

Reaction of Ethylene with Oxygen on a Pt/CeO₂ Catalyst

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A new pathway is suggested for the reaction of ethylene and oxygen. The catalyst used was Pt/CeO₂. The products obtained in addition to carbon monoxide, carbon dioxide, and water were methane and ethane which were formed by the hydrogenation of either carbon monoxide or ethylene. Electron spin resonance was used to show the role performed by lattice oxygen. © 1985 Academic Press, Inc.

INTRODUCTION

The catalytic oxidation of hydrocarbons in general and of olefins in particular provides perhaps one of the most interesting fields in heterogeneous catalysis. Complete oxidation is of interest in the removal of hydrocarbons to prevent air contamination while selective oxidation (1, 2) is an important step in various industrial processes. Platinum supported on alumina or silica is used in catalytic oxidations. The use of "nonclassical" supports may open new horizons and reveal new and different catalytic properties of platinum. The lanthanide oxides exhibit a rich variety of solid-state properties and, along with this versatility, both the low cost and availability make them interesting subjects in catalytic studies. The catalytic properties of these materials have been reviewed by Rosynek (3).

The reaction of ethylene with oxygen on 2% Pt/CeO₂ are reported in the present article. The analysis of gaseous products, in combination with ESR, has assisted in explaining the various steps of the catalytic reaction.

EXPERIMENTAL

Ceria used as the support was prepared

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by the citrate method (4). A solution of cerium(III) nitrate (Fluka 99.9%) in nitric acid (BDH Analar) and citric acid (BDH 99.7%) was prepared. The final ratio of Ce(III) to citrate was 1:1 molar. The solution was heated in a flash evaporator up to the stage when a honey-like mixture was obtained. A vitreous material was obtained by drying in vacuum (~1 Torr) at 343 K for 24 h. Cerium(IV) oxide is obtained by heating in air at 673 K for 90 h. Infrared and XRD showed no evidence for phases other than pure ceria. The platinum catalyst was prepared by impregnation of the support in a suitable volume of chloroplatinic acid (BDH 99.95%) and reduction in a hydrogen (Matheson 99.9%) stream for 3 h at 523 K. The amount of platinum in the catalysts was $1.9 \pm 0.1\%$ by weight as determined by atomic absorption. The BET(N₂) specific surface area was 50 ± 3 m²/g as measured by the conventional method (5) and the platinum dispersion was evaluated by hydrogen adsorption, a correction being made for the adsorption on the support; the H/Pt ratio so obtained was 0.35. ESR spectra were recorded at 77 K on a Varian 4502 X-band spectrometer; the experimental setup was described previously (6).

Ethylene (Matheson 99.5%) was further purified by vacuum distillation. Oxygen (Matheson 99.99%) was used as received. Mixtures of ethylene and oxygen were prepared and diluted in helium (Matheson

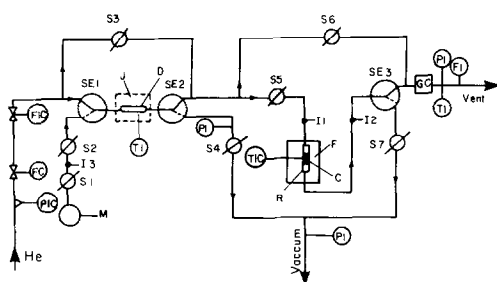


FIG. 1. Flow diagram of the pulse reactor. M, Reaction mixture; J, air jacket; D, calibrated doser; F, furnace; R, reactor; C, catalyst; GC, gas chromatograph; $I_1 \rightarrow I_3$, capillary connection joints; $S_1 \rightarrow S_7$, vacuum valves; $SE_1 \rightarrow SE_3$, three-way selection valves; FIC, flow indication and control; PIC, pressure indication and control; TIC, temperature indication and control.

