

Methane Reforming with Sulfur Dioxide on $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$

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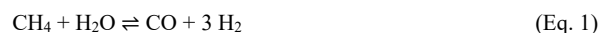
Abstract

In this work we present a study on the methane oxidation reaction on Cr_2O_3 in the presence of sulfur dioxide using both infrared spectroscopy and simulations based on the density functional theory. The purpose of the work is to know the reasons why sulfur dioxide decreases the activation energy of the methane oxidation reaction. We found that sulfur dioxide promotes oxygen dissociation through the formation of sulfite species. Dissociated oxygen favors the dehydrogenation of methane, the formation of methoxy species, formaldehyde, dioxymethylene, and methanol.

Keywords: methane reforming, methanol, formaldehyde.

1. INTRODUCTION

Methane reforming is a method for producing syngas (hydrogen and carbon monoxide) by the reaction of hydrocarbons with water. The main purpose of this technology is hydrogen production. The reaction is represented by

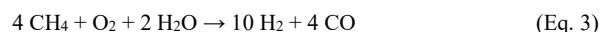


Autothermal reforming (ATR) uses oxygen and carbon dioxide or steam in a reaction with methane to form syngas.

The reactions can be described by the following equations, using CO_2 :



and using steam:



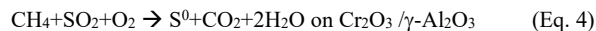
CH_4 is also one of the main greenhouse gases. To reduce its emission to the atmosphere, it can be retained by adsorption before it is released by industrial chimneys. O_2 is present in flue gases, but in the absence of a suitable catalyst, it does not react with CH_4 .

CH_4 oxidation was previously studied on $\text{PdO}(101)$, $\text{RuO}_2(110)$ and $\text{IrO}_2(110)$, $\text{Ni}(111)$ and $\text{MgO}(001)$ on Ni_4 catalysts.

A major difficulty associated with the production of syngas is that the sulfur compounds in the fuel poison certain catalysts, making it difficult to operate this type of system with regular gasoline. We have carried out studies on various oxides, with emphasis on the oxidation of CH_4 and the reduction reactions of SO_2 [1, 6]. It has been concluded that the alumina-supported chromium oxide catalyst ($\text{Cr}_2\text{O}_3 / \text{Al}_2\text{O}_3$) is the most efficient for the adsorption of these greenhouse gases, because it is not deactivated by the presence of acid gases. In [4] we studied the oxidation of CH_4 on $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ and experimentally determined an activation energy of the reaction ($E_a = 0.57 \text{ eV}$). The SO_2 reduces the activation energy to $E_a = 0.31 \text{ eV}$, the lowest value found so far to our knowledge. For example, the catalytic oxidation of methane in the presence and absence of SO_2 was investigated on palladium catalysts supported on Al_2O_3

and $\text{CeO}_2/\text{Al}_2\text{O}_3$ washcoats. The activation energies in the absence of SO_2 were 0.4 ± 0.1 eV and 0.6 ± 0.15 eV for the 3 wt% $\text{Pd}/\text{Al}_2\text{O}_3$ and the 3 wt% $\text{Pd}/12$ wt% $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalysts respectively.

In this work we carried out a combined FTIR + DFT study of the reaction



in order to unveil its kinetic mechanism.

This work continues previous research on the oxidation of CH_4 with oxygen on $\text{Cr}_2\text{O}_3 / \gamma\text{-Al}_2\text{O}_3$ [6]. The main purpose is to reveal the causes for the reduction of the activation energy mentioned above.

Additionally, we found the formation of intermediate species of industrial interest, such as methanol and formaldehyde.

