

An Investigation of the Reaction Mechanism for the Promotion of Propane Oxidation over Pt/Al₂O₃ by SO₂

Andreas Hinz,^{*} Magnus Skoglundh,[†] Erik Fridell,[†] and Arne Andersson^{*,1}

^{*}Department of Chemical Engineering II, Lund University, Center for Chemistry & Chemical Engineering, P.O. Box 124, SE-221 00 Lund, Sweden; and [†]Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden

Received January 23, 2001; revised March 30, 2001; accepted March 30, 2001

Total oxidation of propane with oxygen in the absence and the respective presence of SO₂ in the feed gas was studied over 1 wt% Pt on γ -Al₂O₃ using transient experiments with TAP (temporal analysis of products) and *in situ* DRIFT spectroscopy. The TAP experiments confirm the promoting role of SO₂ on the conversion of propane and, moreover, show an inhibiting effect from SO₂ on the conversion of the intermediate products propene and CO. *In situ* DRIFT spectroscopy reveals the formation of sulphate species on the catalyst surface and indicates the formation of an allylic intermediate in the absence of SO₂ only. Interaction between hydrocarbon intermediates and the sulphate species is confirmed by the appearance of thiol fragments in the mass spectra. The transient experiments show that propane in the first step is irreversibly adsorbed at the surface. Analysis of the surface residence times of the products formed at the propane pulse in pump-probe experiments provides information about the reaction pathways. Without SO₂ in the feed gas, propane reacts consecutively in the sequence propane \rightarrow propene \rightarrow ethane \rightarrow CO \rightarrow CO₂. In the presence of SO₂ the first step of the main route is the breaking of a C–C bond in propane producing ethane and a C₁ fragment, which then form CO and eventually CO₂. It is suggested that the promoting effect by SO₂ on the conversion of propane is due to the formation of an acidic site at the Pt/Al₂O₃/SO₄²⁻ interface.

© 2001 Academic Press

Key Words: propane oxidation; promotion by SO₂; Pt/Al₂O₃; transient experiments; TAP; *in situ* DRIFT; reaction mechanism.

INTRODUCTION

Complete catalytic oxidation is an efficient technique to convert emissions of volatile organic compounds (VOC) into harmless products. In this connection Pt/Al₂O₃ catalysts generally combine high activity with good stability and, consequently, are among the most widely used catalysts for the abatement of VOC emissions. Stable oxygenates and saturated hydrocarbons, like, e.g., ethyl acetate and propane, require however relatively high

temperatures to be completely oxidised over Pt/Al₂O₃ catalysts. Efficient oxidation of such compounds generally requires external preheating of the feed gas, which results in low energy efficiency. Previously, it was shown that small amounts of SO₂ can promote the oxidation of saturated hydrocarbons over Pt/Al₂O₃ (1–6). The oxidation of unsaturated hydrocarbons, like propene, is however inhibited by the presence of SO₂ over this type of catalyst (1, 6). Further, the choice of support material is of major importance for the promotional effect to be seen. Sulphur dioxide promotes the oxidation of ethyl acetate, ethanol, and propane over Pt/Al₂O₃ whereas no significant effect on the conversion of these compounds is observed for silica-supported Pt (4, 6).

The origin of the promotional effect of SO₂ on the conversion of propane is proposed to be related to the formation of surface sulphates on alumina (1), on platinum (3), or in the platinum–alumina interface (4, 5). The surface sulphate groups would then enhance the chemisorption properties for propane, which in turn lead to an increase in the rate of propane combustion (1). Sulphation has also been reported to reduce PtO₂ particles to metallic Pt, with increased activity for propane oxidation (5). In the studies of the effect of SO₂ on the oxidation of propane over unsupported and supported Pt presented so far, the focus has not been on the identification of different reaction pathways. In this respect, transient studies can be a helpful tool for clarifying reaction mechanisms (7).

In this paper we have investigated the effect of SO₂ on the oxidation of propane over Pt/ γ -Al₂O₃ by temporal analysis of products (TAP) using a TAP-2 system (8) and *in situ* diffuse reflectance infrared (DRIFT) spectroscopy. We will show that the oxidation of propane mainly proceeds via two different reaction mechanisms in the absence and respectively presence of SO₂. Without SO₂, the oxidation to CO₂ takes place via the formation of propene, ethane, and CO as intermediates. With SO₂ present, the initial step in the oxidation involves breaking of a carbon–carbon bond of propane, resulting in ethane, CO, and finally CO₂ formation.

¹ To whom correspondence should be addressed. Fax: +46-46-149156. E-mail: Arne.Andersson@chemeng.lth.se.

EXPERIMENTAL

Catalyst Preparation

The catalyst, 1 wt% Pt on γ -Al₂O₃, was prepared by impregnating an alumina support with a platinum precursor followed by drying and calcination (9).

Spheres of γ -Al₂O₃ (1.0 mm in diameter, 163 m²/g from Condea Chemie) were crushed and sieved. The fraction between 250 and 500 μ m was saved and further used (here designated as the support). An amount of 5.0 g of the support was dispersed in 100 g of distilled water under stirring and the pH was adjusted to 10 by the addition of NH₄OH. An aqueous solution of platinum was prepared by dissolving Pt(NH₃)₄(OH)₂ (Johnson Matthey) in distilled water, resulting in a concentration of 10 mg of Pt/g of solution. Pt was deposited on the support by dropwise addition of 5.0 g of Pt solution. The dispersion was then stirred for 1 h, freeze-dried, and finally calcined in air at 550°C for 1.5 h.

TAP-2 Experiments

Pulse experiments were performed using a TAP-2 reactor system (7, 8) to gain insight into the reaction mechanism of propane oxidation over the Pt/ γ -Al₂O₃ catalyst in both the absence and the presence of SO₂. The TAP-2 system consists of a feed station with two blend tanks, a microreactor with four high-speed valves being connected to the blend tanks, a vacuum system, and an UTI 100C mass spectrometer (MS) for analysis of the pulse responses. Two kinds of experiments were performed, namely, multipulse and pump-probe experiments. In the multipulse experiments a mixture with all reactants was pulsed at high frequency with simultaneous scanning of the atomic mass units (amu), being characteristic of the reactants and the products formed, hereinafter referred to as pulse/scan experiments. In the pump-probe experiments the different reactants were alternately pulsed with an offset time of 500 μ s, and the response profiles of selected masses (m/e) were followed using MS analysis. For each profile 100 pulses were averaged. An amount of 17 mg of the Pt/ γ -Al₂O₃ catalyst was loaded into the microreactor in between inert layers of quartz. The pulse size was of the order 10¹⁴ molecules/pulse, and the pulse width was measured to be about 300–420 μ s. The total pressure in the feed tanks was 1140 Torr.

Prior to each experiment the catalyst was conditioned as follows. First, the catalyst was oxidized with oxygen at 450°C for 10 min. Then, the sample was flushed with argon at 450°C for 10 min before being reduced with 10 vol% hydrogen in argon for another period of 10 min at the same temperature.

Oxidation of propane. Pulse/scan experiments were performed at 40, 300, and 500°C, pulsing a mixture of propane and oxygen over the catalyst. To provide an atmosphere that admits the complete conversion of propane

to CO₂ and water, the mole ratio between propane and oxygen was 1 : 7 (12.5 vol% propane).

