of chemicals from methane is dominated by technologies that require first the formation of a mixture of carbon monoxide and hydrogen, which is usually referred to as synthesis gas:

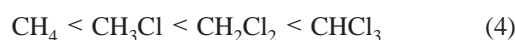


Synthesis gas production is capital intensive, and the breaking of C–H bonds in eqs 1 and 2 has to be substantially reversed in subsequent steps to produce hydrocarbons. A promising alternative technology is oxidative methane coupling, where C₂ and higher products are produced directly from methane in the presence of oxygen:



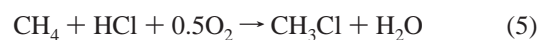
Methane coupling technology has not, however, been commercialized because of low product yields. Reaction 3 occurs partially on the catalytic surface and partially in the gas phase, and the product selectivity rapidly declines as methane conversion increases due to side reactions.³ New ways of activating methane over a heterogeneous catalyst can be advantageous compared to these and other known chemistries, because solid catalysts are usually more economical than liquid-phase ones and since reactions on the surface can be more selective than radical transformations in the gas phase. However, even total methane combustion over solid catalysts presents a major scientific challenge.^{13,14}

One of the methods for functionalizing methane is chlorination, which can proceed in the gas phase without a catalyst. The selectivity to methyl chloride (CH₃Cl) is usually low, because it is a radical reaction where incorporation of each successive chlorine makes the product more reactive, that is, the rate of chlorination increases in the following order:

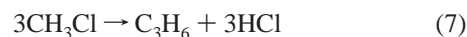


It has been shown^{15,16} that this trend can be reversed, and selectivities to methyl chloride close to 100% can be achieved by using a catalyst that can generate a chlorine atom with a partial positive charge (Cl^{δ+}). Since incorporation of Cl atoms into methane makes the carbon progressively electropositive, the electrophilic reaction with Cl^{δ+} becomes progressively less favorable. Efficient solid catalysts have been identified for this chemistry,¹⁶ but only with chlorine gas as a reactant. It is preferable to use HCl as a chlorine source, because it is usually generated during the second step: the conversion of CH₃Cl to other chemicals. For example, a process where CH₃Cl is produced by oxidative chlorination (eq 5) and then utilized for ethylene production (eq 6), and HCl formed in the second stage (eq 6) is recycled to the first process stage (eq 5) has the potential of being less capital intensive than a process based

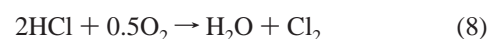
on synthesis gas production:



The overall reaction here is identical to the ethylene formation via oxidative coupling (eq 3). Furthermore, propylene and higher hydrocarbons can be produced from the CH₃Cl intermediate with reactions analogous to eq 6:^{4,5}



Oxidative chlorination chemistry is practiced commercially in the production of vinyl chloride. Catalysts for this reaction are based on a reducible metal, usually copper.^{17,18} The catalytic cycle is believed to proceed through the reduction of CuCl₂ to CuCl on the surface of the catalyst by ethylene followed by oxidation back to CuCl₂ by HCl and O₂.¹⁸ Multiple attempts^{19–23} to adapt this catalytic chemistry for methane conversion (eq 5) had limited success because a reducible metal catalyzes the formation of chlorine gas according to the Deacon reaction:



and methane chlorination proceeds, at least partially, in the gas phase, yielding low selectivity. Furthermore, copper salts are volatile and unstable at the temperatures required for methane activation. Our group at The Dow Chemical Company has discovered that this chemistry can be efficiently catalyzed by irreducible and thermally stable lanthanum compounds. Specifically, lanthanum oxychloride (LaOCl) and derivative compounds with a higher extent of chlorination were found to be selective in catalyzing the conversion of methane to methyl chloride⁶ and ethane to vinyl chloride,⁷ and also to be useful for functionalizing higher alkanes.²⁴ The fully chlorinated form of this catalyst, lanthanum trichloride (LaCl₃), is known to be a promoter for various copper-based formulations,^{18,19,25,26} but it has never been considered as a catalyst by itself, because it is generally accepted that the active catalyst site has to be based on a reducible metal. We here present evidence that catalysis can occur with a metal that does not change its oxidation state (La⁺³) and propose a reaction mechanism that involves a catalytic oxidation–reduction cycle with surface chlorine species.

2. Results and Discussion

2.1. Kinetic Measurements. Kinetic measurements were first used to confirm that the oxidative chlorination of methane (eq 5) is actually catalyzed by LaOCl by comparing reaction rates for two identical parallel reactors: one reactor was filled with LaOCl and another one with quartz chips, which are considered chemically inert but increase the contact surface area to make a valid blank experiment. For all reported experimental condi-

(13) Zarur, A. J.; Ying, J. Y. *Nature* **2000**, *403*, 65.
 (14) Park, S.; Vohs, J. M.; Gorte, R. J. *Nature* **2000**, *404*, 265.
 (15) Olah, G. A.; Gupta, B.; Farina, M.; Felberg, J. D.; Ip, W. M.; Husain, A.; Karpeles, R.; Lammertsma, K.; Melhoira, A. K.; Trivedi, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 7097.
 (16) Olah, G. A. *Acc. Chem. Res.* **1987**, *20*, 422.
 (17) Olah, G. A.; Molnár, A. *Hydrocarbon Chemistry*, 2nd ed.; Wiley Interscience: Hoboken, NJ, 2003.
 (18) Hodnett, B. K. *Heterogeneous Catalytic Oxidation: Fundamental and Technological Aspects of the Selective and Total Oxidation of Organic Compounds*; Wiley & Sons: Chichester, U.K., 2000.

