Decomposition and oxidation of $CH_3{}^{13}CH_2OH$ on Al_2O_3, Pd/Al_2O_3, and PdO/Al_2O_3 catalysts

Eric M. Cordi and John L. Falconer

Department of Chemical Engineering, University of Colorado, Boulder, CO 80309-0424, USA

Received 2 October 1995; accepted 9 January 1996

Temperature-programmed desorption (TPD) and oxidation (TPO) were used to investigate the decomposition and oxidation of ethanol on Al_2O_3, Pd/Al_2O_3, and PdO/Al_2O_3. Ethyl-α-^{13}C alcohol ($CH_3{}^{13}CH_2OH$) was adsorbed on the catalysts so that reaction pathways of the two carbons could be distinguished. Alumina was mainly a dehydration catalyst, but dehydrogenation was also observed and some carbon remained on the surface. In the presence of O_2, Al_2O_3 oxidized the decomposition products and the β-carbon was oxidized faster. Ethanol, which was adsorbed on Al_2O_3, decomposed much faster on Pd/Al_2O_3 by diffusing to Pd and undergoing CO elimination to form CH_4, ^{13}CO, H_2, and surface carbon. On PdO/Al_2O_3, the decomposition was slower than on Pd/Al_2O_3 until lattice oxygen was extracted above 450 K; the decomposition products were oxidized by lattice oxygen. In the presence of gas phase O_2, Pd/Al_2O_3 was an active oxidation catalyst at low temperature, but lattice oxygen had to be extracted from PdO/Al_2O_3 before it had significant oxidation activity.

Keywords: TPD; TPO; ethanol decomposition; Al_2O_3; Pd/Al_2O_3; PdO/Al_2O_3; lattice oxygen; $CH_3{}^{13}CH_2OH$

1. Introduction

Volatile organic compounds (VOCs) are emitted from an increasing number of industrial processes and mobile sources, and catalytic incineration has become an effective means of neutralizing these dilute streams. Catalysts can oxidize VOCs to CO_2 and H_2O at lower temperatures and with less energy consumption than traditional thermal methods of pollution control. Most studies of VOC oxidation have focused on conversion of reactants as a function of temperature and catalyst composition rather than on the oxidation mechanism [1].

The objective of the current study was to compare the activities of Pd/Al_2O_3 and PdO/Al_2O_3 catalysts for decomposition and oxidation of C_2H_5OH. Temperature-programmed desorption and oxidation (TPD, TPO) were used to examine the effect of lattice oxygen on the rate and its ability to be incorporated into the products. Of particular interest in this comparison are the relative reactivities of the two carbons in C_2H_5OH. The products from the two carbons were distinguished by labeling the α-carbon with ^{13}C isotope ($CH_3{}^{13}CH_2OH$) so that the labeled products could be monitored with a mass spectrometer. In these transient experiments, essentially all the C_2H_5OH adsorbs on the Al_2O_3 support of Pd/Al_2O_3 and PdO/Al_2O_3. The C_2H_5OH diffused to the Pd or PdO and reacted, and thus reaction on Al_2O_3 was also studied to ensure that reaction was much slower on the Al_2O_3 surface.

2. Experimental

Temperature-programmed desorption and oxidation experiments were performed on 25 mg samples (60–80 mesh) of Al_2O_3, Pd/Al_2O_3, and PdO/Al_2O_3. The catalysts were located in a 1 cm o.d. tubular quartz reactor. Ethanol was adsorbed on the catalyst at room temperature in He flow. For TPD, the catalyst temperature was raised at 1 K/s in He flow, and for TPO a 3% O_2/1% Ar/96% He flow was used. The catalyst was heated by an electric furnace, and a 0.5 mm o.d., chromel–alumel thermocouple, placed in the center of the catalyst bed, measured catalyst temperature and provided feedback to the temperature programmer for the furnace. The effluent from the reactor was sampled by a capillary inlet system and analyzed by a Balzers QMG 421C quadrupole mass spectrometer that has a computer system for acquisition of multiple mass peaks.

Ethyl-α-^{13}C alcohol ($CH_3{}^{13}CH_2OH$) was obtained from Isotec with a minimum 99% ^{13}C enrichment purity. A sample of isotopically-labeled ethanol was adsorbed on either Al_2O_3, Pd/Al_2O_3, or PdO/Al_2O_3 by injecting a liquid sample into a He flow stream. The liquid evaporated from the side of the quartz reactor, so that only ethanol vapor contacted the catalyst bed. For TPD on all catalysts and for TPO on Al_2O_3, 0.5 μl of liquid $CH_3{}^{13}CH_2OH$ was injected. A 0.1 μl sample was injected for TPO on Pd/Al_2O_3 and PdO/Al_2O_3 since the exothermic reaction affected the linear heating ramp when 0.5 μl was used.