Pump-probe experiments were performed at 200°C, pulsing two valves alternately. One valve was used to pulse 90.9 vol% oxygen in argon over the catalyst while the other valve was used for pulsing 12.5 vol% propane in argon. The following m/e ratios were analyzed during the pump-probe experiments: 17 (water), 26 (ethane, propene, propane), 28 (ethane, propane, CO, CO₂), 29 (propane), 32 (oxygen), 40 (argon), 41 (propene, propane), 43 (propane), and 44 (propane, CO₂). The signals for propene, CO₂, ethane, and CO were obtained considering the fragmentation patterns of the products and propane.

Oxidation of SO₂. Pulse/scan experiments were carried out at 200 and 500°C pulsing a mixture of 33.3 vol% oxygen and 0.67 vol% SO₂ in argon over the catalyst.

Oxidation of propane in the presence of SO₂. Pulse/scan experiments were performed at 200 and 500°C. The pulses consisted of a mixture of 5.5 vol% propane, 38.9 vol% oxygen, and 0.55 vol% SO₂ in argon.

Pump-probe experiments were carried out at 200°C. Besides the m/e ratios being traced in the corresponding propane oxidation without SO₂ (see above), the m/e ratio 64 from SO₂ was analyzed. Two sets of experiments were made, differing in the way of pulsing SO₂. In one case a mixture of 33.3 vol% oxygen and 0.67 vol% SO₂ in argon was pulsed alternately with a pulse of 4.6 vol% propane in argon. In another set of experiments a mixture of 4.4 vol% propane and 0.67 vol% SO₂ in argon was pulsed alternately with a pulse of 33.3 vol% oxygen in argon. The analysis of the mass spectra was performed as described above for the corresponding experiments without SO₂.

FTIR Experiments

The *in situ* FTIR experiments were performed using a BioRad FTS6000 FTIR spectrometer equipped with a continuous flow reaction chamber with CaF₂ windows (Harrick Scientific Praying Mantis DRIFT cell). The Pt/ γ -Al₂O₃ catalyst was ground into powder and mixed thoroughly with KBr. About 30 mg of the sample was applied on a tungsten grid (6.2 × 3.2 mm) placed over the outlet of the reaction chamber. The temperature was measured with a K-type thermocouple and controlled by the power applied over the heater. Spectra were recorded in diffuse reflectance (DRIFT) mode, and 40 scans were collected at a resolution of 1 cm⁻¹.

The sample was initially reduced in 5 vol% H₂ for 15 min at 500°C and then oxidised in 8% O₂ for 15 min at the same temperature. The experiments were performed at 200 and 500°C in a total gas flow of 300 ml/min with Ar as the balance. The sample was first exposed to 3.0 vol% O₂ for 15 min and reference spectra were taken at 500 and 200°C. At 200°C, 0.42 vol% propane was added to the feed

and a spectrum was taken after about 5 min. The oxygen concentration was then successively lowered to 1.5, 0.75, and 0 vol%, and spectra were taken at each level after about 5 min. Finally, also the propane flow was turned off and a spectrum was recorded after 5 min.

The sample was then oxidised in 3.0 vol% O₂ at 500°C for 30 min and at 200°C for 10 min. At 200°C 0.42 vol% propane and 0.06 vol% SO₂ were added to the feed and spectra were recorded for 3.0, 1.5, 0.75, and 0 vol% O₂ as described above. The propane and SO₂ flows were then successively turned off and spectra were recorded. Finally, the sample was exposed to 3.0 vol% O₂ and 0.06 vol% SO₂ for 5 min and a DRIFT spectrum was recorded. After treatment of the catalyst in 3.0 vol% O₂ at 500°C for 30 min, the experiments were repeated at 500°C.

RESULTS

Investigation with the TAP-2 Reactor System

For the TAP experiments without SO₂ the concentrations of oxygen and propane in the pulse are a factor of 2–3 higher than those for the corresponding experiments with SO₂. This choice was made considering that the activity of the catalyst is lower for propane oxidation in the absence of SO₂ and, moreover, SO₂ is corrosive to the pulse valves. Therefore, a gas with 1 vol% SO₂ in Ar is used as supply for SO₂. In spite of the difference in feed concentration, however, the two types of experiments are comparable since the reactor itself is kept under vacuum (10⁻⁸ Torr) and the

pulse size is small compared to the surface of the catalyst being used. Therefore, the relative conversion of propane and the product distribution are unaffected by the pulse size of the reactants.

In Fig. 1 the mass spectra from pulse/scan experiments are shown when pulsing a mixture of oxygen and propane over Pt/γ-Al₂O₃ at different temperatures. The propane (29 and 43 amu) and oxygen (32 amu) responses decrease with increasing temperature, showing the conversion of the reactants. Formation of CO₂ is shown by the concurrent increase of the response at 44 amu. Compared with the masses from propane, the decrease in the response at $m/e = 28$ is less pronounced due to contributions from both propane and the products CO, CO₂, and ethane.

Mass scans in Fig. 2 were recorded in pulse/scan experiments when pulsing a mixture of SO₂ and oxygen over the catalyst at 200 and 500°C. The response from SO₂ at 64 amu is more intense at 500°C than at 200°C, indicating that more SO₂ is adsorbed at the lower temperature. Also, the oxygen response (32 amu) is higher at 500°C than at 200°C. Moreover, the formation of SO₃ (80 amu) is only observed at 500°C.

Figure 3 shows the results from pulse/scan experiments at two temperatures with pulsing of a mixture of propane, oxygen, and SO₂. Compared to the results in Fig. 1 for propane oxidation, the results in Fig. 3 show that the conversion of propane is higher in the presence of SO₂. This becomes obvious, especially when considering that the intensities of the two unique mass peaks from propane at 29 and 43 amu,

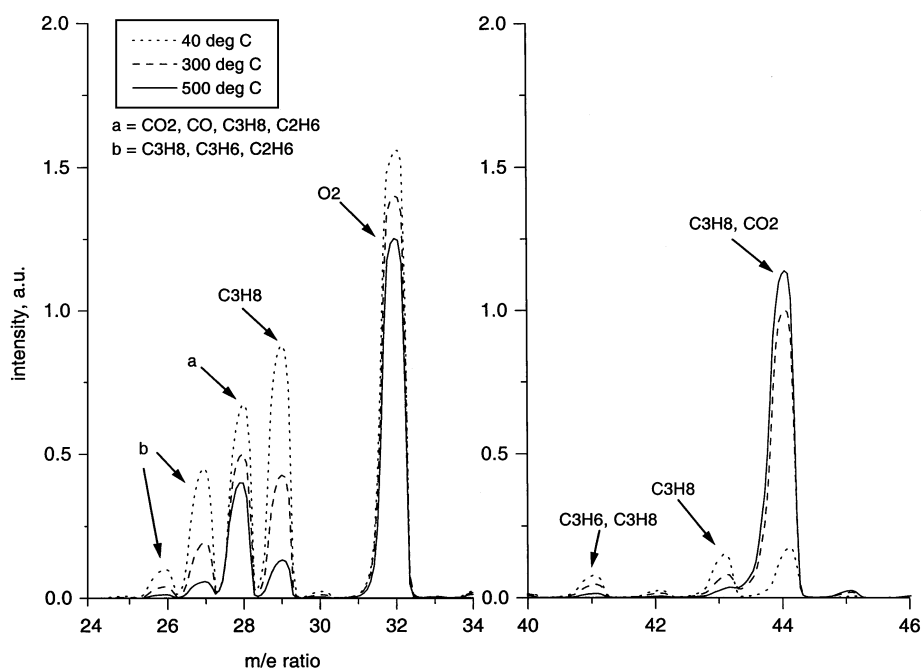


FIG. 1. Mass spectra from pulse/scan experiments with multipulsing of a mixture of 12.5 vol% propane and 87.5 vol% oxygen over Pt/γ-Al₂O₃ at different temperatures.