(19) Pieters, W. J. M.; Conner, W. C.; Carlson, E. J. *Appl. Catal.* **1984**, *11*, 35.
 (20) Ohtsuka, Y.; Tamai, Y. *J. Catal.* **1978**, *51*, 169.
 (21) Noceti, R. P.; Taylor, C. E. *Prepr.-Am. Chem. Soc., Div. Pet. Chem.* **1992**, *37*, 281.
 (22) Rozanov, V. N.; Gvozdz, E. V.; Babich, N. F.; Trushechkin, M. A.; Treger, Yu. A. *Khim. Prom-st. (Moscow)* **1989**, *10*, 726.
 (23) Vlasenko, V. M.; Chernobrivets, V. L. *Zh. Prikl. Khim.* **1998**, *71*, 1321.
 (24) Schweizer, A. E.; Jones, M. E.; Hickman, D. A. U.S. Patent 6984763 B2, 2006.
 (25) Garcia, C. L.; Resasco, D. E. *J. Catal.* **1990**, *122*, 151.
 (26) Taylor, C. E.; Noceti, R. P.; Schehl, R. R. *Stud. Surf. Sci. Catal.* **1988**, *36*, 483.

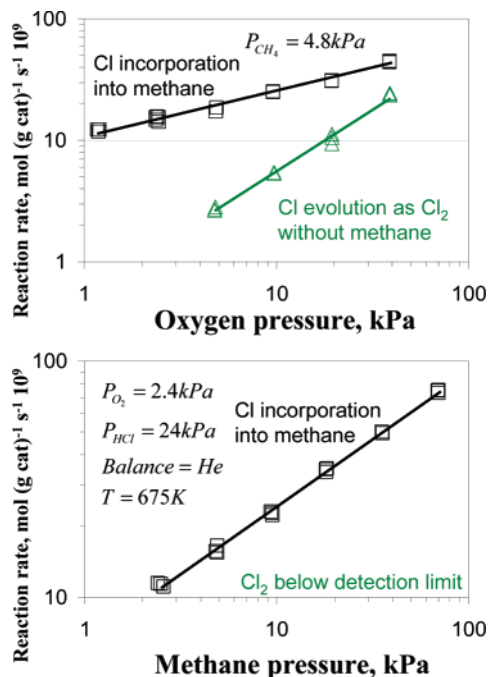


Figure 1. Comparison of reaction rates over LaCl_3 for Cl incorporation into methane and for Cl evolution as Cl_2 without methane in the feed.

tions, the reaction rate without the catalyst did not exceed 5%, and it was usually below 1%, of the reaction rate with the catalyst. The irreducibility of lanthanum (the fact that it does not change its nominal +3 oxidation state) under evaluated reaction conditions was tested with X-ray photoelectron spectroscopic (XPS) measurements. For these measurements, catalyst samples were transferred into a quartz cell under a vacuum of 10^{-6} Pa, and the positions of the La3d peaks were determined. The spectra were similar to those reported for pure and chlorinated La_2O_3 .^{27,28} The positions of the La3d 5/2 doublet at 836.2 and 840.4 eV and the 3/2 doublet at 853.1 and 857.2 eV were practically constant in all tests.

We then considered if the reaction may proceed through generation of gas-phase chlorine (Deacon reaction, eq 8). To test this, the rates of chlorine incorporation into methane and chloromethanes (mostly eq 5) at various conditions were compared to those of chlorine evolution as Cl_2 when there was no methane in the feed (eq 8). No Cl_2 formation was detected in experiments with methane. A comparison of the reaction rates with and without methane in the feed is provided in Figure 1 as a function of O_2 and CH_4 partial pressures at 675 K. Although the rate of Cl incorporation into C_1 products at the highest tested oxygen partial pressure of 39 kPa is comparable to the rate of Cl evolution as Cl_2 in the absence of methane (Figure 1a), the data in Figure 1 show that there is no correlation between the rates of the two reactions. For example, without methane, the rate of Cl_2 formation was below the detection limit at O_2 pressures below 4.8 kPa, but considerable quantities of CH_3Cl were produced at the same conditions when methane was present (Figure 1b). The same kinetic experiments were repeated at 750 K,²⁹ and, similarly, there was no correlation between the rates

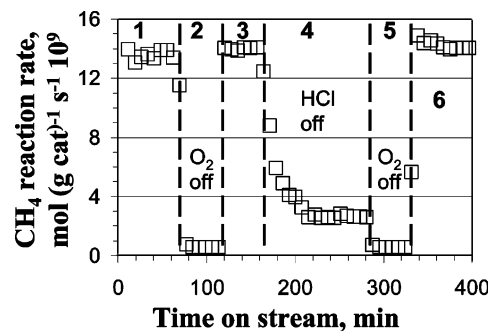


Figure 2. Effect of feed components on the reaction rate over LaCl_3 at 4.8 kPa CH_4 , 2.4 kPa O_2 , and 24 kPa HCl with balance He with a total flow rate of 14 sccm at 675 K. The reaction stops without gas-phase O_2 (2 and 5) but can be sustained without HCl in the feed by Cl diffusion from the bulk onto the catalyst surface (4).

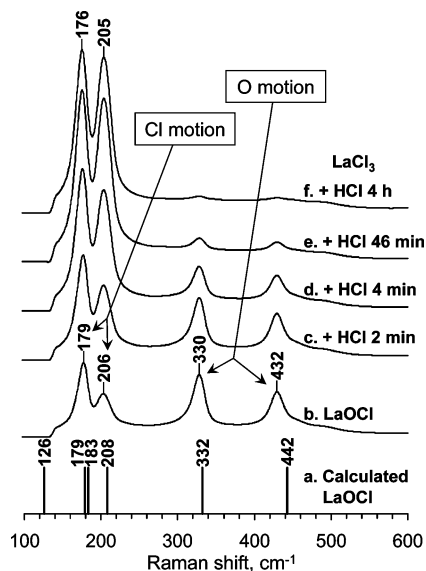


Figure 3. In situ Raman spectra of LaOCl as a function of exposure to HCl flow at 725 K: (a) theoretical vibrational frequencies calculated with the LaOCl model in Figure 5, (b) LaOCl spectrum prior to exposure to HCl flow, (c) after exposure to HCl flow for 2 min, (d) 4 min, (e) 46 min, and (f) 4 h. The spectrum (f) is essentially that of LaCl_3 . DFT calculations suggest that the bands at 179 and 206 cm^{-1} are associated with motion of Cl atoms, and the bands at 330 and 432 cm^{-1} with motion of O atoms.

of the two reactions, suggesting that methane reacts with chlorine on the surface of the catalyst.