99.995%) previous to the reactions. Reactions were performed in a static quartz reactor (approx. vol. 25 cm³) and in a pulse reactor (Fig. 1). As a routine procedure, the catalyst was activated by evacuation at $\sim 10^{-6}$ Torr (1 Torr = 133.33 N m⁻²) at 773 K for 3 h. In the static reactor ~ 50 mg of catalyst were activated and then exposed to the reaction mixture and subsequently heated to the appropriate temperature. Small gaseous samples were withdrawn, at established intervals, and injected into a gas chromatograph directly connected to the reactor. In the pulse reactor ~ 20 mg of the catalyst was used and activated "in situ." In a typical experiment, helium was flowed through the reactor, the reaction mixture (M) was introduced into the previously evacuated doser (D), and temperature and pressure were determined. By appropriate manipulation of the vacuum valves the pulse in D was injected through the catalyst into the gas chromatograph (GC). A similar procedure permitted the analysis of the prereacted mixture. The connection pipes in the reactor were kept at ~ 373 K with a heating tape to prevent the condensation of water or other vapors. Typical pulses contained 1 to 10 μ mol of mixture or pure gases. Pressure at the inlet of the reactor was ~ 1750 Torr and at the outlet ~ 700 Torr. Reactants and products were analyzed using a Gow-Mac 24-101

thermal conductivity cell coupled to a Gow-Mac 24-510 power supply/temperature controller. The gases and vapors were separated by two columns of Porapak (Q or R), with column 1 at 367–373 K and column 2 at 190 K (solid carbon dioxide/acetone slush). Both branches of the thermal conductivity cell were used alternatively as detector or reference. A Varian Mat 311 mass spectrometer was used for the analysis of reactants and products.

RESULTS

The reactions between oxygen and ethylene were carried out in the static and pulse reactor in the temperature range 373–673 K. Pressures were between 150 and 500 Torr and the partial pressure of oxygen and ethylene was less than 40%. The diluent gas was helium.

Reaction at Temperatures Higher than 573 K

The products obtained in this temperature range were carbon dioxide, methane, ethane, and carbon monoxide. Typical results for the static reactor are presented in Table 1 and Fig. 2 (at 623 K). From the results it may be observed that:

(1) The ratio $n_{CO_2}/n_{C_2H_4}^0$ increases rapidly, while the ratio $n_{C_2H_6}/n_{C_2H_4}^0$ increases at the beginning and then stays almost unchanged, as the concentration of C_2H_4 becomes low.

(2) CO is observed only in very low concentrations, after ~ 30 min of reaction,

TABLE I

Reaction between Ethylene and Oxygen over Pt/CeO₂ in a Static Reactor at 623 K and 150 Torr Total Pressure (15% C₂H₄, 29% O₂ in Helium)

Time of reaction (min)	Gas composition (%) ^a					
	C ₂ H ₄	O ₂	CO ₂	CO	CH ₄	C ₂ H ₆
12	13	8.0	67	—	5.3	6.4
30	3.0	0.3	75	0.7	14	6.4
43	—	—	76	2.0	17	5.3
61	—	—	74	2.2	19	4.4

^a Mixture of dry gases ± 0.5 .

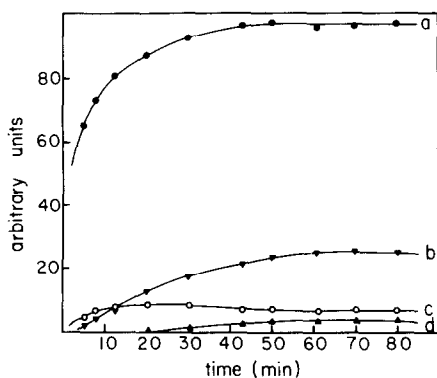


FIG. 2. Reaction of ethylene with oxygen in the static reactor at 623 K and 150 Torr (15% C₂H₄, 29% O₂ in He). (a) $n_{\text{CO}_2}/n_{\text{C}_2\text{H}_4}^0$; (b) $n_{\text{CH}_4}/n_{\text{C}_2\text{H}_4}^0$; (c) $n_{\text{C}_2\text{H}_6}/n_{\text{C}_2\text{H}_4}^0$; (d) $n_{\text{CO}}/n_{\text{C}_2\text{H}_4}^0$; ($n_{\text{C}_2\text{H}_4}^0$ = initial moles of C₂H₄).

when concentrations of CO₂ and CH₄ are relatively high, while C₂H₄ and O₂ have almost disappeared.

