

Low-temperature oxidation reactions of ethane over a Pt/Al₂O₃ catalyst

B. Silberova,^a R. Burch,^b A. Goguet,^b C. Hardacre,^{b,*} and A. Holmen^{a,*}

^a Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway

^b School of Chemistry, Queen's University of Belfast, David Keir Building, Stranmillis Road, Belfast BT 9 5AG, Northern Ireland, UK

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Abstract

Oxidative dehydrogenation of ethane was performed under conventional microreactor and TAP reactor conditions over a Pt/Al₂O₃ catalyst between 100 and 600 °C. During TAP studies, no ethene was produced whereas under flow conditions small but significant ethene formation was observed. This is consistent with a mechanism involving the gas-phase production of ethene rather than via a surface reaction. In comparison, both hydrogen and methane formation were found under TAP conditions and the trends with temperature and surface oxide composition are interpreted in terms of successive dehydrogenation steps on the catalyst surface. It is further observed that periodic introduction of the reactants can minimize deactivation processes.

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1. Introduction

Light olefins such as ethene, propene, and butenes are important reactants widely used in numerous industrial processes. The current method of production is via steam cracking of a hydrocarbon feedstock [1] and although this process is widely applied, it has numerous shortcomings such as the high endothermicity of the reaction, long residence times, and the production of coke on the reactor walls requiring periodic maintenance. In order to alleviate some of these issues, several studies have been performed to find an alternative catalytic route to the production of alkenes. In this regard, the partial oxidation of ethane has been investigated and shows considerable potential [2–18].

The products formed in this reaction are strongly dependent on the reaction conditions, such as the hydrocarbon:O₂ ratio, the catalyst used, and the temperature, and includes oxidative dehydrogenation of ethane to ethene (ODH), partial oxidation of ethane to syngas (CO/H₂) and the total oxidation of ethane to carbon dioxide and water. Despite the

number of studies performed on this reaction, the mechanism is still not fully understood.

A number of investigations have reported high yields of ethene and propene obtained by oxidative dehydrogenation over Pt catalysts using very short contact times [11–18]. For example, Huff and Schmidt achieved selectivities to ethene up to 70% at conversions above 80% on Pt-coated foam monoliths, operating at contact times between 1 and 10 ms and high reaction temperatures (> 700 °C) [13,14]. In these studies, Huff and Schmidt excluded homogeneous gas-phase reactions and a surface mechanism was suggested to explain the formation of ethene and propene. However, several other studies have shown that the high-temperature production of olefins could also be explained by the onset of homogeneous gas phase reactions [15–18]. Lødeng et al. found that oxidative dehydrogenation mainly proceeded in the gas phase and that the role of the Pt and Pt–Rh gauze catalysts used was to facilitate ignition of the reactants and therefore rapidly heat the reaction mixture [17,18]. This is in agreement with recent studies over a Pt monolith catalyst also indicating the importance of homogeneous gas-phase reactions at high temperatures [19].

In order to investigate the role of the catalyst, we have used a Temporal Analysis of Products (TAP) reactor [20] to probe the surface catalytic reactions during the oxida-

* Corresponding authors.

E-mail addresses: c.hardacre@qub.ac.uk (C. Hardacre), holmen@chemeng.ntnu.no (A. Holmen).

tive dehydrogenation of ethane. The TAP system uses gas pulses on the millisecond timescale in such a way as to exclude gas-phase reactions and thus can reveal details of surface reaction mechanisms. For example, it is possible to investigate whether both heterogeneous and homogeneous processes contribute to the ODH reaction; i.e., is the catalyst only used to provide energy through the oxidation of part of the ethane to facilitate homogeneous reaction or is the catalyst involved in the generation of surface radicals that further desorb and react in the gas phase, as has been observed for partial oxidation of propane [21,22]? Recent TAP studies of methane oxidation reactions over noble metal-based catalysts [23–28] as well as oxidative dehydrogenation of ethane over a Ni catalyst [29] were found successful in revealing useful information about reaction mechanisms taking place over these catalysts. In methane oxidation reactions, Mallens et al. [26] showed that oxygen was present in three different forms: platinum oxide, dissolved oxygen, and chemisorbed oxygen, each of them being involved in a specific step of the reaction network. Carbon monoxide and hydrogen were produced directly from the reaction of the methane with the oxygen present as platinum oxide followed by subsequent platinum reoxidation. A Mars–van Krevelen redox-type reaction scheme was postulated. Similar results were obtained by Fathi et al. [28] with a Pt gauze catalyst. They showed that carbon monoxide and hydrogen could be produced with high yields directly from methane and bulk oxidized platinum. At low surface oxygen concentrations, the bulk oxygen diffused back to the platinum surface to react with surface carbon. In this case, the surface lifetimes of carbon monoxide and hydrogen were much shorter than the oxygen diffusion time and no consecutive oxidation reaction occurred.