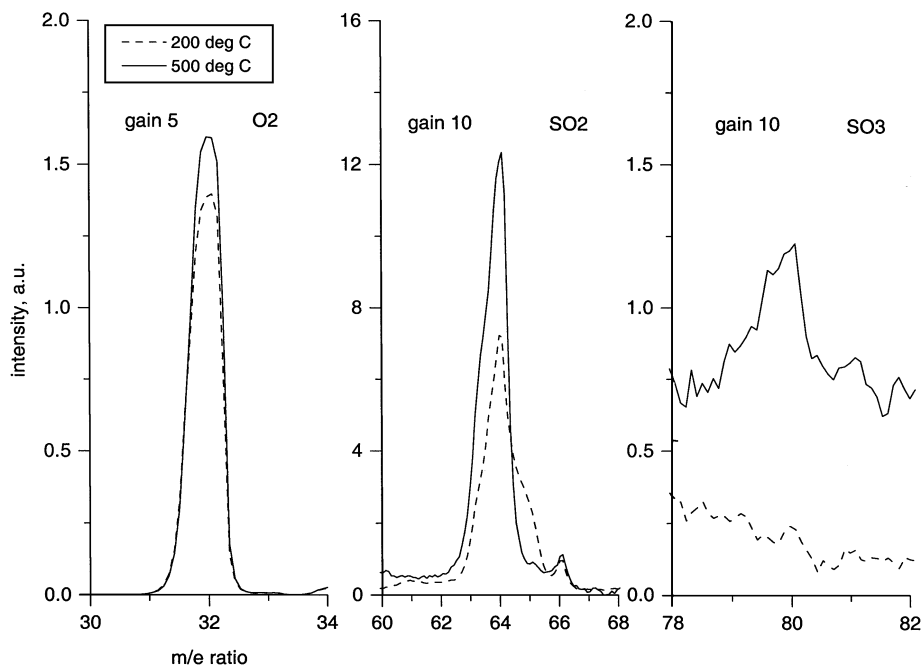


FIG. 2. Mass spectra from pulse/sweep experiments with multipulsing of a mixture of 33.3 vol% oxygen and 0.67 vol% SO₂ in argon over Pt/ γ -Al₂O₃ at different temperatures.

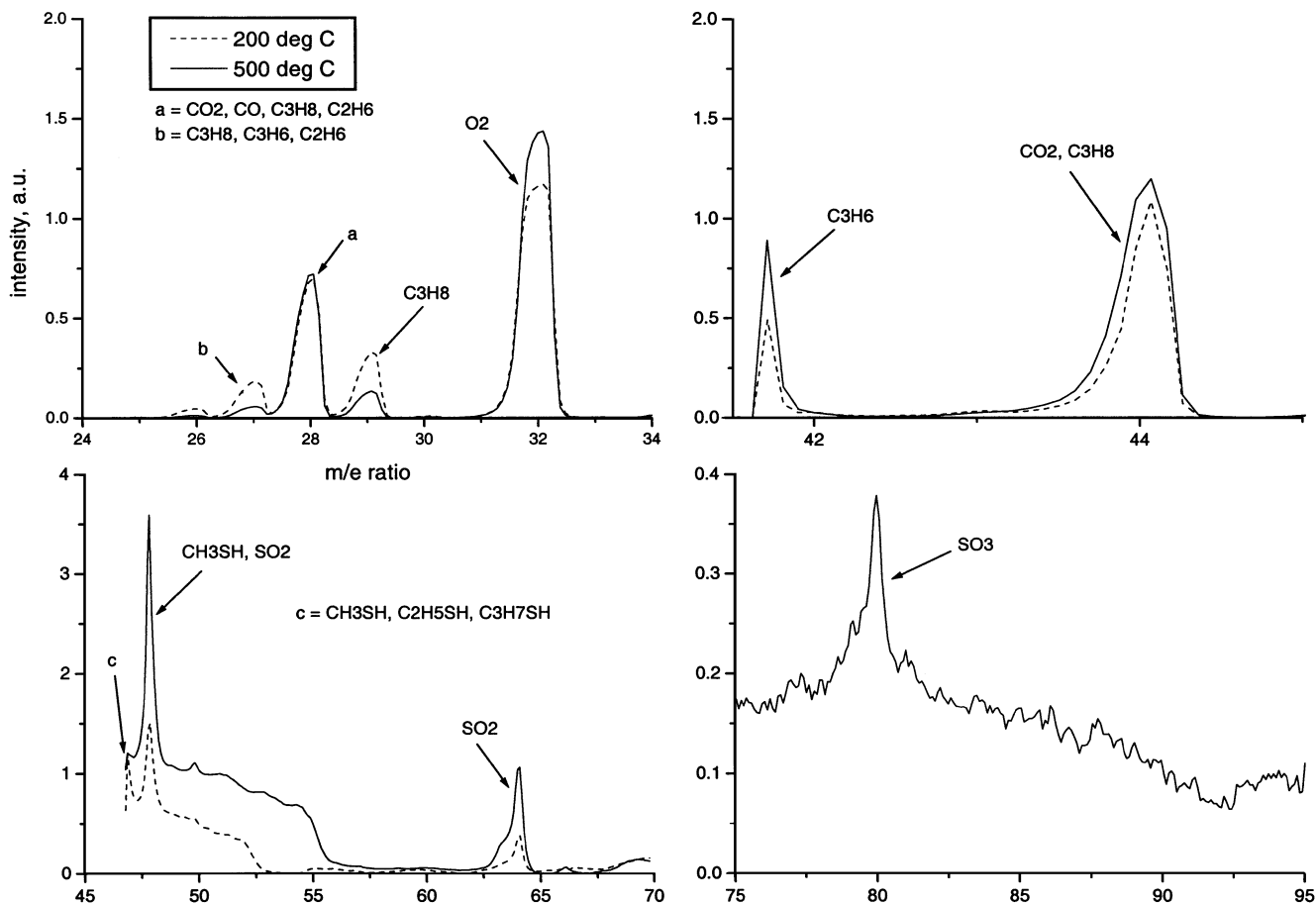


FIG. 3. Mass spectra from pulse/sweep experiments with multipulsing of a mixture of 0.55 vol% SO₂, 5.5 vol% propane, and 38.9 vol% oxygen over Pt/ γ -Al₂O₃ at different temperatures.

