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Abstract: In the present work we experimentally determine the activation energies of CH₄, SO₂ and O₂ reactions on Cr₂O₃/γ-Al₂O₃. To our knowledge there is no previous determination of these parameters, so fundamental information is provided to determine the velocity laws of these reactions and understand their kinetic behavior.γ

Dear Editor,

We are pleased to send you the revised version of our manuscript entitled "Experimental determination of the activation energies of SO₂, CH₄ and O₂ reactions on Cr₂O₃/γ-Al₂O₃."

We expect that you may find our article suitable for publication in Chemical Physics Letters.

Yours sincerely

Isabel Irurzun

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Dear Sir,

The following changes were made to our manuscript Ms. No.: CPLETT-16-697, entitled "Experimental determination of the activation energies of CH₄, SO₂ and O₂ reactions on Cr₂O₃/γ-Al₂O₃".

- (i) Graphical Abstract: the graphical abstract was replaced according to your suggestion.
- (ii) While preparing the new graphical abstract, we realized that there were two major mistakes in the figures, which were corrected in this version. We regret any misunderstanding that these errors may have caused.
 - (a) The CO₂ production curves corresponding to the catalyzed reactions were interchanged, the one in figure 2b corresponded to figure 2c and vice versa
 - (b) The line corresponding to the catalysed reaction in figure 3b was mistakenly included in figure 3c.

We expect that you may find our article suitable for publication in Chemical Physics Letters.