The reaction mechanism was further examined by considering the importance of the feed components. When O_2 was eliminated from the feed mixture, the reaction rate measured over LaCl_3 abruptly declined practically to zero, as shown in Figure 2 (segment 2). When O_2 flow was restored, the reaction rate immediately returned to its original value (segment 3), showing that the presence of gas-phase O_2 is essential for the chemistry. When HCl was eliminated from the feed (segment 4), the reaction rate gradually declined and then stabilized at a lower value. This result shows that chlorine can be supplied by the catalyst surface. When the surface is not regenerated by HCl, a transformation of LaCl_3 into LaOCl begins, as evidenced by in situ Raman measurements (not shown). This transformation proceeds by diffusion of chlorine from the bulk onto the surface, and it is the reverse process of LaOCl chlorination, for which Raman and pulse reaction measurements are presented in Figures 3 and 4. Thus, in the absence of HCl, the reaction rate is limited by the chlorine bulk diffusion, and it can be sustained

- (27) Gruenert, W.; Sauerlandt, U.; Schloegl, R.; Karge, H. G. *J. Phys. Chem.* **1993**, *97*, 1413.
 (28) Weckhuysen, B. M.; Rosynek, M. P.; Lunsford, J. H. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3157.
 (29) Peringer, E.; Podkolzin, S. G.; Jones, M. E.; Olindo, R.; Lercher, J. A. *Topics Catal.* **2006**, *38*, 211.

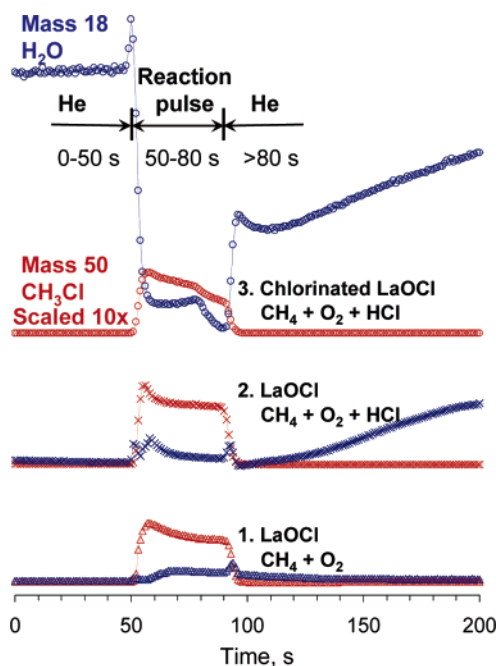


Figure 4. Mass spectrometer traces for mass 50 (CH_3Cl) and mass 18 (H_2O) collected with 30-s reaction pulses: (1) $\text{CH}_4 + \text{O}_2$ pulse over LaOCl injected after collection of the spectrum in Figure 3b, (2) $\text{CH}_4 + \text{O}_2 + \text{HCl}$ pulse over LaOCl injected after completion of the first pulse, (3) $\text{CH}_4 + \text{O}_2 + \text{HCl}$ pulse injected after collection of the spectrum in Figure 3c collected over LaOCl exposed to HCl flow for 2 min. Results of consecutive pulses collected after additional exposure to HCl were similar to (3). The relative scale of the mass 50 traces is increased 10 times for clarity.

for a considerable period of time. Without gas-phase O_2 (segment 5 in Figure 2), the rate again became negligibly small. Finally, when O_2 and HCl flows were restored (segment 6), the reaction rate rapidly reached its original value. The reaction was run for three weeks without noticeable catalyst deactivation. The kinetic experiments of Figure 2 were repeated with another LaOCl sample that had a lower surface area due to a preparation with an organic solvent, and the same qualitative results for the effect of O_2 and HCl were reproduced.²⁹

The ability of the catalyst to sustain methane chlorination in the absence of HCl for an extended period of time (segment 4 in Figure 2) demonstrates that the lanthanum structure can serve as a chlorine reservoir capable of an efficient exchange of lattice chlorine for another anion, in this case oxygen. Notably, as methane conversion decreased in the absence of HCl under the tested conditions, only methyl chloride was detected as a product and, furthermore, the selectivity to methyl chloride remained at 100% as the catalyst continued to dechlorinate. This catalytic property of sustaining the reaction at high selectivity without HCl can be utilized by operating the system in a pulse or swing mode, that is by exposing the catalyst to alternating separate feed streams of first CH_4 plus O_2 and then HCl. Such a mode has a potential advantage of reducing product separation costs.⁶ Whether the role of HCl is limited only to rechlorination of the catalytic surface and whether the product formation is affected by the separation of the feed components can be further studied by comparing selectivities to methyl chloride with and without HCl at similar methane conversion levels. For this comparison, additional data will have to be collected similarly to the results in Figure 6 but only without HCl in the feed.

The ability of La structures to serve as anion reservoirs with efficient bulk diffusion has been known for more than 20 years.

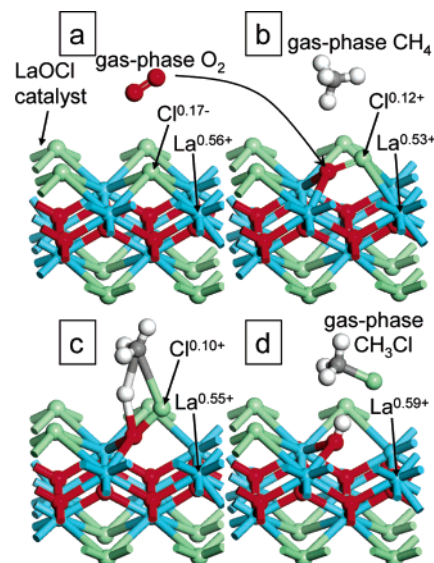


Figure 5. Proposed reaction mechanism for oxidative chlorination of methane over LaOCl catalyst based on DFT calculations: (a) gas-phase oxygen above LaOCl catalyst, (b) dissociative oxygen adsorption with the formation of OCl surface species, (c) reaction of gas-phase methane with surface OCl species, (d) surface OH and gas-phase CH_3Cl . Numbers next to element symbols show partial atom charges calculated with the Hirshfeld method.