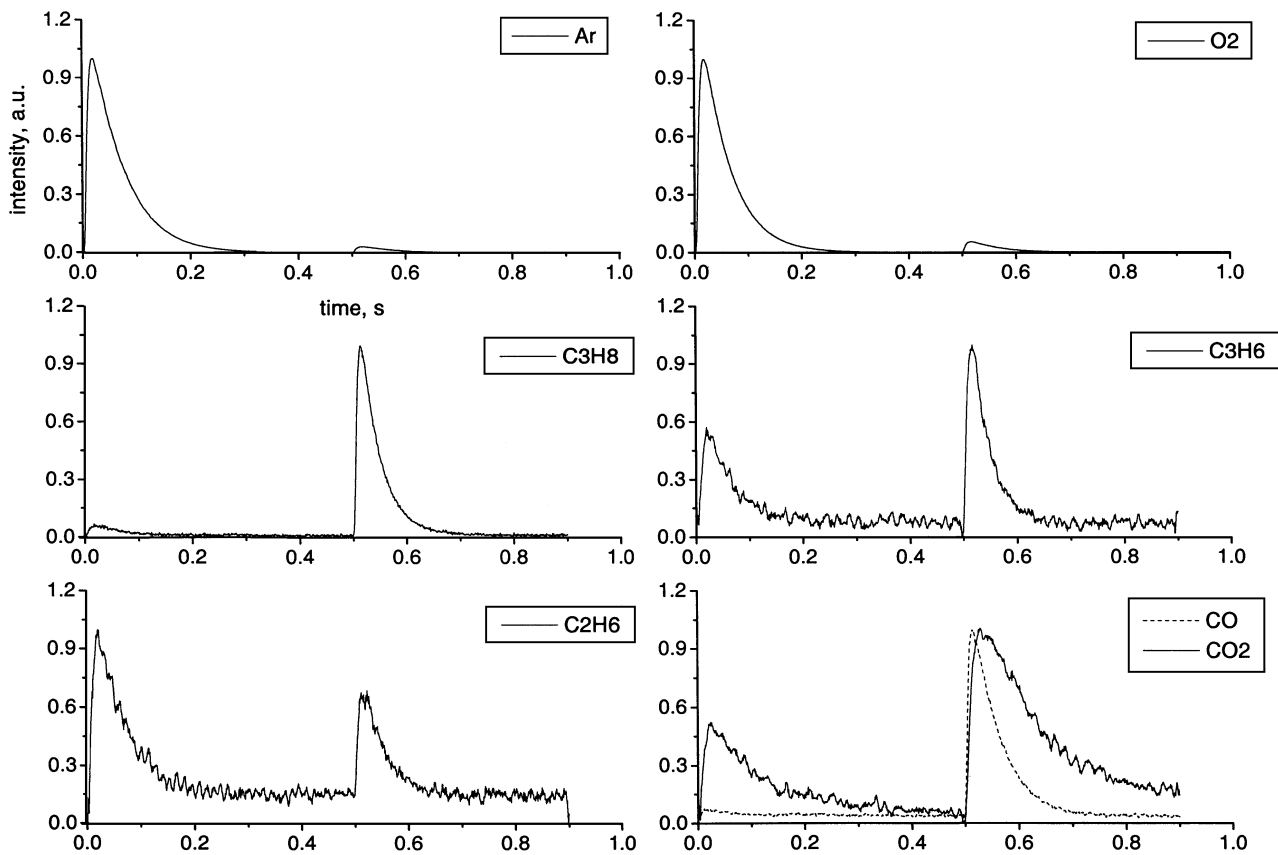


FIG. 4. Height-normalised time-resolved responses recorded in a pump-probe experiment when pulsing 4.6 vol% propane in argon alternately with a mixture of 33.3 vol% oxygen and 0.67 vol% SO₂ in argon over Pt/ γ -Al₂O₃ at 200°C. The pump-probe interval is 500 μ s and each response curve is the average of 100 pulses.

relative the intensities of the peaks at 28, 41, and 44 amu, are much smaller in Fig. 3 (200 and 500°C) than in Fig. 1 (300 and 500°C). With SO₂ in the pulse, the formation of propene also is more evident, as revealed by the intensity of mass 41 amu. It is worth noticing that the oxygen signal (32 amu) in Fig. 3 is more intense at 500°C than at 200°C. Moreover, the masses from SO₂ and SO₃ show behaviour similar to that in Fig. 2. Additionally, two masses at 47 and 48 amu appear.

The results of a pump-probe experiment with alternate pulses of SO₂ in oxygen and propane, respectively, are presented in Fig. 4. From the figure it is clear that more propene, CO, and CO₂ are formed at the propane pulse than at the SO₂/O₂ pulse. The formation of ethane, however, shows the opposite behaviour.

Figure 5 gives the surface residence times of the products being formed at the propane pulse in three different sets of pump-probe experiments. The surface residence time (τ_{surf}) was calculated from the relationship $\tau_{\text{surf}} = \tau - \tau_{\text{diff}}$, where τ is the measured residence time in the reactor and τ_{diff} is the diffusion time through the reactor. The measured residence time (τ) was calculated from the zero (m_0) and first (m_1) moments of the response curves and is equal to

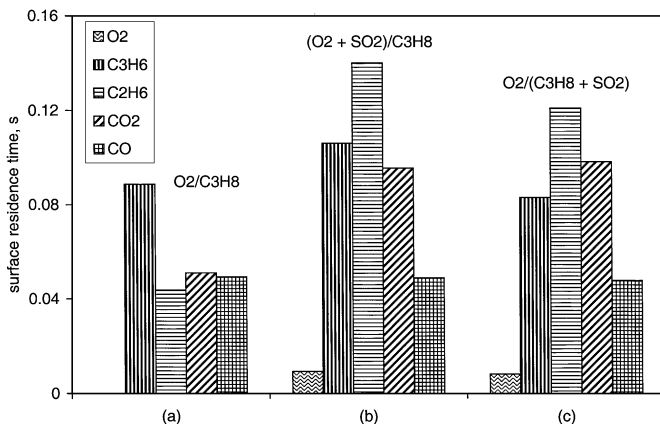


FIG. 5. Surface residence times for the products formed on Pt/ γ -Al₂O₃ at the propane pulse in three different types of pump-probe experiments performed at 200°C. (a) Oxygen (90.9 vol%) in Ar/propane (12.5 vol%) in Ar; (b) oxygen (33.3 vol%) and SO₂ (0.67 vol%) in Ar/propane (4.6 vol%) in Ar; and (c) oxygen (33.3 vol%) in Ar/propane (4.4 vol%) and SO₂ (0.67 vol%) in Ar. The values are the average of 100 pulses and the variance of the calculated residence time is $\pm 4\%$.

TABLE 1

Propane Conversion and Relative Response Areas in Three Different Types of Pump-Probe Experiments Performed at 200°C^a

Component	Relative peak area at the propane pulse in the alternate pulsing of ^b		
	Oxygen/propane	(Oxygen + SO ₂)/propane	Oxygen/(propane + SO ₂)
Propane	1.0×10^0	1.0×10^0	1.0×10^0
Propene	1.8×10^{-2}	8.0×10^{-2}	6.5×10^{-2}
Ethane	6.8×10^{-2}	5.0×10^{-2}	2.7×10^{-2}
CO ₂	4.3×10^{-1}	9.3×10^{-1}	2.7×10^{-1}
CO	4.5×10^{-1}	5.7×10^1	4.4×10^1
O ₂	—	2.9×10^1	2.1×10^1
SO ₂ ^c	—	—	—

^a The corresponding surface residence times of the products are given in Fig. 5.

^b See the legend of Fig. 5 for more experimental details.

^c An SO₂ peak is observed only at the oxygen pulse, even when it is pulsed together with propane.

m_1/m_0 (10). Assuming that the products are formed in the middle of the catalyst bed, τ_{diff} was set to half the residence time as measured for the inert argon after adjustment of the value with regard to the difference in mass between the product and argon (10).