Schuurman et al. studied the oxidative dehydrogenation of ethane over unsupported Ni catalysts [29] under TAP conditions and revealed that the oxygen involved in the reaction was a species irreversibly held by the catalyst at 300 °C, possibly as O⁻. Detailed analysis of their data revealed that ethane was irreversibly adsorbed and that the ethene formed through instantaneous reaction of the ethane surface intermediate. The CO₂ observed was proposed to originate from a parallel-consecutive scheme involving desorption/readsorption of ethene and consecutive surface reaction of the adsorbed ethene to adsorbed CO₂ precursor in equilibrium with CO₂.

Here, we report a comparison of the partial oxidation reactions of ethane over a Pt/Al₂O₃ catalyst under steady-state conditions in a conventional microreactor and under transient conditions using a TAP reactor. The steady-state experiments were performed over a wide range of temperatures 100–700 °C while the TAP experiments were focused in a temperature range (350–550 °C) corresponding to the ignition region observed in the steady-state experiment.

2. Experimental

2.1. Catalyst preparation and characterization

2.1.1. Pt/monolith

A cordierite ceramic monolith (2MgO · 2Al₂O₃ · 5SiO₂; Corning) was used as a support. It consisted of square straight channels with cell density of 62.2 cells cm⁻². Cylindrical pieces of the monolith (10 mm long and 15 mm outer diameter) were washcoated by dipping them into a dispersion of Disperal P2 (specific surface area: 286 m² g⁻¹) (Condea) composite of Al₂O₃. The dispersion was prepared by stirring the powder in deionized water at 60 °C for 30 min. The washcoated monoliths were dried in an oven at 120 °C for 4 h. The monolith was calcined in a flow of air (42 cm³ min⁻¹) at 550 °C for 4.5 h. The specific surface area of the washcoated cordierite monolith was 23.2 m² g⁻¹.

The deposition of the Pt was performed by impregnating the washcoated monolith with an aqueous solution of Pt(NH₃)₄(NO₃)₂ (Alfa products). The impregnated monoliths were then dried at 80 °C in an oven for 4 h and calcined at 550 °C in a flow of air for 4.5 h. The final loading of Pt was found to be ca. 1 wt% by ICP.

2.1.2. Pt/γ-Al₂O₃

This catalyst was prepared by incipient wetness impregnation of γ-Al₂O₃ (Alfa products) by a Pt(NH₃)₄(NO₃)₂ (Alfa products) aqueous solution (0.028 M). The pellets were crushed to a particle size between 300 and 710 μm and, after impregnation, were dried for 12 h at 150 °C in an oven and calcined at 600 °C for 10 h. The specific surface area of the γ-Al₂O₃ support was 198 m² g⁻¹. The Pt loading was found to be 0.5 wt% by ICP and the Pt dispersion, measured by H₂ pulse chemisorption, was 59.8%.

2.2. Conventional flow apparatus

Oxidation reactions of ethane were carried out in a conventional flow apparatus at atmospheric pressure between 100 and 700 °C. The experimental setup has been described in detail elsewhere [30].

The catalyst consisting of a 1% Pt-coated monolith was sandwiched between two inert monolith pieces acting as radiation shields (each 10 mm long and 15 mm outer diameter). The reaction mixture contained 15.4% ethane, 7.7% O₂ (balance argon) with a total flow rate of 2000 N cm³ min⁻¹. The ratio ethane/oxygen of 2:1 corresponded to the stoichiometric ratio according to the oxidative dehydrogenation reaction.

During a typical experiment, the catalyst was first reduced in a flow of hydrogen at 250 °C, then the reactor was cooled down to 100 °C in a flow of argon, and the reaction mixture was introduced into the reactor. The reactor temperature was then increased in steps of 25 °C from 100 to 600 °C. At each temperature, a sample of the reaction mixture was analyzed by online GC. Two water-cooled condensers were

installed at the reactor outlet for the removal of water from the product stream. Consequently, the reactant conversions and product selectivity were calculated from the “dry gas” reactor effluent. The residence time in the reactor was estimated according to the method described by Fathi et al. [31] and was found to be 0.04 s through the monolith piece. All gases used were 99.99% purity and were supplied by AGA.

2.3. TAP setup and experimental procedure

The TAP experiments were performed in a TAP-I reactor (Autoclave Engineers) using a stainless-steel microreactor (41 mm long and 5.5 mm inner diameter). A charge of 0.1 g catalyst diluted with quartz particles was used. Quartz particles were also placed before and after the catalyst bed to act as heat radiation shields. All particles had a size of 250–450 μm . The temperature of the reactor was measured by a thermocouple positioned in the center of the catalyst bed. Reactants and products were recorded at the reactor outlet by a UTI100C quadrupole mass spectrometer.

Prior to each reaction, the catalyst was reduced at 250 °C for 1 h in flowing hydrogen at 1 atmosphere and then heated up to the desired reaction temperature (350, 450, or 550 °C) under vacuum. For studies on an oxidized catalyst, the surface was saturated with oxygen at the desired temperature (350, 450, or 550 °C) and then exposed to consecutive ethane pulses. For experiments over the reduced and oxidized samples, the pulsing of oxygen and ethane was repeated until the ethane pulses exiting the reactor were constant in shape and intensity. For experiments consisting of alternate oxygen and ethane pulses, the catalyst was exposed to sets of alternating pulses of oxygen/ethane with a delay between oxygen and ethane equal to 1.0 s. After 200 oxygen and ethane pulses, sets of altering pulses with shorter delays were performed. The ratio between oxygen and ethane was 1:1 in all experiments. For experiments utilizing simultaneous pulsing of oxygen and ethane, a ratio ethane:oxygen 2:1 was used, corresponding to the stoichiometry of the oxidative dehydrogenation reaction.