II. EXPERIMENTAL WORK

A. Materials and Setup

Methane oxidation on $\text{Cr}_2\text{O}_3 / \gamma\text{-Al}_2\text{O}_3$ and in the presence of SO_2 (Eq. 4) was studied on a fixed-bed reactor consisting of a quartz column of 0.6 cm diameter and 110 cm length placed in an adjustable temperature oven (Fig. 1). Reaction gases were provided by LINDE: SO_2 composition > 99:98%, CH_4 composition > 93%, O_2 composition > 99:5%. They were introduced in the reactor at a constant flow rate and a concentration of 10 ppm in N_2 . In one experiment, a catalyst sample was exposed to the reaction gases at an initial temperature of 293 K, until the concentration of the produced CO_2 reached constant values. Then, the temperature was increased in steps until reaching 573 K. Each catalyst sample was subjected to three of these experiments. Finally, a Fourier transform infrared (FTIR) spectroscopic study was performed on each sample with Vertex 70 equipment from 2008.

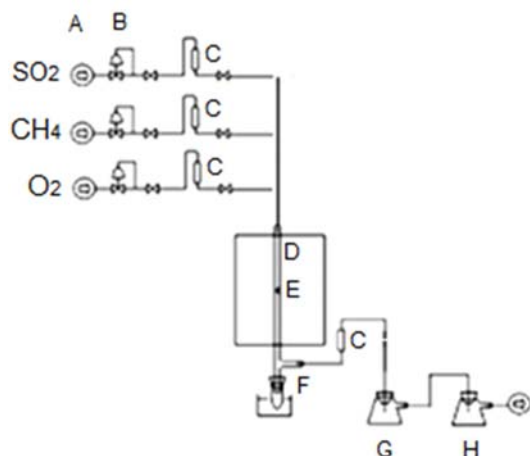


Figure 1. Experimental setup used in the present work. (A) Gas suppliers, (B) safety valves, (C) rotameters, (D) electrically heated oven, (E) reactor (quartz column), (F) sulfur trap, (G) bubbler with distilled water, (H) bubbler with a dilute sodium hydroxide solution.

Results

Figure 2 shows an FTIR spectrum obtained in this work. We identified bands at 2960 cm^{-1} and 2854 cm^{-1} , corresponding to the stretching modes of CH_3 and CH_2 groups respectively. There was also an O-H bond stretching band at $3446\text{-}3465 \text{ cm}^{-1}$.

Stretching frequencies of adsorbed O-S-O bond were at $561\text{-}567 \text{ cm}^{-1}$.

Finally, we found bands at 1126 cm^{-1} and 1655 cm^{-1} . According to our DFT calculations we related them to formaldehyde adsorbed on the surface.

III. THEORETICAL WORK

A. Computational Calculations

First-principles calculations were performed using DFT+U as implemented in the Vienna Ab initio Simulation Package (VASP) code. The Kohn-Sham equations were solved using the projector augmented wave (PAW) method and a plane-wave base set that includes plane waves up to 400 eV. The DFT+U method was used with values $J = 1$ and $U = 5$. The calculations were performed using pseudopotentials based on the generalized gradient approximation (GGA+U). The convergence of each calculation was achieved when the forces on the ions were less than $0.03 \text{ eV} / \text{\AA}$. The periodic boundary conditions applied in all three perpendicular directions. The Hessian matrix of second derivatives was determined for basal structures within the harmonic approximation

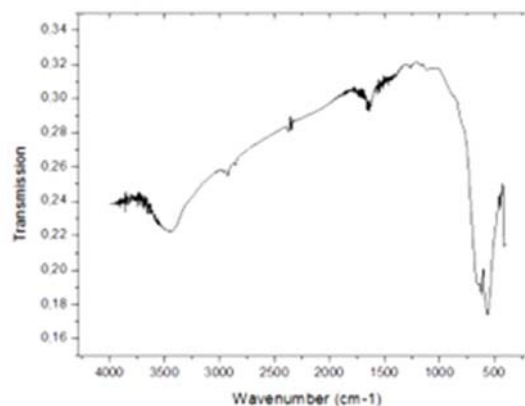


Figure 2. Infrared spectra of a sample used in this work.

by finite two-sided differences, using a displacement step of 0.01 \AA . The adsorbed atoms were displaced in the calculations, and the diagonalization of the dynamic matrix produced the harmonic frequencies.