As the data in Fig. 5 show, there is considerable influence from SO₂ on the values of the surface residence time for ethane and CO₂, which are both considerably increased. In contrast, for propene and CO the influence is negligible. An interesting observation is that oxygen appears at the propane pulse only in the experiments with SO₂ irrespective of whether propane is pulsed together with argon or together with SO₂ and argon.

The propane conversion and the relative response areas of the components, corresponding to the surface residence times in Fig. 5, are given in Table 1. Clearly, the conversion of propane is increased by the presence of sulphur species at the surface of the catalyst. The relative amounts being formed of propene and especially CO are both increased.

FTIR Studies

Figure 6 shows the DRIFT spectra in the range 3900–900 cm⁻¹ recorded while exposing the catalyst at 200°C to propane with different O₂ contents in the feed gas (spectra a to d) and to inert gas (spectrum e). Figure 7 shows DRIFT spectra recorded between 4000 and 1200 cm⁻¹ when the Pt/ γ -Al₂O₃ sample is exposed to either propane and O₂ at 200°C (spectrum a), or propane, O₂, and SO₂ (spectra b and d), or inert gas (spectra c and e) at 200 and 500°C, respectively.

Strong absorption bands around 3510, 3680, and 3730 cm⁻¹ are seen in the spectra of Fig. 6 and spectrum a of Fig. 7. These bands are from surface OH groups on

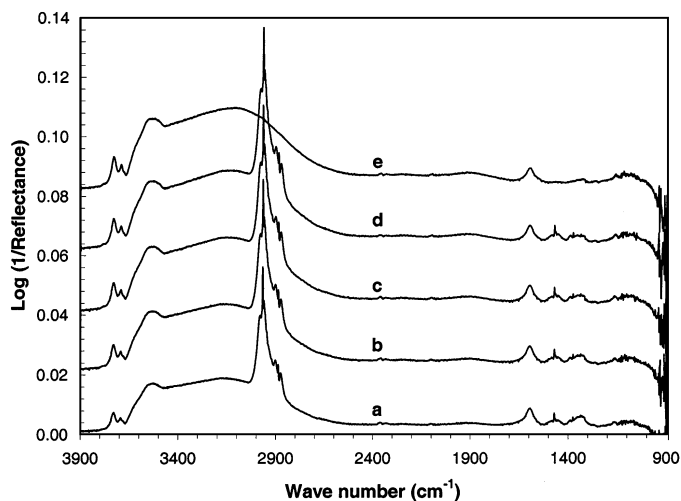


FIG. 6. *In situ* DRIFT spectra recorded at 200°C of Pt/ γ -Al₂O₃ successively exposed to (a) 0.42 vol% C₃H₈ and 3.0 vol% O₂ in N₂; (b) 0.42 vol% C₃H₈ and 1.5 vol% O₂ in N₂; (c) 0.42 vol% C₃H₈ and 0.75 vol% O₂ in N₂; (d) 0.42 vol% C₃H₈ and 0 vol% O₂ in N₂; and (e) N₂. The spectra are offset by 0.02.

γ -Al₂O₃ (11, 12). Upon exposure of the catalyst to SO₂ (Fig. 7), the bands turn negative, which indicate that the hydroxyl groups on the alumina support either interact with SO₂ species or are consumed upon the adsorption of SO₂ (11). All spectra (Figs. 6 and 7) recorded with propane in the feed gas show several sharp peaks around 2969 cm⁻¹ and some weak peaks around 1470 and 1376 cm⁻¹. These bands are not shifted with the temperature and disappear when the propane flow is turned off. The bands are

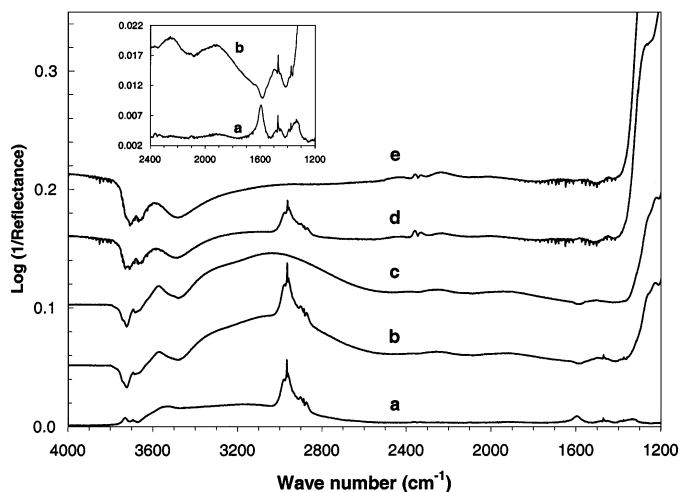


FIG. 7. *In situ* DRIFT spectra of the 4000- to 1200-cm⁻¹ region for Pt/ γ -Al₂O₃ successively exposed to (a) 0.42 vol% C₃H₈ and 3.0 vol% O₂ in N₂ at 200°C; (b) 0.42 vol% C₃H₈, 3.0 vol% O₂, and 0.06 vol% SO₂ in N₂ at 200°C; (c) N₂ at 200°C; (d) 0.42 vol% C₃H₈, 3.0 vol% O₂, and 0.06 vol% SO₂ in N₂ at 500°C; and (e) N₂ at 500°C. The spectra are offset by 0.05. The insert shows the 2400- to 1200-cm⁻¹ spectral region for experiments a and b (offset 0.007).

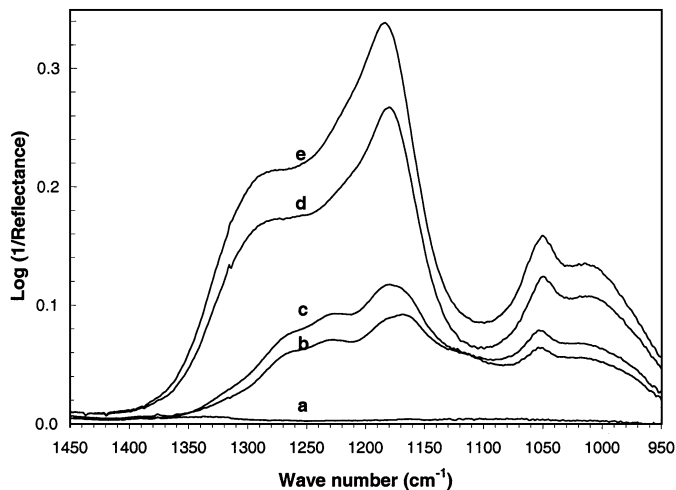


FIG. 8. *In situ* DRIFT spectra of the 1450- to 950-cm⁻¹ region for Pt/γ-Al₂O₃ successively exposed to (a) 0.42 vol% C₃H₈ and 3.0 vol% O₂ in N₂ at 200°C; (b) 0.42 vol% C₃H₈, 3.0 vol% O₂, and 0.06 vol% SO₂ in N₂ at 200°C; (c) N₂ at 200°C; (d) 0.42 vol% C₃H₈, 3.0 vol% O₂, and 0.06 vol% SO₂ in N₂ at 500°C; and (e) N₂ at 500°C.

characteristic of the C-H vibrations of gaseous propane (13). An absorption band is observed at 1601 cm⁻¹ when the sample is exposed to propane and oxygen at 200°C (Fig. 6 and spectrum a in Fig. 7). The interpretation of this band is uncertain. It can be assigned to the formation of a σ -bonded allyl species on the alumina surface (14–16), but there are also reports of carboxylate/carbonate features in this spectral region (17, 18). When the sample is exposed to SO₂, the 1601-cm⁻¹ band disappears and seems to be replaced by a negative band (spectrum b in Fig. 7).