Yours sincerely

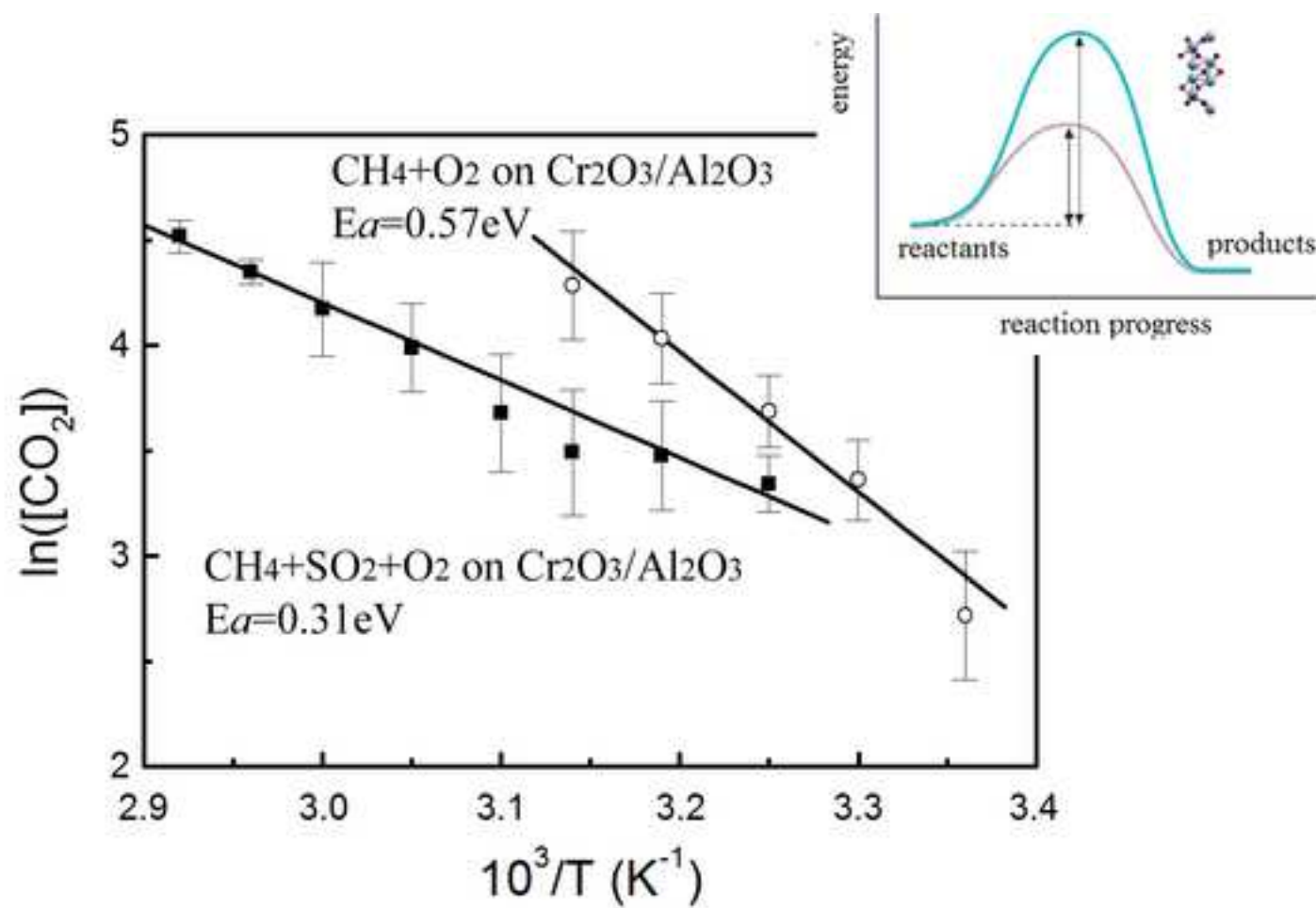
Isabel Irurzun

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***Highlights (for review)**

*Experimental determination of the activation energy of the SO₂ reduction with CH₄ on Cr₂O₃/γ-Al₂O₃

*The oxygen decreases the activation energy of the SO₂ reduction with CH₄ on Cr₂O₃/γ-Al₂O₃



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Experimental determination of the activation energies of CH_4 , SO_2 and O_2 reactions on $Cr_2O_3/\gamma - Al_2O_3$

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Abstract

In the present work we experimentally determine the activation energies of CH_4 , SO_2 and O_2 reactions on $Cr_2O_3/\gamma - Al_2O_3$. To our knowledge there is no previous determination of these parameters, so fundamental information is provided to determine the velocity laws of these reactions and understand their kinetic behavior.

Keywords: Catalysis, methane oxidation, chromium oxide

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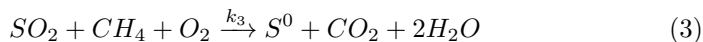
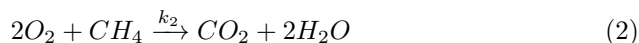
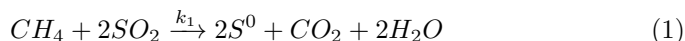
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9 **1. Introduction**

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11 Metal oxide surfaces are of great interest in environmental science as cata-
12 lysts to eliminate harmful molecules (such as SO_2 , NH_3 , CO and NO_x) from
13 polluted air. Among these molecules, SO_2 is one of the substances emitted to
14 the atmosphere from natural and human sources that can be converted into acid
15 rain [1]. Most of the SO_2 that reaches the atmosphere ($\approx 3/4$) is produced by
16 human activities, mainly, the combustion of fossil fuels. More than half of the
17 world production comes from a few developed countries.

18
19 In previous papers, we investigated the adsorption and desorption of SO_2
20 on several polycrystalline transition metal oxides (Co , Ni , Fe , V , Mn , Cr
21 and Mo) supported on alumina [2]. Among them, Cr_2O_3 is the oxide with
22 the maximum capacity to adsorb SO_2 at high temperatures. DFT calculations
23 shows that the adsorption of SO_2 implies the formation of sulfite-like species,
24 while the desorption energy calculated by temperature-programmed desorption
25 (TPD) experiments is 3.12eV [3].

26
27 In the present work, the following reactions are experimentally studied



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46 In the industrial combustion of fossil fuels, the reduction of SO_2 occurs by
47 reaction with CH_4 , while the latter is oxidized to CO_2 by O_2 . This conversion is
48 very important for environmental sciences, and a metal oxide is used as catalyst
49 to favoring the reactions.