For example, a nuclear magnetic resonance (NMR) study on the exchange and diffusion of F and OH anions in LaF_3 , $\text{LaF}_2(\text{OH})$, $\text{LaF}(\text{OH})_2$, and $\text{La}(\text{OH})_3$ was published in 1980.³⁰ Just recently, a reaction of CCl_4 decomposition to CO_2 over La_2O_3 and LaOCl was reported.^{31,32} This reaction can be used to convert chlorohydrocarbon impurities from waste streams into carbon oxides, and the chemistry can be run catalytically, in a pulse or continuous mode, by dechlorinating the catalyst surface with steam and forming HCl as another product. This chemistry can be viewed as the reverse of methyl chloride formation reported here in the sense that the surface and, if not regenerated, the whole bulk of the catalyst can exchange O for Cl anions, resulting in the transformation of La_2O_3 to LaOCl and eventually to LaCl_3 . This year, the same concept of anion exchange and diffusion was reported for a pulse reaction of H_2S over La_2O_3 .³³ In this case, the catalyst exchanges O for S anions, and it can later be regenerated with steam.

Our preliminary results show that methane chlorination can be effectively run not only over LaOCl and LaCl_3 but also over similar compounds of other lanthanide metals.⁶ An interesting case is Ce, which, unlike La, can change its formal oxidation state from +3 to +4. For example, XPS spectra reported for chlorination with CCl_4 show a transformation of CeO_2 into CeCl_3 .²⁸ Our preliminary comparison between La- and Ce-based catalysts, conducted similarly to the experiments in Figure 1, indicates that the rates of Cl evolution as Cl_2 without CH_4 are significantly higher as a fraction of the rates for Cl incorporation into C_1 products with the full feed over chlorinated CeO_2 . This suggests that, in contrast to La, the Deacon reaction (eq 8) may play a significant role for Ce-based catalysts.

(30) Buznik, V. M.; Komissarova, L. N.; Moskvich, Yu. N.; Pushkina, G. Ya. *Zh. Neorg. Khim.* **1980**, *25*, 1488.

(31) Van der Avert, P.; Weckhuysen, B. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4730.

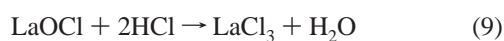
(32) Van der Avert, P.; Podkolzin, S. G.; Manoilova, O.; De Winne, H.; Weckhuysen, B. M. *Chem.-Eur. J.* **2004**, *10*, 1637.

(33) Flytzani-Stephanopoulos, M.; Sakbodin, M.; Wang, Z. *Science* **2006**, *312*, 1508.

2.2. Raman Spectroscopy and Reaction Pulse Measurements. The nature of the catalytic phase and details of catalyst transformation from LaOCl to LaCl₃ were examined with in situ Raman measurements and reaction pulses. Results of a typical run at 725 K are illustrated in Figures 3 and 4. In this run, a Raman spectrum of LaOCl sample was first collected under He flow. This experimental spectrum (Figure 3b) is compared to the theoretical vibrational frequencies (Figure 3a), which were obtained with density-functional theory (DFT) calculations using the LaOCl model in Figure 5. The calculated frequencies are shown in Figure 3a as lines of arbitrary height because the DFT calculations allowed us to estimate the frequencies but not the intensities of the vibrational modes. The experimental bands in Figure 3b are in agreement with the theoretical frequencies in Figure 3a and previously reported experimental results for LaOCl.^{28,32} The calculated frequency at 126 cm⁻¹ in Figure 3a, previously reported based on experimental results,^{28,32} was outside of our current experimental data collection range. The DFT calculations suggest that the experimental bands at 179 and 206 cm⁻¹ in Figure 3b are associated with motion of Cl atoms in LaOCl, and the bands at 330 and 432 cm⁻¹ with motion of O atoms.

After collection of the initial spectrum, the catalyst was probed with a *short* pulse of CH₄ and O₂ (15.0 and 7.5 mol %, respectively, in He) to minimize changes caused by any reactions to the surface composition. The total amount of CH₄ in the pulse was equivalent to 0.02 mol per mol of catalyst. The mass spectrometer traces for H₂O and CH₃Cl collected during the pulse interrogation are presented in Figure 4.1. The concentration of these products was negligible prior to the injection of reactants (0–50 s). Then, during the reaction pulse, between 50 and 80 s, CH₃Cl (red trace in Figure 4.1) and H₂O (blue trace) were formed. This result suggests that Cl species on the surface of LaOCl can react with CH₄ in the presence of gas-phase O₂. This reaction, proceeding through surface Cl species, is similar to the one observed with CH₄ and O₂ flow over LaCl₃ (segment 4 in Figure 2).

After the first pulse, the catalyst was probed with a pulse of CH₄, O₂, and HCl (15.0, 7.5, and 15.0 mol %, respectively, in He) in the stoichiometric ratios based on eq 5, which again produced CH₃Cl and H₂O (Figure 4.2). The total amount of CH₄ introduced in the second pulse was the same as in the first one. Similarly to the first pulse, the conversion of CH₄ and O₂ was low (below 5 mol %), and the amounts of CH₃Cl produced, based on the trace curve areas, were comparable in the two pulses. The difference in the second pulse was the complete consumption of HCl, which resulted in a different H₂O evolution trace: water was slowly evolving long after the completion of the reaction pulse. This behavior can be attributed to catalyst chlorination (eq 9) based on the following additional experiments.



In a separate run, a sample of LaOCl was exposed to a flow of HCl and analyzed *ex situ* for the La-to-Cl ratio by neutron activation. A complete HCl conversion was observed up until the La-to-Cl mol ratio reached a value of about 1:2, and only during the subsequent chlorination was HCl detected in the outlet stream. The HCl consumption stopped when the La-to-Cl mol

ratio became essentially 1:3, indicating the completion of the transformation to LaCl₃.