During TPD and TPO of $CH_3{}^{13}CH_2OH$, multiple mass signals were monitored so that both the ^{12}C and the ^{13}C-containing products were detected. Extensive corrections for cracking in the mass spectrometer were required to obtain the final product signals. Each product, except those containing ^{13}C, was calibrated by injecting a known amount of liquid or vapor into the flow gas between the reactor and mass spectrometer. Products containing ^{13}C were calibrated by using the equivalent ^{12}C compounds. Though H_2O formed from dehydration and oxidation reactions, the H_2O spectra are not presented in the figures so that the other products are easier to see. Only the presence of H_2O as a reaction product was significant since H_2O reabsorbs on Al_2O_3 and its appearance is desorption limited.

The 3.7% Pd/Al_2O_3 catalyst was prepared by impregnating Kaiser A-201 Al_2O_3 to incipient wetness with an aqueous solution of $PdCl_2$ [2]. The impregnated Al_2O_3 was air dried for 24 h and then dried in vacuum at 373–383 K for 24 h. The catalyst was then calcined for 10 min at 573 K, reduced at 573 K for 5 h, and then passivated in 2% O_2/N_2 at 300 K. Finally, the Pd/Al_2O_3 was reduced again at 773 K in H_2 for 5 h. The Pd weight loading was measured by inductively-coupled, plasma mass spectroscopy (ICP).

The Al_2O_3 was pretreated in 3% O_2 at 873 K for 10 min before each experiment to dehydrate it and to oxidize contaminants on the surface. The Pd/Al_2O_3 catalyst was pretreated by oxidation in 3% O_2 at 773 K for 30 min. When a PdO/Al_2O_3 sample was desired, this was the only pretreatment necessary. Palladium oxidized above 600 K during TPO of Pd/Al_2O_3; the uptake of O_2 was observed between 600 and 773 K [3]. The Pd particles were fully oxidized by this treatment since no further O_2 uptake was observed during a repeat TPO. The PdO was stable on Al_2O_3 since O_2 did not desorb when the temperature was raised to 773 K. Previous studies [4,5] detected decomposition of PdO supported on Al_2O_3 near 1073 K. To obtain Pd/Al_2O_3, the sample was reduced in H_2 flow at 573 K for 30 min, the flow was switched to He at 573 K, and the temperature was slowly raised to 773 K and held there 10 min to remove H_2 and H_2O from the catalyst. The oxygen treatment redispersed Pd on the surface, and low-temperature reduction prevented sintering, which occurs above 573 K in H_2 [6]. The dispersion of Pd, determined by CO adsorption, was approximately 0.15.

3. Results and discussion

3.1. Temperature-programmed desorption (TPD)

On Al_2O_3, ethanol mostly dehydrated to ethylene and water, as shown in fig. 1. In addition, a small fraction of adsorbed ethanol dehydrogenated to acetaldehyde. More H_2 was seen then expected from acetaldehyde formation, indicating further dehydrogenation with the carbon-containing product remaining on the surface. A mass balance indicated that about 20% of the carbon in the original ethanol remained on the Al_2O_3 at the end of TPD. Some carbon–carbon bond cleavage took place since $^{13}CO_2$ but not CO_2 formed above 800 K. That is, only the α-carbon in ethanol