Ethylene was also reacted on the catalyst but without the presence of gaseous oxygen and the same results were obtained in this temperature range.

Reaction at Temperatures below 573 K

It was found that at temperatures below 573 K the reaction between ethylene and oxygen results in complete oxidation to carbon dioxide and water (Fig. 3, Table 2).

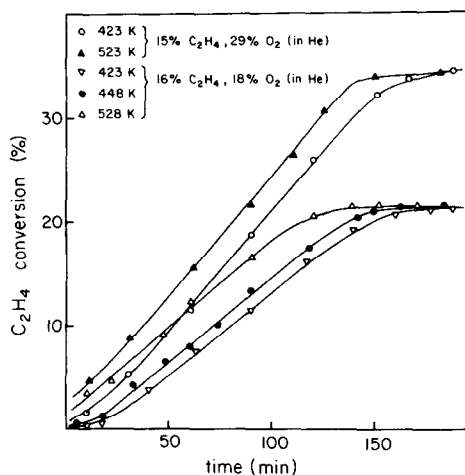


FIG. 3. Reaction of ethylene with oxygen in the static reactor at temperatures lower than 573 K and 150 Torr total pressure.

TABLE 2

Reaction between Ethylene and Oxygen over Pt/CeO₂ in the Static Reactor, at 448 K, 150 Torr Total Pressure (16% C₂H₄, 18% O₂ in Helium)

Time of reaction (min)	Gas composition (%) ^a		
	C ₂ H ₄	O ₂	CO ₂
5	62	37	0.4
17	63	36	1.3
32	61	34	5.5
72	74	10	17
117	69	1.3	29
162	65	0	35

^a Mixture of dry gases ± 0.5 .

Ethane, methane, and carbon monoxide were not detected under these conditions. In the absence of gaseous oxygen no gaseous products were observed by gas chromatography.

Experiments in the Pulse Reactor

The injection of various mixtures of ethylene and oxygen at temperatures between 423 and 673 K yield carbon dioxide and water. The conversion of ethylene decreases with the first few pulses and then stays almost constant for at least 30 pulses (Fig. 4). Ethane and methane could be obtained only at very low flow rates (i.e., higher residence time) accompanied with carbon monoxide and carbon dioxide. Under these flow rate

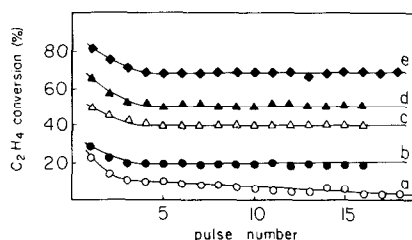


FIG. 4. Reaction of ethylene with oxygen in the pulse reactor at 46 ml(STP)/min. (a) pulses of pure ethylene at 573 K; (b) pulses of a 1:1 mixture C₂H₄:O₂ at 573 K; (c) pulses of a 1:2 mixture C₂H₄:O₂ at 573 K; (d) pulses of a 1:3 mixture C₂H₄:O₂ at 473 K; (e) pulses of a 1:3 mixture C₂H₄:O₂ at 573 K.

TABLE 3
Experiments in the Pulse Reactor, with Pure Gases Injected on to the Catalyst

Pulse injected	Preceding conditions: vacuum activation (V.A.) or preceding pulse	Gases identified by GC	Temperature of catalyst (K)	Flow rate [cm ³ (STP)/min]	Material balance		Basis for the material balance ^a
					μmol ± 0.2 In	Out	
C ₂ H ₄	V.A.	C ₂ H ₄ , CO ₂ , CO, CH ₄ , C ₂ H ₆	573	50	2.0	1.6	C
C ₂ H ₄	V.A.	C ₂ H ₄ , CO ₂ , CO, CH ₄ , C ₂ H ₆	623	50	2.1	1.9	C
O ₂	V.A.	O ₂	623	51	2.5	1.7	O
O ₂	O ₂	O ₂	623	51	2.3	2.3	O
O ₂	C ₂ H ₄	CO ₂ , O ₂	623	51	2.3	1.2	O
H ₂	C ₂ H ₄	H ₂ , traces C ₂ H ₆	623	50	—	—	—