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52 CH_4 adsorption on Cr_2O_3 was previously studied by IR spectroscopy in the
53 presence of H_2 . Both molecules are adsorbed on Cr^{3+} sites, and electrostatic
54 forces are mainly involved [4].
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9 The adsorption and desorption of SO_2 on $\gamma-Al_2O_3$ and $Pt/\gamma-Al_2O_3$ were
10 recently studied in [5] to further understand the oxidation of SO_2 on $Pt/\gamma-$
11 Al_2O_3 catalysts [6].

12
13 The reduction of SO_2 with H_2 and C_2H_4 , as catalyzed by different transition-
14 metal oxides supported on γ -alumina, was also studied [7, 8]. On $NiO/\gamma-Al_2O_3$
15 ,nickel sulfide species were identified during the reaction process.

16
17 The catalytic oxidation of methane in the presence and absence of SO_2
18 was investigated on palladium catalysts supported on Al_2O_3 and CeO_2/Al_2O_3
19 washcoats [9, 10]. The activation energies in absence of SO_2 were $0.4 \pm 0.1 eV$ and
20 $0.6 \pm 0.15 eV$ for the 3 wt.% Pd/Al_2O_3 and the 3 wt.% $Pd/12$ wt.% $CeO_2/\gamma-$
21 Al_2O_3 catalyst respectively.

22
23 To our knowledge, there are no previous studies of the reduction of SO_2 with
24 CH_4 and O_2 on $Cr_2O_3/\gamma-Al_2O_3$. In the present work we approach the study
25 of this system by determining the activation energies of the reactions (1)-(3),
26 under stoichiometric conditions, with and without $Cr_2O_3/\gamma-Al_2O_3$ as catalyst.

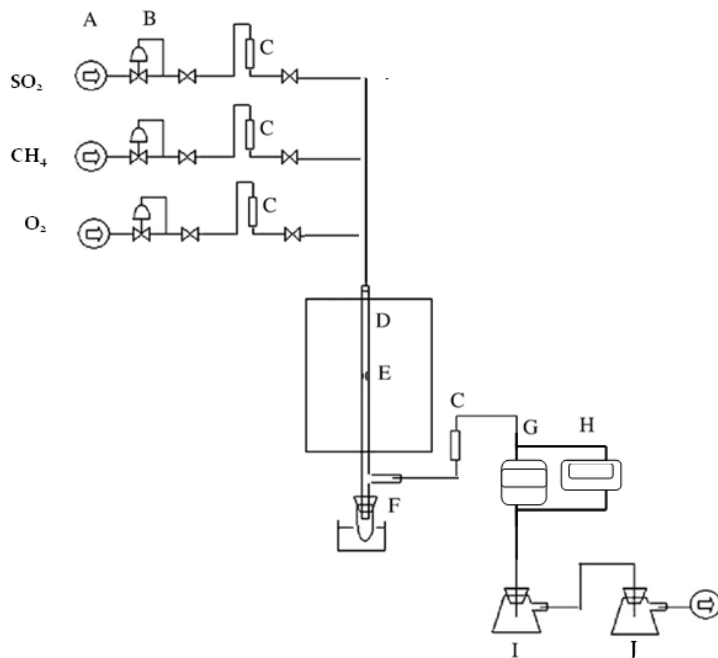
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28 In the next section we present the experimental setup, results are presented
29 in Section 3 and the discussion of our results and conclusions are in Section 4.

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The experimental setup is shown in Fig 1. The fixed bed reactor consists of
a quartz column of 0.6 cm diameter and 110 cm length placed in an adjustable
temperature oven [2]. The column is narrowed in the middle to support the
catalyst between two layers of glass wool. Thus, the gases are warmed prior to
the reaction.

Reaction gases were provided by LINDE: SO_2 composition $> 99.98\%$, CH_4
composition $> 93\%$, O_2 composition $> 99.5\%$. They are introduced in the
reactor at a constant flow rate and a concentration of 10 ppm in N_2 . At the
reactor exit, SO_2 and CO_2 concentrations are measured. The SO_2 register is
an electrochemical cell SafeLog 100, Quest Technologies, capable of detecting
down to less than 10 ppm of SO_2 in the out-coming gas mixture. The CO_2

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9 detector is TES 1370 with a precision of 1 ppm.