For the recordings presented in Fig. 7 spectra of the 1450- to 950-cm⁻¹ region are shown in Fig. 8. Only weak absorption bands are observed in this region when the Pt/γ-Al₂O₃ sample is exposed to propane and oxygen at 200°C (spectrum a). However, when the sample is exposed to a mixture with propane, SO₂, and O₂ at 200°C (spectrum b), absorption bands appear at 1261, 1230, 1170, 1055, and 1016 cm⁻¹. The two most pronounced bands are located at 1170 and 1055 cm⁻¹. The intensity of all bands was observed to increase with increasing SO₂ exposure time. The band at 1170 cm⁻¹ is gradually shifted to 1181 cm⁻¹ after removal of O₂, propane, and SO₂ (spectrum c).

When the catalyst is exposed to propane, SO₂, and O₂ simultaneously at 500°C (Fig. 8, spectrum d), absorption bands at 1278, 1182, 1051, and 1016 cm⁻¹ are observed. The bands were found to remain and become more intense with increasing SO₂ exposure time during the experiment. The two most pronounced absorption bands are located at 1182 and 1051 cm⁻¹. The former band is successively shifted to 1187 cm⁻¹ after removal of O₂, propane, and SO₂ from the gas phase (spectrum e).

The absorption band at 1055 cm⁻¹, which is slightly shifted to 1051 cm⁻¹ at 500°C, is assigned to a surface-

bonded aluminium sulphite or sulphate species in accord with previous studies (11, 19–21). Most bands associated with sulphite are expected to appear below 1000 cm⁻¹, but these cannot be observed due to the strong absorption by alumina in this region. The free SO₃²⁻ ion has been reported giving bands at 960 and 1010 cm⁻¹ (20). The latter position is close to that of the shoulder at 1016 cm⁻¹, which is observed in Fig. 8.

The strong absorption band in the 1170- to 1187-cm⁻¹ region (Fig. 8) can be attributed to a sulphate species since bulk aluminium sulphate gives an intense absorption band at approximately 1190 cm⁻¹ (19). The position of the band in Fig. 8 shifts to higher wavenumber both when the temperature is increased and when SO₂ is removed from the gas phase, indicating a transition from surface sulphate to bulk aluminium sulphate. Moreover, the shoulder bands at 1260–1280 cm⁻¹ (spectra b–e) and 1230 cm⁻¹ (spectra b and c) have been observed in previous studies and assigned to sulphate and sulphite species, respectively (1, 19).

DISCUSSION

It is well known from the literature that SO₂ promotes the oxidation of propane over both Pt on alumina (1, 4, 5, 22) and unsupported Pt (3). In this regard, the results of the present investigation are in perfect agreement. A comparison of the results of the pulse/scan experiments in Figs. 1 (propane and oxygen) and 3 (propane, oxygen, and SO₂) reveals that the propane conversion is higher when propane is oxidised in the presence of SO₂. This is apparent, especially at 200–300°C, when comparing the ratio of the masses from propane at 29 and 43 amu with those of the products. The data in Table 1 for pump-probe experiments performed at 200°C show that relatively more CO and propene are formed in the presence of SO₂. The observed effect on the product distribution agrees with previous reports (1, 22), showing that the oxidations of propene and CO, as opposed to the propane oxidation, are inhibited by the presence of SO₂ in the feed gas.

Considering the intensities of the signals from SO₂ (64 amu) and SO₃ (80 amu) in the pulse/scan experimental results in Fig. 2, it is obvious that more SO₂ is adsorbed on the catalyst surface at 200°C than at 500°C since the intensity of the SO₂ signal is smaller at the lower temperature together with no SO₃ being formed. The same figure, moreover, reveals that the oxygen signal (32 amu) is less intense at 200°C than at 500°C. It is noteworthy that the oxygen signal (gain 5) is larger than the SO₂ signal (gain 10) by a factor of 10⁵, a fact which excludes a possible contribution from SO₂ to the oxygen signal. Considering that the ratio O₂:SO₂ in the experiment is 50, the oxidation of SO₂ only cannot fully explain the substantial difference in the oxygen signal between the two temperatures. Separate experiments

pulsing O₂ alone and O₂ with SO₂ over the catalyst showed in both cases that the oxygen adsorption increased with the temperature. The presence of SO₂ did hardly affect the oxygen adsorption at 200°C; however, at 500°C the presence of SO₂ caused decreased oxygen adsorption. Therefore, the results in Fig. 2 suggest that formed sulphate species affect either the sticking probability or the desorption temperature of oxygen from the catalyst. The mass spectra in Fig. 3 agree completely with the trends in Fig. 2 concerning the oxygen, SO₂, and SO₃ signals. From the results of Figs. 2 and 3 and the DRIFT spectra in Fig. 8 it can be proposed that SO₂ is adsorbed at the surface in the form of sulphate species, which at 500°C desorb partly as SO₃. A difference between the DRIFT results in Fig. 8 and the pulse/scan results in Figs. 2 and 3 is that the DRIFT spectra show that the amount of sulphate species increases when the temperature is increased from 200 to 500°C while the pulse/scan experiments indicate less SO₂ adsorption at the higher temperature. The difference may be explained by the fact that the DRIFT spectra give an average picture of the whole surface including the alumina. The sulphate species formed on average cannot be desorbed at 500°C whereas that in contact with Pt can be.

It is well known that SO₂ is adsorbed on alumina in the form of sulphite and sulphate species (1, 11, 19–21, 23–25), and sulphate formation also has been observed to occur on the Pt(111) surface (26). In a previous investigation (1) it was observed using infrared spectroscopy that SO₂ at room temperature is adsorbed on γ -Al₂O₃ forming sulphite species, which in the presence of oxygen are transformed to sulphate species at 500°C. When Pt is supported on the alumina, it was found that Pt catalyses the oxidation of sulphite to sulphate and the latter species is formed at 200°C, which is consistent with the spectral features in Fig. 8. Bulk aluminium sulphate has previously been reported having an intense absorption band at approximately 1190 cm⁻¹ (19). However, previous studies of oxidised SO₂ on pressed alumina pellets using transmission infrared spectroscopy reported two intense absorption bands at 1380–1400 and 1045–1090 cm⁻¹, which are attributed to a surface sulphate (20, 23). The absence of a band in the 1380- to 1400-cm⁻¹ region in this investigation is in accordance with DRIFT results by Mitchell *et al.* (19). The authors report the arising of an intense band at 1190 cm⁻¹ and a corresponding disappearance of a 1060-cm⁻¹ band when SO₂, chemisorbed on γ -alumina powder, is oxidised at 400°C. On the other hand, when the alumina powder was pressed to a pellet, exposed to SO₂ and oxidised in the DRIFT cell, strong absorption at 1380 cm⁻¹ was observed (19). Therefore, the strong absorption band in the 1170- to 1189-cm⁻¹ region in this investigation is attributed to a sulphate species.

The question arises whether it is sulphate on the Pt or the alumina that causes the improved activity for propane com-

bustion. In this regard, it is important to consider the observation (2, 4) that no corresponding effect on the propane combustion was observed for Pt supported on silica. In recent works (4, 5) it is agreed that an interfacial sulphate species plays a key role in the activation of propane, and Pt sites are required for the activation of oxygen and the subsequent oxidation of alkyl species. The mass spectrum in Fig. 3, showing mass peaks at 47 and 48 amu, which can be from methane-, ethane-, or propanethiol, gives some support for a sulphate species reacting with propane. Clearly, the intensity of the peak at 48 amu has a considerable contribution from methanethiol since for SO₂ this mass peak is small compared to that at 64 amu.