In all experiments, oxygen and ethane pulses were diluted by argon in a ratio of 1:1 and masses characteristic of all reactants and possible products (CO, CO₂, C₂H₄, C₂H₆, CH₄, H₂, H₂O) were followed. All gases used were > 99% purity and were supplied by BOC.

The variation in each reactant and product was extracted from the output from the mass spectrometer using standard fragmentation patterns and sensitivity factors.

In the Knudsen diffusion flow regime, the product pulse shape is independent of the pulse intensity [20]. Consequently, to ensure that the flow in the reactor was in the Knudsen diffusion regime for all experiments and in order to set the parameters for the pulsing valves accordingly, a preliminary test was performed. It consisted of injecting successive pulses of pure Ar with decreasing intensities. When the product pulse shapes were independent of the intensity this indicated that the Knudsen diffusion regime was reached.

3. Results

3.1. Oxidative dehydrogenation of ethane in the conventional flow apparatus

Fig. 1a shows the conversion of reactants and reactor temperature as a function of the furnace temperature. Figs. 1b and 1c show the product distribution variation with respect to the reactor temperature following the introduction of ethane and oxygen over the monolith-supported catalyst. No conversion of ethane and oxygen was observed below a furnace temperature of 150 °C; however, above 200 °C, a rapid increase in the conversion is observed together with a sharp increase in the reactor temperature corresponding to the ignition point of the ethane/air mixture (Fig. 1a). Above the ignition point, the ethane and oxygen conversion increased gradually with increasing temperature forming CO₂, CO, C₂H₄, CH₄, and H₂. The amount of CO₂ was found to decrease with increasing temperature, whereas both CO and H₂ gradually increased (Figs. 1b and c). Although not detected due to the presence of the water-cooled condensers, the remaining hydrogen mass balance from the reaction is likely to be water. Using this assumption, Fig. 1c also shows that the water decreases with increasing reactor temperature. Over the temperature range studied, both CH₄ and C₂H₄ were formed at a low but significant level, approximately 1.5 and 3.0%, respectively.

3.2. Ethane pulsing on an oxygen-saturated catalyst in the TAP reactor

An examination of the reoxidation behavior of the catalyst and its oxygen capacity was performed by pulsing oxygen over the prereduced catalyst. As expected, at all temperatures, the intensity of the oxygen peak gradually increased before stabilizing, showing progressive saturation by oxygen. However, the adsorption mode (reversible or irreversible) did vary with temperature. The average size of the “constant pulses” of oxygen observed after saturation of the catalyst was compared with model pulses of oxygen [20,32]. At 350 °C, the experimental pulse was very similar to the model, whereas at higher temperatures (450 and 550 °C) the pulses were broadened and their maxima shifted to a longer time leading to a crossover of the experimental and model curves. Fig. 2 shows a typical example at 450 °C. The shift in the intersection point and the maxima are consistent with reversible adsorption involving a fast adsorption step followed by a slow desorption [32].

The ratios of oxygen atoms adsorbed per total number of platinum atoms present in the catalyst ($N_{\text{O}}/N_{\text{Pt}}^{\text{total}}$) and per surface platinum atom ($N_{\text{O}}/N_{\text{Pt}}^{\text{s}}$) were evaluated and the results are summarized in Table 1. Clearly, the amount of adsorbed oxygen increases with increasing temperature. At low temperatures (≤ 450 °C), the ratio $N_{\text{O}}/N_{\text{Pt}}^{\text{s}}$ does not exceed 1, indicating that adsorption of oxygen is limited to the