35 Figure 1: Experimental setup used in the present work. (A) Gas suppliers, (B) Safety valves,
36 (C) Rotameters, (D) Electrically heated oven, (E) Reactor (column quartz) (F) Sulfur trap,
37 (G) Sulfur dioxide concentration register SafeLog 100, (H) Carbon dioxide concentra-
38 tion register (I) Bubbler with distilled water, (J) Bubbler with a dilute sodium hydroxide solution.
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41 γ -Alumina (catalyst support) was first dried overnight at 105 °C and then
42 burnt at 600 °C. Cr_2O_3 was prepared in a precipitation flask from an aqueous
43 solution of chromium nitrate $Cr(NO_3)_3 \cdot 9H_2O$, FLUKA trademark. The sup-
44 port, previously prepared, was then impregnated with the Cr_2O_3 in a rotameter.
45 The amount of catalyst employed was the amount necessary to produce a 10%
46 w/w mixture with the alumina. The rotameter used is a Buchi, Waterbath
47 model B-480. Water is evaporated at 70 °C under a pressure of 0.3 bar. After
48 evaporation every sample was dried overnight in a stove at 105 °C within a
49 covered porcelain container. After that, every sample was burnt in a Carbolite
50 furnace.
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9 The catalyst samples were characterized by X-ray diffraction, atomic ad-
10 sorption spectroscopy, nitrogen BET specific surface determination and X-ray
11 photoelectron spectroscopy. The crystalline structure is 85% rhombohedral at
12 973K, with a specific surface of 164 m²/gr at 873K.
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15 16 17 **3. Results**

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19 The reactions in Eqs. (1)-(3) were carried out under stoichiometric condi-
20 tions. The reactor was first cleaned by passing a current of N_2 while heating it
21 by steps until 500K. The presence of SO_2 and CO_2 was monitored at the reac-
22 tor exit, and the reactor was considered clean when the concentration of these
23 gases became zero at a given temperature. Experiments were performed by
24 pumping the reaction gases into the reactor at constant flow rate and constant
25 temperature. The CO_2 and SO_2 concentrations were monitored at the reactor
26 exit until they reached constant values. Then, the temperature was increased
27 and the procedure was repeated again. The production of CO_2 was finally plot-
28 ted as a function of temperature. In our continuous flow reactor, the flow rate
29 determines (at constant reactor length) the residence time in the reactor, i.e.,
30 the time during which the reagents are in contact and therefore the extent of
31 reaction.
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35 Figure 2 shows curves concerning reactions (1)-(3) with and without $Cr_2O_3/\gamma-$
36 Al_2O_3 as catalyst. The reaction in Eq. (2) does not occur without catalyst.
37 Each curve was obtained by averaging about 10 independent experiments (done
38 with new catalyst samples) and the error bars indicate the standard deviations.
39 The surface of the $Cr_2O_3/\gamma - Al_2O_3$ catalyst changes with the temperature and
40 exposure time (variations in the nitrogen BET specific surface were detected by
41 measuring the catalyst samples before and after controlled heating experiments).
42 This effect was studied and considered in the present study, and the experi-
43 mental conditions were adjusted to avoid significant catalyst aging during the
44 experiments. Our test results revealed that two different experiments done with
45 the same catalyst sample, in the present experimental conditions, give similar
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CO_2 production curves. As temperature increases, the CO_2 amount produced by reaction during the residence time grows until a constant value, which is reached when the reactive gases are completely consumed by the reaction, i.e., when the reaction rate prevails over the flow rate in the reactor.

As temperature increases the CO_2 amount produced by reaction during the residence time grows until a constant value which is reached when the reactive gases are completely consumed by reaction that is when the reaction rate dominates on the flow rate in the reactor.

As temperature increases, the CO_2 amount produced by reaction during the residence time grows until a constant value, which is reached when the reactive gases are completely consumed by the reaction, i.e., when the reaction rate prevails over the flow rate in the reactor.