^a C, carbon balance; O, oxygen balance.

conditions the chromatographic separation is very difficult in the pulse experiments, making this quantitative analysis very uncertain.

When ethylene was injected through the catalyst at temperatures higher than 573 K *in the absence of gaseous oxygen*, the activity of the catalyst decreased continuously (Fig. 4a). The products observed were carbon dioxide, carbon monoxide, methane, and ethane (Table 3). At temperatures below 573 K no reaction was observed.

When oxygen was injected after activation, it was partially retained on the catalyst.

Injection of oxygen pulses after ethylene pulses yielded carbon dioxide.

Injection of hydrogen pulses after ethylene gave only traces of ethane.

Reactions on CeO₂

Similar experiments to those described above were carried out on CeO₂ without platinum. The reaction was complete oxidation to carbon dioxide and water over *the whole temperature range*. Methane, ethane, and carbon monoxide were not observed in this case.

ESR

The vacuum activation of the Pt/CeO₂ at 773 K results in the appearance of a signal at $g = 2.004$ (7).

This signal grows with time. Gas chromatographic analysis shows that the gas evolved after the preliminary activation is oxygen. The signal at $g = 2.004$ grows at this temperature in parallel with the evolution of the oxygen.

It was observed that the $g = 2.004$ signal grew when the catalyst was heated in ethylene. When the catalyst was heated in a mixture of ethylene and oxygen, the growth of the signal depended on the amount of oxygen in the mixture.

Four mixtures were used, having the following ratios of oxygen to ethylene: 3:1 (stoichiometric relation for complete oxidation), 2:1, 1:1, and 0:1. The change in the signal at $g = 2.004$ was recorded. The experiments were performed at 573 K. The mixtures of the gases or the ethylene alone were heated after quenching to 77 K. No change in the intensity of the $g = 2.004$ signal was observed when the stoichiometric mixture of 3:1 was reacted (Fig. 5a). When the ratio was 2:1 (Fig. 5b) an increase in the signal was obtained and the same applied also with 1:1 mixture (Fig. 5c). When ethylene alone was used (Fig. 5d) the increase in the signal was the highest (80%). These experiments were carried out with a reproducibility of 5%.

It is interesting to point out that no paramagnetic species were observed as a result of the addition of ethylene or by its reaction with oxygen. However, the adsorption of

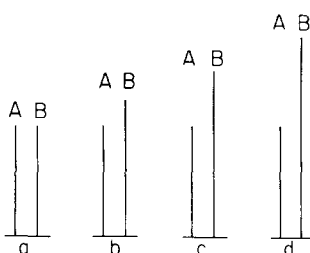


FIG. 5. Influence of the ratio C₂H₄:O₂ in the reaction mixture on the $g = 2.004$ signal. (A) After vacuum activation. (B) After adding the reaction mixture and heating at 573 K for 10 min. C₂H₄:O₂ mixtures: (a) 1:3; (b) 1:2; (c) 1:1; (d) 1:0.

oxygen on this catalyst leads to the formation of paramagnetic species of oxygen (7). This subject will not be discussed in this work.

Other Observations

Hydrogen. Small amounts were detected by gas chromatography during the reactions of ethylene and oxygen at temperatures higher than 573 K. It should be emphasized that hydrogen was always accompanied by carbon monoxide, carbon dioxide, methane, and ethane at temperatures higher than 573 K. The same applies when ethylene without oxygen reacted with the catalyst.