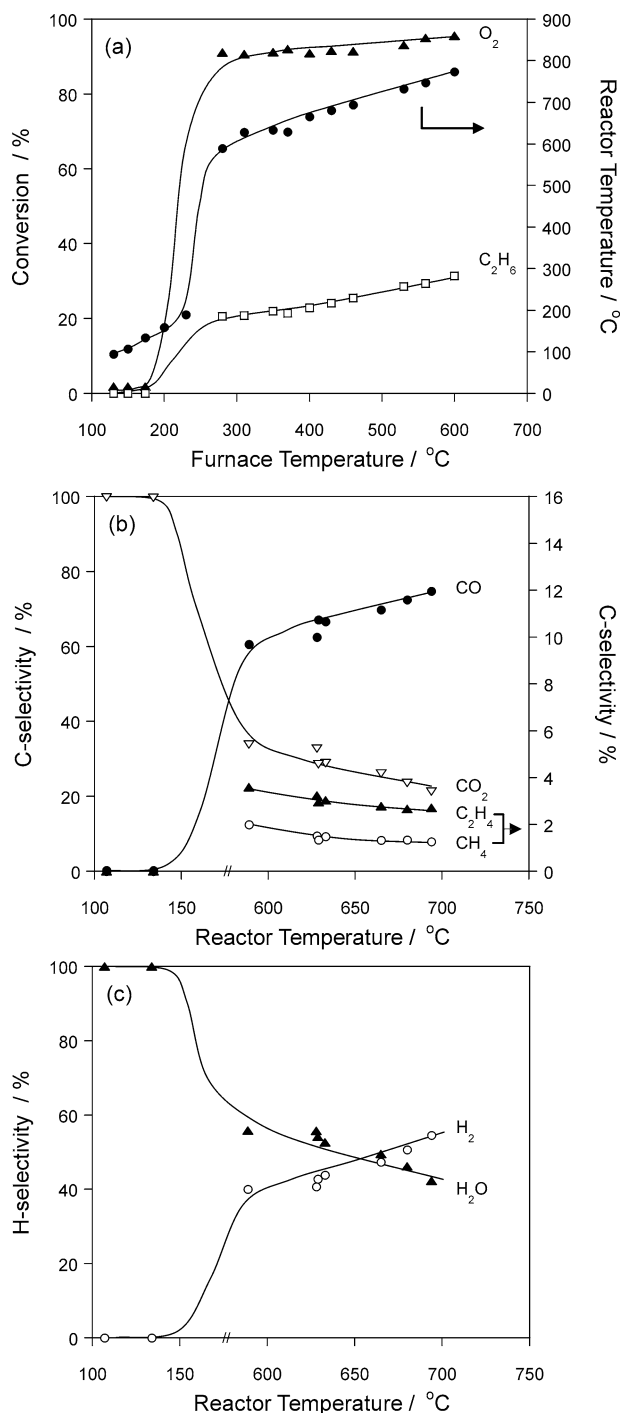


Fig. 1. Oxidative dehydrogenation of ethane in the conventional flow apparatus over the Pt monolithic catalyst showing the variation in (a) O₂ (▲), C₂H₆ (□), and reactor temperature (●) as a function of furnace temperature; (b) CO (●), CO₂ (▽), C₂H₄ (▲), and CH₄ (○); and (c) H₂ (○) and H₂O (▲) as a function of the reactor temperature using the flow rates, C₂H₆ (308 N cm³ min⁻¹), air (733 N cm³ min⁻¹), and Ar (959 N cm³ min⁻¹), and a total flow rate of 2000 N cm³ min⁻¹.

Pt surface. At higher temperatures, the ratio $N_{\text{O}}/N_{\text{Pt}}^{\text{S}}$ is significantly greater than 1, showing that the diffusion of oxygen into the subsurface region, i.e., bulk oxidation, occurs. These results are consistent with previous studies [33,34].

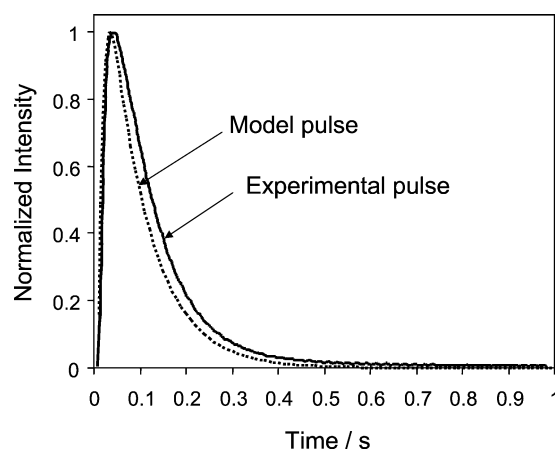


Fig. 2. Height-normalized intensities of model (dotted) and experimental (solid) pulses obtained during the oxygen pulsing at 450 °C over reduced Pt/Al₂O₃.

Table 1

Oxygen uptake on the reduced Pt/Al₂O₃, calculated ratios of $N_{\text{O}}/N_{\text{Pt}}^{\text{total}}$ and $N_{\text{O}}/N_{\text{Pt}}^{\text{S}}$, and ethane reacted over the oxidized and prereduced catalyst at 350, 450, and 550 °C

Temperature (°C)	O ₂ uptake (molecules)	$N_{\text{O}}/N_{\text{Pt}}^{\text{total}}$	$N_{\text{O}}/N_{\text{Pt}}^{\text{S}}$	C ₂ H ₆ reacted (molecules)	
				Oxidized	Reduced
350	2.33×10^{17}	0.15	0.26	3.52×10^{16}	1.26×10^{16}
450	7.55×10^{17}	0.49	0.83	8.01×10^{17}	4.36×10^{17}
550	3.80×10^{18}	2.46	4.17	9.72×10^{17}	5.41×10^{17}

Wang and Yeh showed that a surface oxide layer was formed following adsorption of oxygen on Pt/Al₂O₃, which prevented diffusion of oxygen into the bulk of the platinum. The penetration of adsorbed oxygen ions was limited below 427 °C; however, complete oxidation forming a stable oxide was observed between 427 and 627 °C [33,34].