Concerning the surface residence times in Fig. 5, it can be mentioned that it is zero for the reactant propane. This fact proves that the propane that passes unreacted through the catalyst bed has not been adsorbed/desorbed at the surface of the catalyst. Thus, irreversible adsorption of propane must occur since products from propane are formed, indicating chemisorption by way of hydrogen abstraction. The surface residence times in Fig. 5, which were measured at the propane pulse, and the corresponding data in Table 1 provide information about the reaction pathways. In the present case using a metal catalyst there is a limited amount of oxygen at the surface from the oxygen pulse, which is then consumed at the propane pulse. Therefore, the first part of the propane pulse being chemisorbed at the surface meets a surrounding area that is relatively rich in oxygen. At this stage, initial and reactive intermediates can quickly react to form end products while passing through the catalyst bed. As the oxygen is being consumed with time, the surface becomes progressively depleted of oxygen. Consequently, the initial products of the reaction sequence can be detected at the latter part of the propane pulse since now there will not be enough of oxygen for them to consecutively react to products being subsequent in the reaction pathway. Thus, considering the present results on propane oxidation in the absence of S-containing species, case a in Fig. 5, ethane, CO, and CO₂ have similar surface residence times. Like propane, possibly ethane is irreversibly adsorbed at the surface and the surface residence time in Fig. 5 for ethane is unaffected by readsorption/desorption processes and corresponds to the average reaction time. Compared to the surface residence time for ethane, those of CO and CO₂ are slightly longer, indicating that the latter products are rapidly formed from chemisorbed ethane as long as the oxygen coverage of the surface is high. The residence time for propene is the longest due to propene being the initial product, which can be detected only for the latter part of the propane pulse being chemisorbed at a surface that has become depleted of oxygen. Figure 9 summarises what products are formed at high and low oxygen coverage of the Pt/ γ -Al₂O₃ surface, respectively, and shows the reaction pathway that can be concluded from the experiment. In the absence

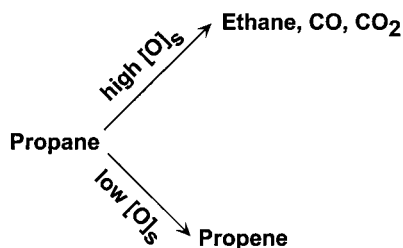
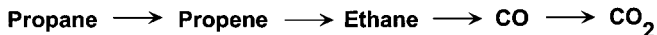
**Reaction pathway:**

FIG. 9. Propane oxidation over Pt/ γ -Al₂O₃. Summary of the oxygen/propane pump-probe experiment (Fig. 5, case a), showing the products being detected at high and low oxygen coverage [O]_s of the surface. The reaction pathway, being concluded on the basis of the experimental results, is indicated.

of any sulphur species at the surface the propane oxidation proceeds over the initial intermediate propene, which then consecutively reacts over ethane and CO to eventually form CO₂.

For propane oxidation in the presence of sulphur species the results in Fig. 5 and Table 1 are similar, irrespective of whether SO₂ is being pulsed at the oxygen or the propane pulse. This observation is consistent with the report that the promoting effect from SO₂ remains for a while after the supply of SO₂ is stopped (6). In the presence of sulphur species the surface residence times for ethane and CO₂ (case b and c in Fig. 5) clearly differ from those that were obtained when no sulphur species were present (case a in Fig. 5). This observation supports the belief that the sulphur species at the surface participate in the reaction. Considering the previous discussion of the importance of the oxygen coverage, Fig. 10 shows the relationship between the oxygen coverage of the catalyst surface and the product formation as it appears from cases b and c of Fig. 5. The results can be explained as follows. CO is rapidly formed since propane from the initial part of the propane pulse chemisorbs at a surface having a relatively high concentration of oxygen species. Compared to propane oxidation in the absence of sulphur species, the data in Table 1 show that in the presence of sulphur species more propane is converted, forming considerably more CO. The formation of CO depletes the surface with oxygen and the transformation of CO to CO₂, which also can be affected by the adsorption of SO₂ on Pt (1), is slowed down. Consequently, compared with case a in Fig. 5, the surface residence time for CO₂ will be longer in cases b and c. As the concentration of the oxygen species at the surface is reduced, the intermediate product propene also appears. Finally, the latter part of the propane pulse, which chemisorbs at an oxygen-poor surface, will admit the detection of the initial intermediate. As

Fig. 5 (cases b and c) shows, this intermediate is ethane. Although ethane presents a longer surface residence time than propene, it is unlikely that propene can form from ethane. Consequently, in the case of the SO₂-promoted oxidation of propane, there are two reaction pathways, as indicated in Fig. 10. The minor pathway from propane to CO₂ passes over the intermediate products propene, ethane, and CO. Considering that ethane is an initial intermediate, being detectable only at low concentration of surface oxygen, the major route comprises an initial attack on a C-C bond of propane. As a result, ethane and a C₁ species are produced, which in excess of oxygen are eventually transformed to CO₂. That the oxidation of ethane, likewise the oxidation of propane, is promoted by SO₂ agrees with previous results (27).

The finding that in the absence of sulphur species the reaction pathway goes through an initial hydrogen abstraction from propane is confirmed by the DRIFT spectra in Fig. 6, assuming that the band at 1601 cm⁻¹ is from an allylic species (14). The band becomes negative (Fig. 7) when the sample is exposed to SO₂, and therefore, it can be concluded that propene is a major intermediate in the total oxidation of propane only in the absence of SO₂.

When the reaction pathways in Figs. 9 and 10 are compared, it is seen that the minor reaction pathway occurring in the presence of sulphur species is identical to the pathway being followed in the absence of such species. This similarity seems reasonable, showing that the concentration of sulphur species is not optimal for conversion of propane; i.e., a part of the propane is converted without involvement of the sulphur species. However, it

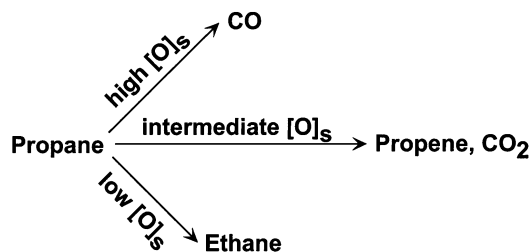
**Reaction pathways:**

FIG. 10. Propane oxidation over Pt/ γ -Al₂O₃ in the presence of SO₂. Summary of the oxygen/propane pump-probe experiments with SO₂ (Fig. 5, case b and c), showing the products being detected at high, intermediate, and low oxygen coverage [O]_s of the surface. The reaction pathways, being concluded on the basis of the experimental results, are indicated.