Ethane. Hydrogenation of ethylene to ethane took place on the Pt/CeO₂ catalyst at temperatures between 298 and 673 K and atmospheric pressure. Ethane was only obtained, however, at higher temperatures (>623 K); methane was observed in trace amounts (Fig. 6). Hydrogenations with deuterium gave C₂H₄D₂ as the main product together with small quantities of C₂H₃D₃ and C₂H₂D₄. No C₂D₅H or C₂D₆ were detected.

DISCUSSION

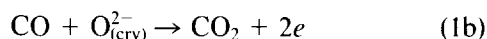
In the reaction of mixtures of ethylene and oxygen and of ethylene alone on the 2% platinum impregnated on ceria catalyst the products obtained at 573–673 K were methane and ethane in addition to carbon monoxide and carbon dioxide, and traces of hy-

drogen. The formation of ethane and methane from ethylene on metallic catalysts (8, 9) can be explained by a self-hydrogenation mechanism. We propose here a pathway for the formation of methane and ethane at temperatures higher than 573 K based on the formation of hydrogen by the secondary reaction of carbon monoxide and water. The hydrogen may react either with carbon monoxide or ethylene to produce methane and ethane, respectively. The results are explained on the basis of a redox mechanism via lattice oxygen (10). A general scheme describing this pathway is as follows, with lattice oxygen designated as O_(cry)²⁻:

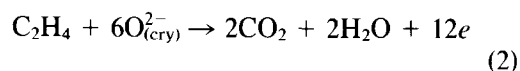
Reduction of the Catalyst



and

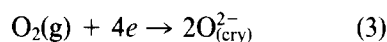


or



Oxidation of the Catalyst

In the presence of gaseous oxygen



Formation of Methane

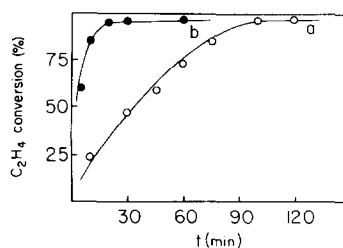
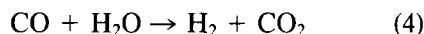
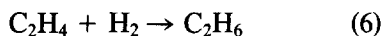


FIG. 6. Hydrogenation of ethylene over Pt/CeO₂ in the static reactor, 1:1 mixture of C₂H₄:H₂. (a) 298 K and 135 Torr; (b) 623 K and 238 Torr.

Formation of Ethane

One of the products obtained by the reaction of ethylene on this catalyst was carbon monoxide, accompanied by hydrogen and the other gases mentioned above. The hydrogen is obtained by Reaction (4). In a subsequent reaction, the hydrogen reacts with another molecule of carbon monoxide to form methane (Reaction (5)).

The water formed can react again with carbon monoxide by Reaction (4). The hydrogen can also hydrogenate ethylene to ethane (Reaction 6).

The possibility of formation of hydrogen and coke by the reaction



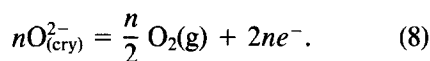
((C_2H_x)_{ads} = adsorbed ethylene residue)

cannot be neglected. However, when hydrogen was detected it was always accompanied by carbon monoxide, carbon dioxide, methane, and ethane, even in the absence of gaseous oxygen. As can be observed from the carbon balance (Table 2), small amounts of ethylene are retained on the catalyst. It is suggested here that the ethylene retained on the catalyst is mostly a result of the reaction of ethylene with lattice oxygen forming a surface adsorbed species which yields oxidation products by decomposition or further reaction with oxygen (12). As can be realized from Table 2, the retained ethylene reacts readily with oxygen pulses yielding oxidation products, while they are almost inactive to the reaction with hydrogen pulses. Also in the experiments of ethylene with deuterium, from the absence of C_2D_6 and $\text{C}_2\text{D}_5\text{H}$ it can be realized that the replacement of hydrogen by deuterium is rather low under these conditions. This may indicate that there is little dissociative adsorption of ethylene (Reaction (7)) and hence the extent of the self-hydrogenation reaction is small. If a hydrogenolysis reaction takes place at all its extent is very low as can be concluded from

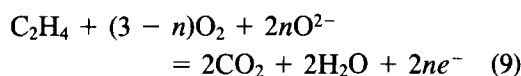
the blank reaction of hydrogen and ethylene at higher temperatures in which only trace amounts of methane were detected.