Having saturated the Pt surface with oxygen, subsequent pulsing of ethane showed that the pulses were completely consumed initially; however, once detected, the ethane pulses gradually increased in intensity before stabilizing. The number of pulses required before ethane was observed was found to be strongly dependent on the reaction temperature with ethane pulses only detected after 10 pulses at 350 °C, 110 pulses at 450 °C, and 130 pulses at 550 °C. At all temperatures, in contrast to the behavior with the oxygen pulses described above, the shapes of the ethane pulses were similar to the model and the flow curve was situated inside the standard model curve, indicating irreversible adsorption/reaction [32]. Table 1 also summarizes the number of ethane molecules that reacted at each temperature. As expected, the number of ethane molecules that reacted increased with increasing temperature.

Fig. 3 shows that on pulsing ethane, methane, carbon monoxide, and hydrogen were the major products formed. The production of hydrogen increased with increasing temperature from 350 to 550 °C, while methane was produced predominantly at 450 °C. It is important to note that no

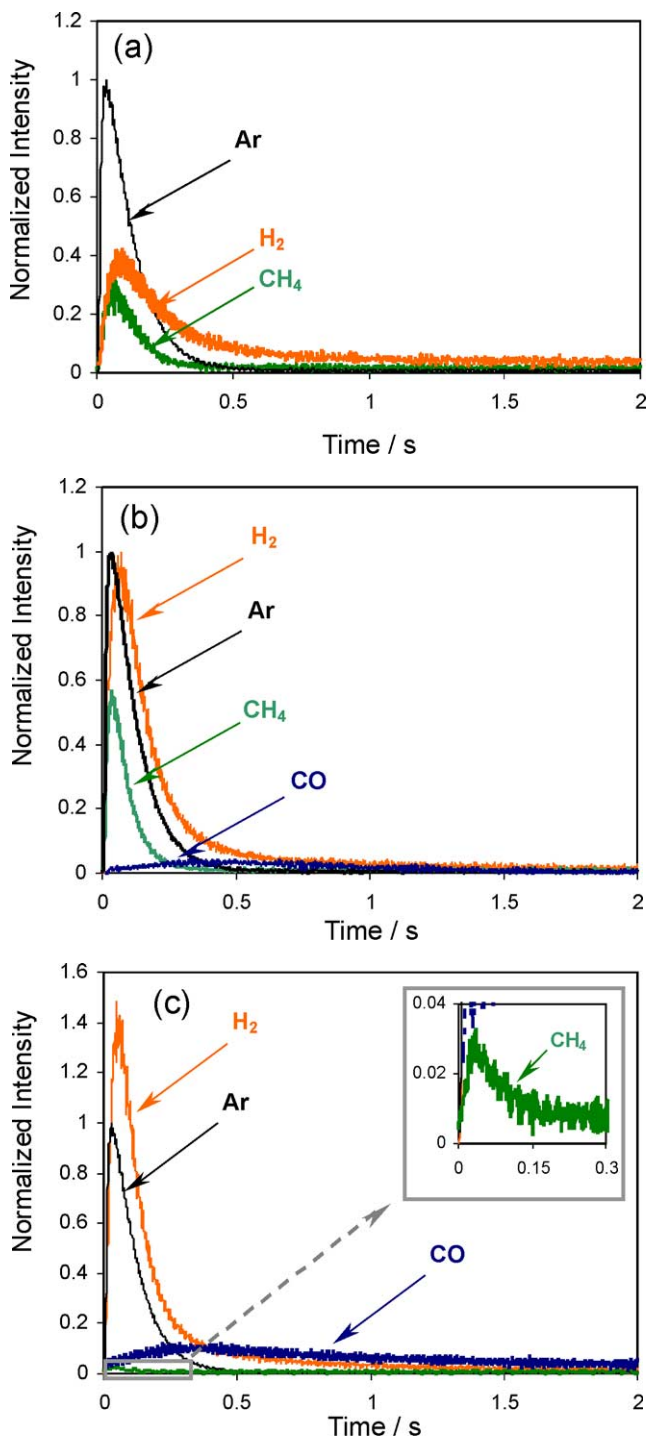


Fig. 3. Variation in the reactants and products during the pulsing of ethane after oxygen uptake on the reduced Pt/Al₂O₃ at (a) 350 °C, (b) 450 °C, and (c) 550 °C. The pulses are normalized with respect to the argon pulse. All the ethane is consumed at each temperature and the ethane trace is not shown for clarity.

ethene was detected at any reaction temperature under these transient conditions.

Both methane and hydrogen were formed during the first pulses at all temperatures; however, the amount of these products decreased sharply with increasing ethane pulsing

before reaching a low but steady-state intensity between 100 and 250 pulses at 350 and 550 °C, respectively. Carbon monoxide was also detected during the first ethane pulses but only at 450 and 550 °C. It is worth noting that, although the pulsing of ethane was performed on a catalyst fully saturated with oxygen, carbon monoxide was the only oxygen-containing product formed.

3.3. Ethane pulsing over a reduced catalyst in the TAP reactor

When pulsing ethane over a reduced catalyst, the amount of ethane adsorption/reaction was found to increase with increasing temperature. Methane and hydrogen were observed as the main products, but, as expected, no carbon monoxide was detected. A similar variation in hydrogen and methane formation as in the case of the oxidized sample was observed, with the amount of hydrogen increasing with increasing temperature and the methane showing a maximum at 450 °C. However, at all temperatures, the reaction of ethane and formation of methane and hydrogen were always significantly lower in the case of the reduced catalyst. The ethane conversion results for each temperature are compared in Table 1. Once again, ethene was not detected at any reaction temperature.