The $\text{Cr}_2\text{O}_3(0001)$ surface was modeled as a rhomboid supercell with an edge size of 4.954 \AA and 20 \AA high. Each substrate layer was composed of one chromium atom, three oxygen atoms and one chromium atom, and was 2.263 \AA thick (Fig. 3).

The face (0001) was selected because in its natural state, Cr_2O_3 has this type of structure in 97.20% of its volume, which is maintained up to temperatures of approximately 973 K (see Fig. 4).

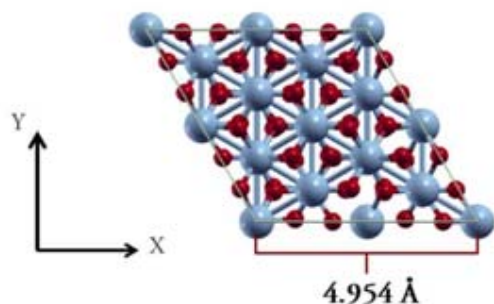


Figure 3. $\text{Cr}_2\text{O}_3(0001)$ supercell [3]. Red: oxygen atoms, gray: chromium atoms.

The first Brillouin zone was sampled with a (331) gamma point centered mesh, and only the gamma point was used for the cubic supercell used for the optimization of isolated molecules.

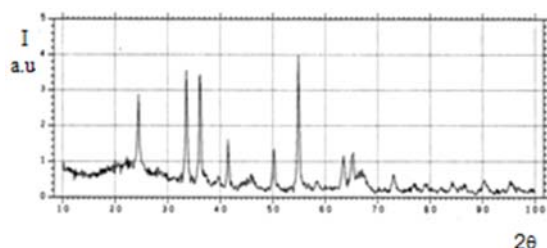


Figure 4. X-ray spectrum of a Cr_2O_3 sample calcined at 973 K.

The adsorption energy of each adsorbate molecule was calculated as

$$E_a = E(\text{Adsorbate}/\text{Cr}_2\text{O}_3) - E(\text{Adsorbate}) - E(\text{Cr}_2\text{O}_3)$$

The first term is the energy of the optimized configuration for the relaxed adsorbate molecule bonded to the clean surface. The second term is the energy of the optimized gas-phase adsorbate molecule (isolated), and the third term is the energy of the optimized surface. Based on this definition, negative values of E_a correspond to stable configurations.

B. Results

SO_2 is adsorbed onto $\text{Cr}_2\text{O}_3(0001)$ by bonding its two oxygen atoms to two different chromium atoms on the surface. The sulfur atom may or may not be attached to a surface oxygen atom. The first sulfite-like structure is the most stable and can be formed at various sites on the surface. The vibrational frequencies of the O-S-O bond are similar in all of these sites and for the asymmetric stretching they take values between 1000 and 940 cm^{-1} , for the symmetric stretching, about 600 cm^{-1} , and for the bending, around 490 cm^{-1} .

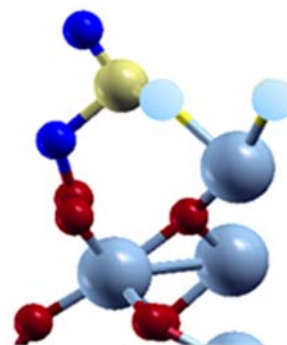


Figure 5. Sulfite-like species formed between SO_2 and oxygen previously adsorbed in molecular state. Gray: chromium atoms, red: surface oxygen atoms, yellow: sulfur atom, blue: oxygen atoms from SO_2 , light blue: preadsorbed oxygen atoms.

The second structure, in which the sulfur atom is not bound to the surface, is an intermediate configuration, in a local minimum of energy, but it participates in the dissociation of adsorbed oxygen and in the dehydrogenation of methane, as explained below.

Oxygen is adsorbed on the clean surface of $\text{Cr}_2\text{O}_3(0001)$ both in molecular state and in dissociated form, the latter being the most stable. In the molecular state it has two stable configurations, with only one oxygen atom attached to a surface chromium atom, or with both oxygen atoms attached to a single chromium atom. In the dissociated state the two oxygen atoms are attached to the same chromium atom.