After the second pulse in Figure 4.2, the catalyst was exposed to a flow of HCl for 2 min, which was equivalent to 0.2 mol of HCl per mol of catalyst, and then the Raman spectrum in Figure 3c was collected. This spectrum shows that the intensity of the bands associated with Cl motion increased and those associated with O motion decreased, confirming a higher extent of catalyst chlorination after the reaction with HCl. Following the spectrum acquisition, the catalyst was again probed with another pulse of CH₄, O₂, and HCl (Figure 4.3). The sequence of exposing the catalyst to HCl flow for 2 min, then acquiring a spectrum and interrogating with a reaction pulse was repeated multiple times. Selected spectra from this sequence, acquired after 4 min, 46 min, and 4 h of cumulative exposure to HCl flow, are presented in Figures 3d–f. These spectra show a trend of gradual catalyst chlorination. The last shown spectrum collected after 4 h of HCl exposure (Figure 3f) with two dominant bands at 176 and 205 cm⁻¹ is consistent with those reported for LaCl₃.^{28,32} Thus, the experimental spectral series in Figure 3 represent a gradual transformation of LaOCl to LaCl₃. The results of subsequent pulse measurements in the series were all similar to the traces shown in Figure 4.3. CH₃Cl formation was detected during the reaction pulse in quantities comparable to those for the initial LaOCl, and H₂O formation was dominated by the catalyst chlorination. Significant amounts of H₂O were evolving from the catalyst even after the HCl flow was stopped and the catalyst was kept under He flow during spectra acquisition and prior to the reaction pulse introduction, as can be seen in the segment from 0 to 50 s in Figure 4.3. During the pulse, the concentration of H₂O in the outlet actually decreased, which can be attributed to suppression of the continuous and relatively slow catalyst chlorination and subsequent dehydration by methane activation. After the completion of the reaction pulse, the segment after 80 s in Figure 4.3, the H₂O evolution from the catalyst resumed. The delay and relatively slow rate of H₂O evolution from the catalyst after exposure to HCl flow is similar to the trailing of the H₂O trace after the completion of the very first pulse with HCl in Figure 4.2. Importantly, however, the Raman spectra in Figure 3 and the results of pulse measurements in Figure 4 suggest that LaOCl, LaCl₃, and La phases with an intermediate extent of chlorination are all catalytically active and that the only essential element for methane activation is the presence of chlorine surface species that can be activated by gas-phase oxygen.

2.3. Density-Functional Theory Calculations. A possible reaction mechanism was evaluated with electronic-structure calculations using DFT, and the results are summarized in Figure 5. Figure 5a shows a gas-phase O₂ molecule above a model LaOCl surface terminated with Cl atoms. Calculations suggest that molecular oxygen can react with the surface by splitting and adsorbing dissociatively with the formation of *OCI*⁻ surface species (Figure 5b, eq 10). The formal oxidation state of the activated surface Cl atom in this step changes from -1 to +1, and this transformation is reflected in the change of the calculated partial atomic charge on the Cl atom from 0.17- to 0.12+, as shown in, correspondingly, Figures 5a and 5b. Since our attempts to characterize these *OCI*⁻ species with static adsorption, temperature-programmed desorption (TPD), and infrared and Raman spectroscopic measurements were not

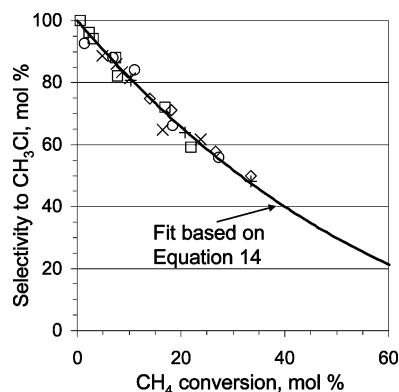
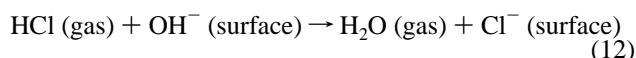
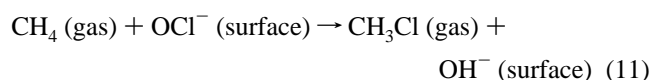
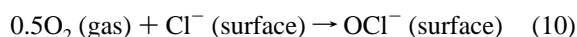


Figure 6. Dependence of selectivity to CH₃Cl on CH₄ conversion. The data were collected by varying the space velocity and feed composition at 800 K and also by varying the temperature from 680 to 825 K at a constant space velocity with LaOCl catalysts prepared with different bases (Table 1): (□) NH₄OH in water under Ar, (×) NH₄OH in ethanol, (◇) TEOH, (+) TPAOH, (○) TBAOH.

successful, we conclude that these species are transient (i.e., oxygen readily desorbs into the gas phase or displaces chlorine and becomes a part of the lattice). Additional calculations suggest that methane can react with OCl^- by exchanging a proton for Cl^+ (Figure 5c) and by forming a hydroxyl group on the surface (Figure 5d, eq 11). Although the intermediate structure in Figure 5c was obtained by linear geometric interpolation of the configurations in Figures 5b and 5d and was not confirmed as a transition state, it shows a possible mechanism of methane activation by surface OCl^- species. The catalytic site in Figure 5d can be regenerated by the reaction between the hydroxyl group and gas-phase HCl with the formation of gas-phase water and restoration of the Cl-terminated surface of Figure 5a (eq 12).



The partial atomic charge on surface La atoms for all the structures in Figure 5 changes only slightly: within 0.53+ and 0.59+. The proposed catalytic cycle, thus, involves oxidation of surface chlorine without any changes in the oxidation state of the underlying metal, which is significantly different from known mechanisms for oxidative chlorination.