3.4. Alternating pulsing of oxygen/ethane in the TAP reactor

Fig. 4 shows the results from alternating pulses of oxygen and ethane. It should be noted, that although the pulses had a 1.0 s delay, changes in the delay between 0.5 and 2.0 s did not affect the results significantly. During all pulses, no oxygen was observed over the reduced Pt catalyst at all temperatures even after extended oxygen/ethane pulse cycles. Similarly above 350 °C, no ethane was detected, and at 350 °C only small amounts of unreacted ethane were observed.

During the ethane pulses, methane, hydrogen, and carbon monoxide were formed with the hydrogen production increasing with increasing temperature and methane showing a maximum at 450 °C. Carbon monoxide was formed above 350 °C and increased with increasing temperature. During the pulsing of oxygen, only carbon dioxide was observed but mainly at 350 °C. Once again, no ethene was observed during either type of pulse at any temperature.

3.5. Simultaneous pulsing of ethane and oxygen in the TAP reactor

Simultaneously pulsing ethane and oxygen lead to little adsorption/reaction of ethane at 350 °C; however, significant reaction/adsorption was observed at 450 and 550 °C. As shown in all the scenarios described above, methane and hydrogen were formed with hydrogen formation greatest at high temperature and the methane formation reach-

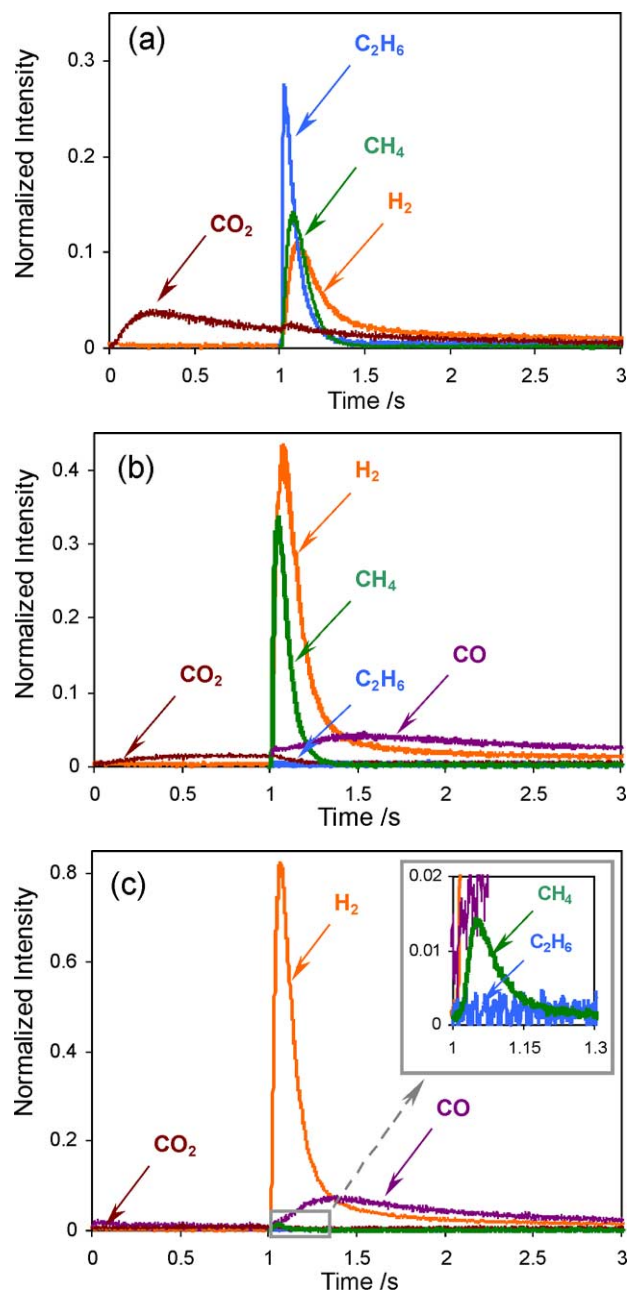


Fig. 4. Variation in the reactants and products during alternating pulsing of oxygen/ethane over the reduced Pt/Al₂O₃ with a 1.0-s delay at (a) 350 °C, (b) 450 °C, and (c) 550 °C. The pulses are normalized with respect to the argon pulse, not shown for clarity. All the oxygen is consumed at each temperature and the oxygen trace is also not shown for clarity.

ing a maximum at 450 °C. The product distribution found was comparable to that found for reaction over the oxygen-saturated catalyst. No ethene was detected at the reaction temperatures studied.

4. Discussion

Comparing the results described above, the most striking feature is the absence of ethene formation during the

experiments performed under all conditions using the TAP reactor whereas during the conventional flow investigation, ethene was detected above 200 °C. This is significant since, although it is not clear what the exact oxidation state of the platinum is under flow conditions, the TAP results clearly show that whether the catalyst is fully reduced, partially oxidized, or fully oxidized, dehydrogenation of ethane does not occur. Therefore as the TAP reactor excludes gas-phase reactions, these results strongly suggest that at low catalyst temperatures, below 600 °C, any ethene is formed homogeneously and not on the catalyst surface. The role of the catalyst may simply be to heat the reaction mixture in the gas phase via the exothermic surface reaction between ethane and oxygen and facilitate the homogeneous reaction in the catalyst void volume at this locally elevated temperature.