To determine the activation energies (E_i), we assumed an Arrhenius dependence on temperature for the reaction constants (k_i).

$$\log(k_i) = \log(A_i) - \frac{E_i}{kT} \quad (4)$$

where $k = 8.6173324(78) \times 10^{-5} eV/K$ is the Boltzman constant, T the absolute temperature and A_i 's are the pre-exponential constant.

Figure 3 shows the Arrhenius plots obtained from Figure 2.

To determine the activation energies from linear plots, our reactor must be operating in a regime where the reaction proceeds slowly and the reagent amounts consumed inside the reactor are small. Then, the reaction rate only depends on temperature.

As the temperature increases, the reaction rate depends on the local concentration of the reagents inside the reactor, and concentration gradients may appear. Finally, CO_2 production will tend to a constant value as discussed above. In fact, this limits the temperature range in which E_i can be determined, which is specified in each case in Table 1.

Finally, we note that reactions (1) and (3) occur also in the gas phase without catalyst. To determine the activation energies with the catalyst, the CO_2 curve

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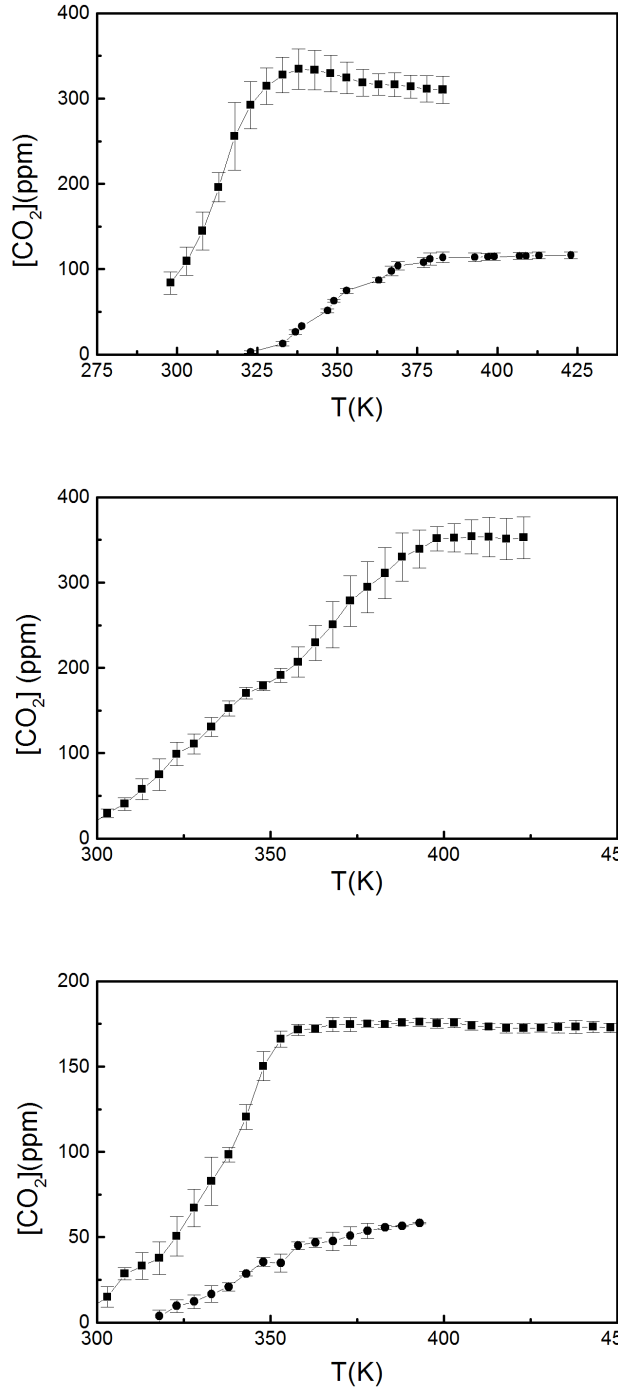


Figure 2: CO₂ production during the reactions of SO₂, CH₄ and O₂ as a function of temperature without catalyst (circles) and with Cr₂O₃/γ-Al₂O₃ (squares). (a) SO₂ + CH₄ (Eq. 1), (b) CH₄ + O₂ (Eq. 2), (c) SO₂ + CH₄ + O₂ (Eq. 3).