Carbon dioxide can be formed on this catalyst in two ways. The first is by the direct oxidation of the ethylene (Reaction (1a)), or by partial oxidation to carbon monoxide (Reaction (1b)) and subsequently the carbon monoxide may react with lattice oxygen (Reaction (2)), or with water (Reaction (4)). No reaction between carbon dioxide and hydrogen was observed (9).

It is suggested here that at temperatures higher than 573 K the reaction proceeds via a redox mechanism using oxidic oxygen of the cerium oxide support. When gaseous oxygen is available then there is a continuous supply of oxygen to replace the oxidic oxygen used (Reaction (3)). This is supported by the ESR results. The signal at $g = 2.004$ is formed when oxidic oxygen is abstracted from the ceria support and its intensity is proportional to the number of electrons trapped on the surface as described by



When ethylene without gaseous oxygen reacted at temperatures higher than 573 K the signal grew by ~80%. However, when a stoichiometric mixture of 3:1 (oxygen to ethylene) was reacted no change was observed in the signal (Fig. 5a) because all the oxidic oxygen used by Reactions 1 and 2 was replaced by oxygen (Reaction (3)). For the intermediary ratios of oxygen to ethylene the changes in the signal were larger than those presented in Fig. 5a because a partial replacement of the oxide ion by the gaseous oxygen took place. The reactions suggested can be described by



describing, in fact, a complete oxidation reaction. The ratio of ethylene to oxygen in this reaction is $1/(3 - n)$. In a stoichiometric

TABLE 4

Correlation of the Number of Moles of Electrons to 1 mol of Ethylene

Mole of electrons to 1 mol of ethylene in Reaction (8)	Increase in ESR signal at $g = 2.004$ ($\pm 5\%$)	Ratio ethylene to oxygen $1/(3 - n)$
0	0	1/3
4	27	1/2
8	50	1/1
12	80	Pure ethylene

reaction the value of n in Reaction (9) becomes zero and thus there is no change in the signal. When ethylene alone reacts with the catalyst then for every mole of ethylene six moles of electrons will be released (Table 4).

Additional evidence for the participation of lattice oxygen is found in the pulse experiments, which show clearly that pulses of ethylene injected without oxygen yield carbon monoxide and carbon dioxide in addition to methane and ethane (Table 3).

At temperatures lower than 573 K, no reaction was detected between ethylene and lattice oxygen. It can be realized from the results in the static reactor, when ethylene was in excess (Fig. 3), that the conversion of C₂H₄ remains constant when oxygen is no longer present in the gas phase. This may indicate that at temperatures below 573 K, the complete oxidation reaction of ethylene takes place with no participation of lattice oxygen of the ceria. This is in agreement with the results in the pulse reactor which show that no products were observed when ethylene was injected without oxygen, at temperatures below 573 K.

Reaction on CeO₂

Oxidation to carbon dioxide and water was the only reaction observed on CeO₂. Reactions (1) and (2) occur on CeO₂. However, carbon monoxide does not react with water or hydrogen under similar conditions and reacts only with lattice oxygen (Reac-

tion (1b)) producing carbon dioxide as a final product (9).

Support for the assumption that methane derives from the hydrogenation of carbon monoxide was obtained by direct reaction of both carbon monoxide with water and carbon monoxide with hydrogen on Pt/CeO₂ (9), when methane was obtained. In the reaction of carbon monoxide with water, hydrogen and methane were detected at temperatures higher than 573 K; therefore, methane and ethane were observed in the experiments with oxygen and ethylene only above this temperature. Reactions (4) and (5) do not occur on the CeO₂ support under similar conditions, and from this it may be concluded that these reactions take place on platinum sites or by a synergic effect of platinum acting in concert with the ceria support.

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