This conclusion is in agreement with other studies [15–18], in particular with those of Lødeng et al. [17,18]. Burch and Crabb also showed that oxidative dehydrogenation could proceed without a catalyst in an empty quartz tube reactor [8]. For an ethane to oxygen ratio of 2:1 and at temperatures as low as 550 °C, although the ethane conversion was small, ~ 3.6%, selectivities for ethene as high as 95.9% were achieved. At higher temperatures, the conversion increased but the selectivity decreased because of the increase in CO formation. The homogeneous reaction was reduced, however, by filling the reactor with quartz wool or SiC: radical termination reactions via the surface occur and ethene is not formed. In the flow system studied here, termination reactions should be limited since the catalyst was supported on a monolith. In addition, heat transfer from the catalyst is likely to be poor which should increase the likelihood of strong localized heating within the monolith channels, thus allowing gaseous reactions to take place.

While it is likely that the surface does not directly form ethene, it is still important to understand the surface processes, which give rise to the large exotherm observed. From the TAP experiments, it is clear that although oxygen increases the reaction of ethane on the catalyst, the presence of oxygen is not required to activate the ethane even at low temperatures. Both hydrogen and methane are formed over the reduced catalyst during the TAP experiments, suggesting that dissociative adsorption of ethane on the catalyst leads to C–H and C–C bond cleavage followed by H–H and C–H recombination. This hypothesis appears to be confirmed by the observed increase and decrease of hydrogen and methane production, respectively, at high temperature. This variation can be explained using a mechanism proposed by Cortright et al. [35] who reported that, although the formation of highly dehydrogenated C₂H_{x,ads} was shown to be favored at high temperature, the major C–C cleavage pathways occurred via less dehydrogenated activated complexes based on ethyl (C₂H₅) and ethylidene (CHCH₃) species, for example. Consequently, an increase in the reaction temperature effectively

leads to an increase in hydrogen production due to greater hydrogen abstraction from the adsorbed ethyl group. However, increasing temperature also decreases the probability of C–C cleavage due to the formation of the highly dehydrogenated complexes. The maximum shown in methane formation can therefore be explained by the balance between having a sufficiently high temperature for an initial hydrogen abstraction and too high a temperature for further dehydrogenation. Sufficient dehydrogenation activity leads to the formation of surface carbon and progressive catalyst deactivation as observed during the pulsing. The variation in the formation of methane at these temperatures can only be understood if a surface reaction is invoked. Equilibrium gas-phase calculations show no such variation with temperature [36].

The formation of CO in the presence of oxygen with an increase in the H₂ and methane production suggests that the role of adsorbed oxygen is simply to clean off surface deposited carbon and free up the active surface sites allowing further ethane adsorption to occur. On pulsing ethane over the oxygen-saturated catalyst, a two-stage deactivation was observed: initially, a slow deactivation, possibly due to slow depletion of the preadsorbed oxygen through reaction with the surface carbon, and then a second, more rapid, deactivation process through carbon deposition on the “rereduced” or oxygen-depleted catalyst. Therefore the presence of oxygen on the surface of the catalyst only delays the strong deactivation taking place through carbon deposition. Whereas simultaneous pulsing of ethane and oxygen shows a similar loss in activity, alternating the oxygen and ethane pulses allows the catalyst to maintain high activity throughout the duration of the experiment. In the latter case, the oxygen pulse has sufficient time to react with surface carbon and prevents substantial carbonaceous deposits building up. In the simultaneous pulsing, the dehydrogenation reaction outweighs the clean off process and deactivation occurs. From this observation, alternative pulsing may be a way of maintaining catalyst activity under flow conditions but this requires further investigation.

In the TAP experiment using alternating pulses of O₂ and ethane, the absence of CO at 350 °C is probably due to the low mobility of the oxygen on the platinum surface. Since oxygen is likely to preferentially react with hydrogen and since at this temperature the hydrogen formed during the ethane pulse has a low rate of desorption, hydroxy species are formed leaving the carbon deposit unreacted. Subsequently, during the oxygen pulse, the surface carbon oxidizes to form CO₂. In contrast, at 450 and 550 °C, both the rate of hydrogen desorption and the surface mobility of oxygen are sufficiently high to facilitate carbon oxidation during the ethane pulse to again form CO. The amount of carbon remaining on the surface during the oxygen pulse is low and neither CO nor CO₂ are observed.

5. Conclusion

This comparative study of oxidative dehydrogenation of ethane over Pt/Al₂O₃ catalysts, under conventional flow or TAP reactor conditions, has shown that ethene produced during the ODH of ethane at low temperatures in the flow microreactor is formed in the gas-phase and not via a surface reaction. This is in contrast to the production of methane which is thought to be formed on the catalyst. Trends in the deactivation behavior with temperature and surface oxygen concentration are consistent with a balance between successive dehydrogenation steps leading to the eventual formation of surface carbon and substantial loss in activity.