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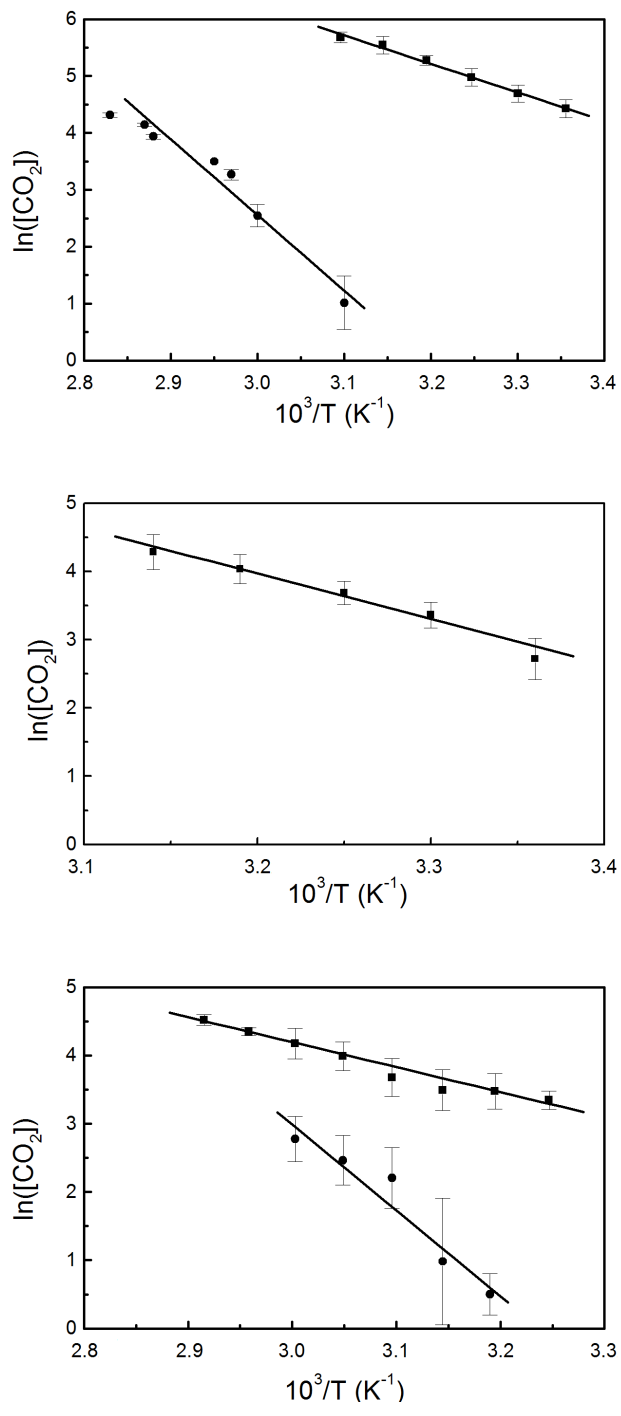


Figure 3: Arrhenius plots for the reactions of SO_2 , CH_4 and O_2 without catalyst (circles) and with $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ (squares). (a) $\text{S}_2\text{O}_8 + \text{CH}_4$ (Eq. 1), (b) $\text{CH}_4 + \text{O}_2$ (Eq. 2), (c) $\text{SO}_2 + \text{CH}_4 + \text{O}_2$ (Eq. 3).