2.4. Methyl Chloride Selectivity Measurements and Modeling. Since a reaction between methane and electrophilic chlorine surface species ($Cl^{\delta+}$ in Figure 5c) should provide an opportunity for achieving high selectivities to methyl chloride, we attempted to compare reaction selectivities over La-based catalysts and those reported for radical gas-phase chlorination. In kinetics experiments in Figure 1, methane conversion was kept below 10 mol % by adjusting the flow rate, so that a differential reactor model could be used in the data analysis. In addition, the catalyst was kept in the chlorinated LaCl₃ form by supplying a large HCl excess, with the state of the catalyst being confirmed by in situ Raman spectroscopy measurements and by control reaction rate measurements at even larger HCl concentrations. At these conditions, the selectivity to CH₃Cl was

90% or higher, mostly 98% or higher, with the rest of the product being CH₂Cl₂. Additional selectivity measurements were performed at methane conversion levels up to 34% with the HCl-to-O₂ feed ratio of 2:1 (based on the stoichiometry of eq 5). At those conditions, CO₂ formation was observed for methane conversions above 1 mol %, and CO formation was observed for methane conversions above 10 mol %. The main product was always CH₃Cl followed by CH₂Cl₂; small amounts of CHCl₃ were observed, and CCl₄ was never detected. The absence of CO or CO₂ at low methane conversion suggests that these products are formed not directly from methane but through decomposition of chloromethanes. This supposition was tested with temperature-programmed reaction (TPR) measurements over a prechlorinated catalyst.²⁹ In the first TPR experiment with CH₄ and O₂ as reactants, the formation of CH₃Cl was observed at about 600 K, while the formation of carbon oxides was not detected until the temperature reached about 675 K. In the second TPR experiment with CH₂Cl₂ and O₂ as reactants, carbon oxides were observed already at 625 K, and no other products were detected except for trace amounts of CHCl₃. These TPR results are consistent with methane first forming CH₃Cl, and then CH₃Cl either chlorinating further or decomposing to carbon oxides:



Published studies on the relative activity of chloromethanes in decomposition over La-based catalysts indicate that the reactivity increases with the extent of hydrocarbon chlorination.³⁴ Therefore, if a significant fraction of CH₂Cl₂ decomposes to carbon oxides under our oxidative chlorination conditions, any formed CHCl₃ can be expected to produce exclusively carbon oxides, so that CCl₄ would never form or would exist only as a transient intermediate. The active site for the formation of carbon oxides in oxidative chlorination is likely to be a terminal lattice oxygen atom, the active site proposed for decomposition of chloromethanes over dechlorinated surfaces of La-based catalysts.^{32,35} Our reported DFT model for the LaOCl terminal lattice oxygen site was generated by substituting two surface Cl atoms in the model in Figure 5a for one O atom.^{35,36} Our similarly constructed partially dechlorinated surface of LaCl₃ was also computationally shown to be active in decomposition of CCl₄.³⁵ The absence of carbon oxides in our kinetic experiments with a large HCl excess (Figure 1) is consistent with this proposed mechanism where decomposition of chloromethanes requires at least partial surface dechlorination to form active oxygen sites.

The analysis of eq 13 can be simplified by assuming that the main product of CH₃Cl is CH₂Cl₂ and, correspondingly, that only minor quantities of carbon oxides are produced directly from CH₃Cl. If we further assume that the reaction rates for CH₄ and CH₃Cl are first-order in the concentrations of the respective hydrocarbon and the source of chlorine, the dependence of selectivity to CH₃Cl (S) on CH₄ conversion (C) for this consecutive reaction can be derived as a closed-form

(34) Van der Avert, P.; Weckhuysen, B. M. *Phys. Chem. Chem. Phys.* **2004**, *6*, 5256.

(35) Podkolzin, S. G.; Manoilova, O. V.; Weckhuysen, B. M. *J. Phys. Chem. B* **2005**, *109*, 11634.

(36) Manoilova, O. V.; Podkolzin, S. G.; Tope, B.; Lercher, J.; Stangland, E. E.; Goupil, J.-M.; Weckhuysen, B. M. *J. Phys. Chem. B* **2004**, *108*, 15770.

solution that depends only on the ratio of rate constants $k_{\text{CH}_3\text{Cl}}/k_{\text{CH}_4}$. Modeling our tubular reactor as an ideal plug flow reactor gives the following dependence:

$$S = \frac{1 - C/100 - (1 - C/100) \frac{k_{\text{CH}_3\text{Cl}}}{k_{\text{CH}_4}}}{C/100 \left(\frac{k_{\text{CH}_3\text{Cl}}}{k_{\text{CH}_4}} - 1 \right)} 100 \quad (14)$$

where $S = [(\text{CH}_3\text{Cl})_{\text{out}}]/[(\text{CH}_4)_{\text{in}} - (\text{CH}_4)_{\text{out}}]100$, mol % and $C = [(\text{CH}_4)_{\text{in}} - (\text{CH}_4)_{\text{out}}]/[(\text{CH}_4)_{\text{in}}]100$, mol %.

This expression was used to fit the selectivity versus conversion data in Figure 6. The measurements in Figure 6 were collected with multiple catalysts by varying the space velocity and feed composition at 800 K and also by varying the temperature from 680 to 825 K at a constant space velocity. Catalyst samples for this study were prepared by using different bases in the precipitation of LaOCl, resulting in materials with BET surface areas between 39 and 125 $\text{m}^2 \text{g}^{-1}$ based on N_2 adsorption, as summarized in Table 1. All catalysts were converted to LaCl_3 by exposure to HCl prior to activity measurements. The surface area after chlorination could not be easily measured due to hygroscopicity of LaCl_3 , but it was estimated to be on the order of 5–20 $\text{m}^2 \text{g}^{-1}$. Despite the dramatic reduction in the surface area on the transformation from LaOCl to LaCl_3 , the differences in activity for the catalysts in Table 1 suggest that the morphology of the initial LaOCl material can still influence the reactivity of the chlorinated phase. The similarity of the trend for selectivity versus conversion for catalysts with various activities in Figure 6 and the accuracy of the fit based on eq 14 suggest that the reaction mechanism is the same for all the materials and that this mechanism is consistent with eq 13. The fit in Figure 6 was obtained with the ratio of rate constants $k_{\text{CH}_3\text{Cl}}/k_{\text{CH}_4}$ of 3.9. Our analysis of literature data^{37–39} on the kinetics of radical gas-phase chlorination of CH_4 and CH_3Cl suggests that the ratio of rate constants $k_{\text{CH}_3\text{Cl}}/k_{\text{CH}_4}$ for the consecutive reaction with Cl_2 at 250–450 K is 3.2–4.2. Since the value of 3.9 for the oxidative chlorination falls within this range, it appears that catalysts based on pure lanthanum compounds do not provide a selectivity advantage compared to gas-phase chlorination. We note that this conclusion does not contradict our proposed mechanism for methane activation through surface $\text{Cl}^{\delta+}$ species because methyl chloride can potentially react through an additional pathway. Specifically, while methane has to be activated to be present on the surface and to react with chlorine, methyl chloride, in contrast, should be coordinated, even if very weakly, with the surface on formation and, therefore, can potentially react further through an additional pathway. We further note that, unlike gas-phase radical chemistry, properties of active sites on the surface of La-based catalysts can be modified, for example with promoters, to tune the chemistry by changing the site geometry, its charge distribution, and propensity for dechlorination to achieve better selectivities. Furthermore, the chemistry over La-based catalysts can be operated at low methane conversions with the selectivity approaching 100%, whereas operation of gas-phase chlorination