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References

- [1] L.F. Albright, B.L. Crynes, W.H. Corcoran, *Pyrolysis: Theory and Industrial Practice*, Academic Press, London, 1983.
- [2] Z. Dang, J. Gu, J. Lin, D. Yang, *Catal. Lett.* 54 (1998) 129.
- [3] D.W. Flick, M.C. Huff, *J. Catal.* 179 (1998) 315.
- [4] J.M. Lopez Nieto, V.A. Zazhigalov, B. Solsona, I.V. Bacherikova, *Stud. Surf. Sci. Catal.* 130 (2000) 1853.
- [5] S. Wang, K. Murata, T. Hayakawa, S. Hamakawa, K. Suzuki, *Stud. Surf. Sci. Catal.* 130 (2000) 1829.
- [6] T. Chen, W. Li, C. Yu, R. Jin, H. Xu, *Stud. Surf. Sci. Catal.* 130 (2000) 1847.
- [7] S.A.R. Mulla, B.S. Uphade, V.R. Choudary, *Stud. Surf. Sci. Catal.* 113 (1998) 1023.
- [8] R. Burch, E.M. Crabb, *Appl. Catal. A* 97 (1993) 49.
- [9] D.W. Flick, M.C. Huff, *Appl. Catal. A* 187 (1999) 13.
- [10] A.S. Bodke, D.A. Olschki, L.D. Schmidt, E. Ranzi, *Science* 285 (1999) 712.
- [11] M.C. Huff, I.P. Androulakis, J.H. Sinfelt, S.C. Reyes, *J. Catal.* 191 (2000) 46.
- [12] D.A. Goetsch, P.M. Witt, L.D. Schmidt, *Am. Chem. Soc. Div. Petrol. Chem.* 41 (1996) 150.
- [13] M. Huff, L.D. Schmidt, *J. Phys. Chem.* 97 (1993) 11815.
- [14] M. Huff, L.D. Schmidt, *J. Catal.* 149 (1994) 127.
- [15] A. Beretta, E. Ranzi, P. Forzatti, *Catal. Today* 64 (2001) 103.
- [16] A. Beretta, E. Ranzi, P. Forzatti, *Chem. Eng. Sci.* 56 (2001) 779.
- [17] R. Lødeng, O.A. Lindvåg, S. Kvisle, H. Reier-Nielsen, A. Holmen, *Stud. Surf. Sci. Catal.* 119 (1998) 641.
- [18] R. Lødeng, O.A. Lindvåg, S. Kvisle, H. Reier-Nielsen, A. Holmen, *Appl. Catal.* 187 (1999) 25.
- [19] B. Silberova, M. Fathi, A. Holmen, *Appl. Catal. A*, to appear.
- [20] J.T. Gleaves, J.R. Ebner, T.C. Kuechler, *Catal. Rev.-Sci. Eng.* 30 (1) (1988) 49.
- [21] D.J. Driscoll, K.D. Campbell, J.H. Lunsford, *Adv. Catal.* 35 (1987) 139.
- [22] C.C. McCain, G.W. Godin, *Nature (London)* 202 (1964) 692.
- [23] D. Wang, O. Dewaele, A.M.D. Groot, G.F. Froment, *J. Catal.* 159 (1996) 418.
- [24] E.V. Kondratenko, O.V. Buyevskaya, M. Soick, M. Baerns, *Catal. Lett.* 63 (1999) 153.

- [25] E.P.J. Mallens, J.H.B.J. Hoebink, G.B. Marin, *J. Catal.* 167 (1997) 43.
- [26] E.P.J. Mallens, J.H.B.J. Hoebink, G.B. Marin, *Catal. Lett.* 33 (1995) 291.
- [27] M. Soick, O. Buyevskaya, M. Hohenberger, D. Wolf, *Catal. Today* 32 (1996) 163.
- [28] M. Fathi, F. Monnet, Y. Schuurman, A. Holmen, C. Mirodatos, *J. Catal.* 190 (2000) 439.
- [29] Y. Schuurman, V. Ducarme, T. Chen, W. Li, C. Mirodatos, G.A. Martin, *Appl. Catal.* 163 (1997) 227.
- [30] K.H. Hofstad, O.A. Rokstad, A. Holmen, *Catal. Lett.* 36 (1996) 25.
- [31] M. Fathi, R. Lødeng, E.S. Nilsen, B. Silberova, A. Holmen, *Catal. Today* 64 (2001) 113.
- [32] J.T. Gleaves, G.S. Yablonskii, P. Phanawadee, Y. Schuurman, *Appl. Catal.* 160 (1997) 55.
- [33] C.B. Wang, C.T. Yeh, *Appl. Catal.* 209 (2001) 1.
- [34] C.B. Wang, C.T. Yeh, *J. Catal.* 178 (1998) 450.
- [35] R.D. Cortright, R.M. Watwe, B.E. Spiewak, J.A. Dumesic, *Catal. Today* 53 (1999) 395.
- [36] Data calculated using the HSC Chemistry Software, ÓA. Roine, Outokumpu Research Oy Peri, Finland, 1992.