Reaction	Catalyst mass (gr)	E_i (eV)	Temperature range (K)
$CH_4 + 2SO_2 \rightarrow 2S^0 + CO_2 + 2H_2O$	0	1.0 ± 0.1	313 – 333
$CH_4 + 2SO_2 \rightarrow 2S^0 + CO_2 + 2H_2O$	0.1	0.43 ± 0.02	298 – 319
$2O_2 + CH_4 \rightarrow CO_2 + 2H_2O$	0	No reaction	298 – 1273
$2O_2 + CH_4 \rightarrow CO_2 + 2H_2O$	0.1	0.57 ± 0.06	298 – 319
$SO_2 + CH_4 + O_2 \rightarrow S^0 + CO_2 + 2H_2O$	0	1.1 ± 0.1	323 – 354
$SO_2 + CH_4 + O_2 \rightarrow S^0 + CO_2 + 2H_2O$	0.1	0.31 ± 0.04	308 – 338

Table 1: Activation energies E_i with and without catalyst determined in the present work.

must be corrected by subtracting the amount of CO_2 produced without catalyst at each temperature.

4. Discussion and Conclusions

In this work the activation energies of the reactions (1) - (3) on $Cr_2O_3/\gamma - Al_2O_3$ were experimentally determined under stoichiometric conditions.

Preliminary results (not shown here for simplicity) indicate that E_i 's values in Table 1 are independent of the catalyst mass but dependent on the reactants flux relationship.

To determine the velocity laws of these reactions, experiments and simulations are being performed to simultaneously calculate the reaction orders and pre-exponential factors A_i . Results will be presented in further work.

To our knowledge, there are no previous studies on the reduction of SO_2 with CH_4 and O_2 on $Cr_2O_3/\gamma - Al_2O_3$. In Ref. [10] activation energies for the catalytic oxidation of methane in the presence and absence of SO_2 on palladium catalysts supported on $\gamma - Al_2O_3$ and $CeO_2/\gamma - Al_2O_3$ washcoats are reported. Values in the absence of SO_2 were $0.4 + / - 0.1eV$ and $0.6 + / - 0.15eV$ for the 3%wt and the 3%wt catalysts, respectively. They must be compared with the $0.57 + / - 0.06eV$ value obtained in the present work. The presence of SO_2 seems to deactivate the palladium catalyst, while we observed that SO_2 favors methane oxidation on the chromium oxide catalyst, decreasing the activation

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9 energy to $0.31 + / - 0.04eV$, the lowest value found so far. The molecular
10 chemisorption of SO_2 on $Cr_2O_3/\gamma - Al_2O_3$ was studied in a previous paper
11 within the DFT+U framework, showing the formation of sulphite-like species
12 involving surface oxygen atoms [5]. The sulfur atom binds to an oxygen atom
13 on the surface, while SO_2 oxygen atoms bind to chromium atoms. Preliminary
14 DFT+U theoretical studies also indicated that the adsorption of SO_2 and CH_4
15 on $Cr_2O_3/\gamma - Al_2O_3$ is favored by co-adsorbed atomic oxygen [11]. Also CH_4
16 adsorption on $Cr_2O_3/\gamma - Al_2O_3$ is favored by co-adsorbed SO_2 , explaining the
17 catalytic activity for reaction (1) (CH_4 does not adsorb on clean $Cr_2O_3/\gamma -$
18 Al_2O_3).

19 We also performed FT-IR spectroscopy studies on the catalyst samples used
20 in the present work [11]. We could identify CH_x ($x=1, 2, 3$) and OH species
21 chemically adsorbed on the surface, as well as $S - O$ and $C = C$ bonds. These
22 studies are being analyzed together with theoretical DFT+U calculations and
23 will be presented in a future work.

24 We hope that the information presented in this work will inspire further
25 research and applications of this system.

26 Acknowledgments

27 This work was supported by Consejo de Investigaciones Científicas y Técnicas
28 (CONICET), Agencia Nacional de Promoción Científica y Tecnológica (AN-
29 PCyT), Universidad Nacional de La Plata and the Faculty of Chemistry and
30 Engineering Fray Roger Bacon

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10 *reducción catalítica de SO_2 sobre óxido de cromo soportado sobre alúmina*
11 *en presencia de CH_4 y O_2 a altas temperaturas*. PhD thesis, University of
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