Table 1. Properties of Catalysts Prepared with Different Bases

base used in LaOCl preparation	surface area of initial LaOCl, $\text{m}^2 \text{g}^{-1}$	activity ^a of chlorinated phase at 800 K, $\text{mol CH}_4 (\text{g cat})^{-1} \text{s}^{-1}$
NH_4OH in water under Ar	39	1.5×10^{-7}
NH_4OH in ethanol	21	6.8×10^{-7}
TEAOH	125	9.4×10^{-7}
TPAOH	118	1.1×10^{-6}
TBAOH	78	6.5×10^{-7}

^a Activity measured with feed CH_4 , HCl, O_2 at, respectively, 20, 20, 10 mol % in He.

at similar conversion levels would be impractical due to process stability and the requirement of a separate stage for HCl conversion to Cl_2 . Moreover, La-based catalysts exhibit stability and complete conversion of reacting chlorine species into chloromethanes, in contrast with known reducible-metal catalysts, which are volatile and, therefore, unstable and which usually produce Cl_2 in addition to chloromethanes. The new catalytic chemistry, thus, presents a promising opportunity for functionalizing alkanes and, specifically, for selective production of methyl chloride from methane.

3. Methods

LaOCl was prepared by reacting $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (Aldrich, 99.999%) with an aqueous solution of ammonium hydroxide (Aldrich, ACS reagent) under argon (BOC, 99.999%) atmosphere. The resulting precipitate was washed with water, dried, and then calcined under synthetic air at 823 K for 8 h. For selectivity measurements in Figure 6, additional LaOCl catalysts were prepared with ammonium hydroxide in ethanol under ambient conditions and with three organic bases (Table 1): tetraethyl ammonium hydroxide (TEAOH, Merck, 20% aqueous solution), tetrapropyl ammonium hydroxide (TPAOH, Merck, 40% aqueous solution), and tetrabutyl ammonium hydroxide (TBAOH, Aldrich, 20% aqueous solution). For these additional catalysts, the precipitate was centrifuged, washed with ethanol, freeze-dried, and finally calcined. The LaOCl composition was confirmed with X-ray diffraction and with elemental analysis by neutron activation.

Catalytic activity was tested in a tubular fixed-bed nickel-alloy reactor with a length-to-diameter ratio of 28.6. The catalyst was sized to ensure greater than 10 particles per reactor diameter. The reactor outlet pressure was atmospheric. The effluent was analyzed with gas chromatography, which allowed closure of carbon, oxygen, and chlorine mass balances. The detection limit for feed and product components was 0.01 mol %. Prior to kinetic measurements with CH_4 (BOC, 99.999%), O_2 (BOC, 99.6%), HCl (BOC, 99.99%), and N_2 (BOC, 99.999%), the catalyst was chlorinated in situ with 5 mol % HCl in He (BOC, 99.999%) at the total weight hourly space velocity (WHSV) of 0.53 h^{-1} at 675 K for 24 h. The complete transformation to LaCl_3 was confirmed with Raman spectroscopy, X-ray diffraction, and elemental analysis. For kinetic measurements in Figure 1, the order of experiments was randomized, and measurements at each of the reported conditions were collected at least twice. Selectivity measurements in Figure 6 were performed at 800 K for the catalyst prepared with NH_4OH in water under Ar using the following CH_4 , HCl, O_2 , and N_2 inlet concentrations in mol %: 76.0, 16.0, 8.0, 0; 88.0, 8.0, 4.0, 0; 94.0, 4.0, 2.0, 0; 94.0, 4.0, 2.0, 0; 80.0, 16.0, 4.0, 0; and 36.0, 36.0, 18.0, 10.0 at WHSV of 0.12–7.38 h^{-1} . Selectivity measurements for other catalysts were collected by first pretreating in He at 823 K for 1 h, chlorinating in situ with 20% mol HCl in He at total WHSV of 1.89 h^{-1} at 675 K for 10–12 h, and then running the reaction by increasing the temperature from 680 to 825 K using a constant feed composition of CH_4 , HCl, O_2 , N_2 , and He in mol %: 20.0, 20.0, 10.0, 10.0, 40.0 at WHSV of 0.92 h^{-1} . The catalyst activity throughout the text is quoted based on the weight of LaOCl initially loaded for testing.

(37) McBee, E. T.; Hass, H. B.; Neher, C. M.; Strickland, H. J. *Ind. Eng. Chem. (Washington, D. C.)* **1942**, *34*, 296.

(38) Clyne, M. A. A.; Walker, R. F. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1547.

(39) Keyser, L. F. *J. Chem. Phys.* **1978**, *69*, 214.