can be difficult to find an optimal range since the results in Table 1 and those of other investigators (1, 19) indicate that the conversion of CO to CO₂ is inhibited by the presence of SO₂ in the gas. Without SO₂ in the gas, according to the reaction pathway in Fig. 9, the initial step of the mechanism for propane oxidation should be the abstraction of two hydrogen atoms from propane forming propene. In contrast, with SO₂ in the gas (Fig. 10) the initial step of the major pathway comprises the cracking of propane, forming ethane and a C₁ fragment. The catalytic cracking of hydrocarbons usually involves acidic sites of Lewis or Brønsted type (28). Consequently, from the results of the present work it can be proposed that the promoting effect of SO₂ for propane oxidation is due to the formation of a basic sulphate species (SO₄²⁻) at the Pt/Al₂O₃ interface, creating an adjacent acidic counterion. Formation of sulphate species is shown by the DRIFT spectra in Fig. 8, and the disappearance of hydroxyl vibrations upon SO₂ adsorption (Fig. 7) can be due to a rearrangement creating an acidic site. Indeed, it has been reported that not only the activity of Pt/Al₂O₃ is increased upon sulphation but also the acidity of the catalyst (29). A complication in this regard is that no general correlation was observed between the activity for propane oxidation and the acidity of the catalyst when comparing Pd and Pt on sulphated and nonsulphated alumina and zirconia supports (29). This apparent inconsistency indicates that the structural features and properties of the Pt–Al–S–O system with the elements in close proximity may be unique. The formation of oxygen at the propane pulse (Fig. 5 and Table 1) cannot be explained in detail from the present results and needs further investigation; however, it can be a result of the surface restructuring that occurs when propane is being chemisorbed.

CONCLUSIONS

Concerning the promoting effect on propane oxidation from sulphur species on Pt/Al₂O₃, previous studies have not focused on the identification of the reaction pathways and reaction mechanism. To fill the gap, this report concerns the study of the reaction pathways using a TAP reactor system for transient experiments. Considering the experimental results, the following conclusions are drawn.

A promoting effect from SO₂ on the activity of Pt/γ-Al₂O₃ for propane oxidation is confirmed. Pulsing of a mixture of SO₂ and oxygen over the catalyst demonstrates that SO₂ is adsorbed on the catalyst surface, and *in situ* DRIFT spectra show the formation of sulphate species.

Pump-probe experiments reveal that different reaction mechanisms operate in the respective absence and presence of SO₂ in the gas. In the former case, the combustion

of propane passes over propene, ethane, and CO to produce CO₂. With SO₂ in the feed gas, the initial step of the mechanism involves the breaking of a carbon–carbon bond of propane. The active site is suggested as being an acidic site at the Pt/Al₂O₃/SO₄²⁻ interface.

ACKNOWLEDGMENTS

Financial support from the Swedish National Research Council for Engineering Sciences is gratefully acknowledged. The Competence Centre for Catalysis is financially supported by the Swedish National Energy Administration and the member companies AB Volvo, Johnson Matthey-CSD, Saab Automobile AB, Perstorp AB, MTC AB, and Eka Chemicals.

REFERENCES

1. Yao, H. C., Stepien, H. K., and Gandhi, H. S., *J. Catal.* **67**, 231 (1981).
2. Hubbard, C. P., Otto, K., Gandhi, H. S., and Ng, K. Y. S., *J. Catal.* **144**, 484 (1993).
3. Wilson, K., Hardacre, C., and Lambert, R. M., *J. Phys. Chem.* **99**, 13755 (1995).
4. Burch, R., Halpin, E., Hayes, M., Ruth, K., and Sullivan, J. A., *Appl. Catal. B* **19**, 199 (1998).
5. Lee, A. F., Wilson, K., Lambert, R. M., Hubbard, C. P., Hurley, R. G., McCabe, R. W., and Gandhi, H. S., *J. Catal.* **184**, 491 (1999).
6. Skoglundh, M., Ljungqvist, A., Petersson, M., Fridell, E., Cruise, N., Augustsson, O., and Jobson, E., *Appl. Catal. B* **30**, 315 (2001).
7. Hinz, A., and Andersson, A., *Chem. Eng. Sci.* **54**, 4407 (1999).
8. Gleaves, J. T., Yablonski, G. S., Phanawadee, P., and Schuurman, Y., *Appl. Catal. A* **160**, 55 (1997).
9. Acke, F., Westerberg, B., Eriksson, L., Johansson, S., Skoglundh, M., Fridell, E., and Smedler, G., in "Catalysis and Automotive Pollution Control IV" (N. Krause, A. Frennet, and J.-M. Bastin, Eds.), Studies in Surface Science and Catalysis, Vol. 116, p. 285. Elsevier, Amsterdam, 1998.
10. Gleaves, J. T., Ebner, J. R., and Kuechler, T. C., *Catal. Rev.-Sci. Eng.* **30**, 49 (1988).
11. Datta, A., Cavell, R. G., Tower, R. W., and George, Z. M., *J. Phys. Chem.* **89**, 443 (1985).
12. Busca, G., *Phys. Chem. Chem. Phys.* **1**, 723 (1999).
13. Shimanouchi, T., "Tables of Molecular Vibrational Frequencies Consolidated," Vol. 1, pp. 1–160. National Bureau of Standards, Washington, 1972.
14. Busca, G., Finocchio, E., Lorenzelli, V., Trombetta, M., and Rossini, S. A., *J. Chem. Soc. Faraday Trans.* **92**, 4687 (1996).
15. Sourisseau, C., Guillermet, J., and Pasquier, B., *Chem. Phys. Lett.* **26**, 564 (1974).
16. Hoffmann, E. G., Kallweit, R., Schroth, G., Seevogel, K., Stempfle, W., and Wilke, G., *J. Organomet. Chem.* **97**, 183 (1975).
17. Erimini, V., Finocchio, E., Sechi, S., Busca, G., and Rossini, S., *Appl. Catal. A* **190**, 157 (2000).
18. Jackson, S. D., Hussain, N., and Munro, S., *J. Chem. Soc. Faraday Trans.* **94** (1998) 955.
19. Mitchell, M. B., Sheinker, V. N., and White, M. G., *J. Phys. Chem.* **100**, 7550 (1996).
20. Chang, C. C., *J. Catal.* **53**, 374 (1978).
21. Amberntsson, A., Westerberg, B., Engström, P., Fridell, E., and Skoglundh, M., in "Catalyst Deactivation" (B. Delmon and G. F.

- Froment, Eds.), *Studies in Surface Science and Catalysis*, Vol. 126, p. 317. Elsevier, Amsterdam, 1999.
22. Gandhi, H. S., and Shelef, M., *Appl. Catal.* **77**, 175 (1991).
 23. Saur, O., Bensitel, M., Saad, A. B. M., Lavalley, J. C., Tripp, C. P., and Morrow, B. A., *J. Catal.* **99**, 104 (1986).
 24. Pieplu, A., Saur, O., Lavalley, J.-C., Pijolat, M., and Legendre, O., *J. Catal.* **159**, 394 (1996).
 25. Rao, S. N. R., Waddell, E., Mitchell, M. B., and White, M. G., *J. Catal.* **163**, 176 (1996).
 26. Wilson, K., Hardacre, C., Baddeley, C. J., Lüdecke, J., Woodruff, D. P., and Lambert, R. M., *Surf. Sci.* **372**, 279 (1997).
 27. Bart, J., Pentenero, A., and Prigent, M., in "Catalytic Control of Air Pollution" (R. G. Silver, J. E. Sawyer, and J. C. Summers, Eds.), ACS Symposium Series, Vol. 495, p. 42. Am. Chem. Soc., Washington, D.C., 1992.
 28. Scherzer, J., *Catal. Rev.-Sci. Eng.* **31**, 215 (1989).
 29. Hubbard, C. P., Otto, K., Gandhi, H. S., and Ng, K. Y. S., *Catal. Lett.* **30**, 41 (1995).