The presence of adsorbed SO_2 promotes the dissociation of oxygen and the formation of sulfite species (Fig. 5).

Methane does not adsorb on the clean $\text{Cr}_2\text{O}_3(0001)$ surface or in the presence of molecular oxygen. However, it interacts with oxygen in a dissociated state, leading to the formation of both hydroxyl and methoxy species, the latter through the binding of the methyl group and a surface oxygen atom. The characteristic frequency of the CH_3 d-stretching mode is in the range 2960–3000 cm^{-1} .

The interaction between methane and adsorbed sulfur dioxide facilitates the dehydrogenation of methane. In this case, the methyl groups are attached to the sulfur atom not bound to the surface, but this configuration, although stable, is intermediate and should lead to the formation of methoxy and sulfite-type species.

Methoxy species can form at various sites on the surface, and their interaction with oxygen in the dissociated state promotes their dehydrogenation. The oxymethylene species then have a characteristic frequency of symmetric stretching around 2860 cm^{-1} (Fig.6).

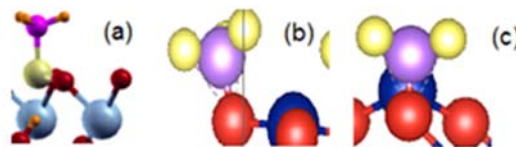


Figure 6. (a) Dehydrogenation of methane in the presence of sulfur dioxide, (b) methoxy species, (c) oxymethylene species

The subsequent oxidation of these species leads to the formation of dioxymethylene and formaldehyde.

According to [7,8] the adsorption of formaldehyde on $\text{Cr}_2\text{O}_3(0001)$ would give rise to spectroscopic bands at 1650 cm^{-1} and 1126 cm^{-1} .

Interestingly, the methoxy species can interact with hydroxyl, leading to the formation of methanol, which in turn can react with the adsorbed species (Fig. 7).

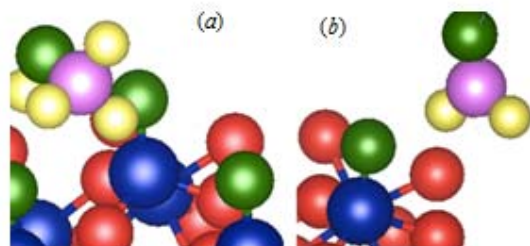
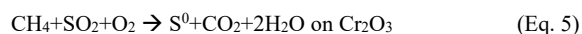


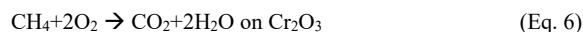
Figure 7. Formation of methanol (a) and formaldehyde (b) on $\text{Cr}_2\text{O}_3(0001)$ surface.

IV. CONCLUSIONS

In this work we presented a theoretical-experimental study of the methane oxidation reaction in the presence of sulfur dioxide on $\text{Cr}_2\text{O}_3 / \gamma\text{-Al}_2\text{O}_3$



The global activation energy of this reaction is lower than that of the oxidation reaction



and to our knowledge, it is the lowest found so far in different catalysts. Our objective was to try to unveil the role of sulfur dioxide as well as to detect intermediate species of possible industrial interest.

Sulfur dioxide is adsorbed on $\text{Cr}_2\text{O}_3(0001)$ in two different configurations, in both the oxygen atoms are attached to chromium atoms, but the sulfur atom may or may not attach to a surface oxygen atom. The sulfite configuration is the most stable, but it is the other one that acts as an intermediate to promote the dissociation of molecularly adsorbed oxygen or the dehydrogenation of methane. This effect facilitates the formation and subsequent oxidation of methoxy species up to the formation of dioxymethylene, formaldehyde, and methanol.

Our results suggest that the possibility of oxidizing methane on chromium oxide in the presence of sulfur dioxide deserves to be considered in the development of syngas production technologies.

Our research also points to an additional alternative to the green formation of methanol that deserves to be explored.

V. ACKNOWLEDGMENTS

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VI. REFERENCES

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