Pulse and spectroscopic Raman measurements were performed with a reactor system that had two feed lines, each equipped with a separate set of mass flow controllers. The two feed lines were connected with a multipoint switch valve, which allowed the feed composition to be changed in a pulse mode. The temperature of the catalyst was initially increased at a ramp rate of 10 K min^{-1} to 950 K under He flow, held at 950 K for 2 h, lowered to 725 K , and then maintained at this value for all measurements. The He flow between reaction pulses and exposure to HCl flow was maintained at WHSV of 0.31 h^{-1} . The exposure to HCl in flow mode was performed in 2-min increments at the concentration of 20 mol % in He at total WHSV of 1.35 h^{-1} . In situ Raman spectra were collected with a Kaiser Optical Systems, Inc., Holoprobe 532/633 spectrometer equipped with a frequency-doubled Nd/YAG 532-nm laser, grating, and EEV CCD detector chip with 278×1024 pixels. The exposure time and number of accumulations were optimized for an 80% CCD detector pixel fill. The laser power output was about 35 mW.

Oxygen adsorption measurements were performed with a Micromeritics 2010 apparatus. Infrared spectroscopic and TPD measurements for oxygen adsorption were conducted similarly to characterization of CO_2 on the surface of LaOCl .³⁶ X-ray photoelectron spectra were collected with a Kratos AXIS instrument using monochromatic Al K α radiation with an anode current of 15 mA and 14 keV and an aperture slot of $3 \times 10\text{ mm}$. The pass energy was set at 80 eV for the survey and 40 eV for the analyzer scans. The analysis area for 16–84% signal level was $0.4 \times 0.2\text{ mm}$. Binding energies were referenced to the Cl 1s peak of adventitious carbon, which was set to 285.0 eV.

The DMol3 code in Materials Studio 2.1 software by Accelrys was used to perform gradient-corrected spin-polarized periodic DFT calculations with the same model and settings as those utilized in the study of LaOCl surface acidity and basicity and relative activity of CCl_4 decomposition over La phase.^{35,36} An infinite $\text{LaOCl}(001)$ stoichiometric model was constructed using a 2×2 unit cell with 12 layers (48 atoms total) with a vacuum spacing of 1.5 nm. Only half of the surface layers are shown in Figure 5 for clarity. The bottom eight layers were constrained during the calculations to simulate bulk properties, and the remaining top layers were optimized with an adsorbate. The calculations used the double numerical with polarization (DNP) basis set and the generalized gradient-corrected Perdew–Wang (GGA PW91) functional. Tightly bound core electrons for La were represented with semi-core pseudopotentials. Reciprocal-space integration over the Brillouin zone was approximated through k -point sampling with a separation of 0.5 nm^{-1} using the $2 \times 2 \times 1$ Monkhorst-Pack grid. An orbital cutoff distance of 0.5 nm was used for all atoms. All adsorption and surface reaction energies were calculated at 0 K without zero-energy corrections.

4. Conclusions

Activity and spectroscopic measurements demonstrate that La-based catalysts (LaOCl , LaCl_3 , and La phases with an intermediate extent of chlorination) are active for methane conversion to methyl chloride in the presence of hydrogen chloride and oxygen (Figures 2–4). These La-based catalysts appear to be very stable: no deactivation was detected after three weeks of testing. Although LaCl_3 was known as a catalyst promoter for hydrocarbon chlorination, it was never considered as a catalyst by itself because it was believed that a reducible metal was required for a catalytic site. The irreducibility of La (the fact that it does not change its nominal +3 oxidation state) under evaluated reaction conditions was tested with XPS measurements.

At methane conversions below 1–2 mol %, the catalyst was 100% selective toward CH_3Cl . At higher conversions, CH_3Cl was always the main product but CH_2Cl_2 , CO, and CO_2 were also observed. Only trace amounts of CHCl_3 were detected, and CCl_4 was never detected. The dependence of CO and CO_2 formation rates on methane conversion and the results of TPR experiments, which compared the stability of CH_4 and CH_2Cl_2 at the reaction conditions, suggest that carbon oxides are formed through decomposition of chloromethanes. The dependence of selectivity to CH_3Cl as a function of CH_4 conversion for La-based catalysts appears to be in line with that expected for gas-phase chlorination based on kinetic modeling of relative reaction rates for CH_4 and CH_3Cl chlorination (Figure 6).

Kinetic measurements were performed for the reactions of (1) Cl incorporation into C_1 hydrocarbons when CH_4 , O_2 , and HCl were fed and (2) Cl evolution as Cl_2 when O_2 and HCl were fed (Figure 1). Formation of Cl_2 was not detected in the presence of CH_4 . When CH_4 was not present in the feed, the rates of Cl_2 formation were usually significantly lower than those for CH_4 chlorination under similar conditions. In addition, apparent reaction orders in reactants were different for the two reactions, suggesting that they are not correlated and that CH_4 activation proceeds through a surface reaction.

Flow and pulse experiments using CH_4 and O_2 as feed show that CH_3Cl can be formed using chlorine from the catalyst surface (Figures 2 and 4). The presence of HCl, thus, is not required for activity, and its role appears to be limited to maintaining the extent of catalyst chlorination. In contrast, the presence of gas-phase O_2 is essential for catalytic activity (Figure 2). Based on this evidence, methane chlorination is proposed to proceed through the surface chlorine species that can be activated by oxygen.

DFT calculations suggest that O_2 can activate surface Cl^- species by dissociatively adsorbing and forming OCl^- species, with the formal oxidation state of Cl changing from -1 to $+1$ (Figure 5). The formation of OCl^- species was not detected using static adsorption, TPD, and infrared and Raman spectroscopic measurements, and therefore, these species are assumed to be transient. DFT calculations suggest that these OCl^- species can serve as an active site for methane activation. The proposed catalytic cycle, thus, involves oxidation of a surface chlorine without any changes in the oxidation state of the underlying metal (eqs 10–12), which is significantly different from known mechanisms of oxidative chlorination.

Acknowledgment. This work would not have been possible without the support of The Dow Chemical Company and many Dow colleagues. In particular, we thank D. M. Millar for anaerobic LaOCl preparation, M. A. Leugers and J. J. Maj for spectroscopic measurements, M. M. Olken for adsorption measurements, and S. E. Beyer for both spectroscopic measurements and GC experimental expertise. The work at the Technische Universität München was partially funded by The Dow Chemical Company.

JA066913W