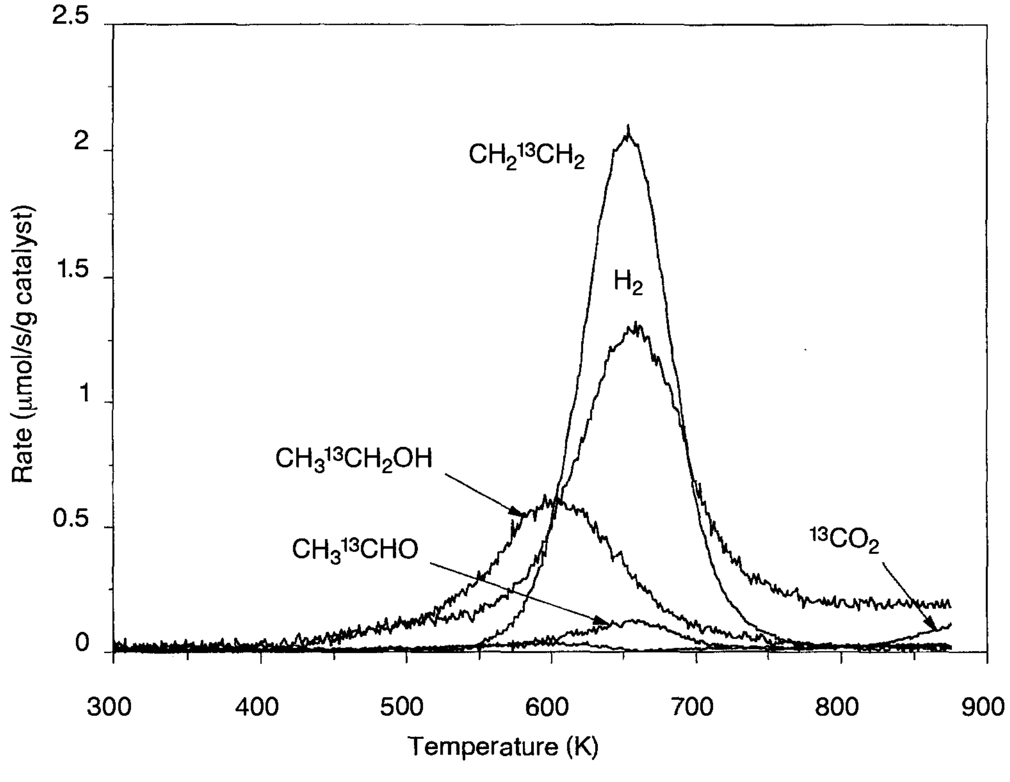

Fig. 1. TPD of $CH_3{}^{13}CH_2OH$ on Al_2O_3.

formed carbon dioxide by 873 K, and the corresponding β-carbon-containing species remained on the surface.

The presence of Pd significantly increased the rate of decomposition of ethanol and changed the product distribution, as shown in fig. 2. Since the amount of ethanol adsorbed on Pd/Al_2O_3 was the same as adsorbed on Al_2O_3, and since the Al_2O_3 surface are was much larger than the Pd, almost all the ethanol was adsorbed on Al_2O_3. Thus, these changes in activity and selectivity indicate that ethanol diffused across the Al_2O_3 surface to the Pd crystallites where it decomposed. Similar decomposition behavior was observed for ethanol adsorbed on Ni/Al_2O_3 catalysts [7]. On Pd/Al_2O_3, ethanol underwent CO elimination to form CH_4, ^{13}CO, and H_2 as the main products. The CH_4 and H_2 appeared in the gas phase below 400 K, but ^{13}CO was delayed; carbon monoxide adsorbs more strongly on Pd than does CH_4 or H_2, and thus ^{13}CO formation was likely desorption limited at low temperature. Smaller amounts of ethylene and acetaldehyde also formed, and at lower temperatures than on Al_2O_3. At high temperatures, small amounts of CO_2 and $^{13}CO_2$ formed, with $^{13}CO_2$ initially forming twice as fast as CO_2. About 75% of the ^{13}C was seen in ^{13}CO, and nearly all the ^{13}C was seen in products that desorbed by the end of TPD. In contrast, only 43% of ^{12}C appeared as CH_4, and less than 70% of ^{12}C was seen in products by the end of TPD; the other 30% remained on the surface. That is, the α-carbon formed predominately CO and the β-carbon formed methane and surface carbon. Table 1 shows the amounts of products formed during TPD.

Davis and Barteau [8] reported that ethanol undergoes CO elimination to form CO, H_2, and CH_4 on Pd(111). Since they observed reaction below 250 K, and since ethanol is adsorbed on Al_2O_3, the decomposition rate of ethanol on Pd/Al_2O_3 during TPD must be limited by surface diffusion or spillover from the Al_2O_3 to the Pd crystallites [7]. Surface carbon was also observed on Pd(111), but the fraction of ethanol that decomposed to surface carbon was much smaller than on Pd/Al_2O_3. Decomposition on Pd(111) took place at much lower temperature where the dehydrogenation rate was lower than hydrogenation rate, apparently because hydrogen remained adsorbed on Pd(111) at low temperature.

The product distribution changed significantly when the Pd was oxidized. Ethanol still underwent CO elimination during TPD to form CH_4, ^{13}CO, and H_2, but these reaction products were oxidized by lattice oxygen in PdO. As shown in fig. 3, much less H_2 formed, and the H_2 had a higher peak temperature than the other products because the hydrogen atoms reacted with the lattice oxygen to form H_2O, which is not shown in fig. 3. As lattice oxygen was depleted and Pd metal formed, H_2 desorbed. Less ^{13}CO was observed on PdO/Al_2O_3 than on Pd/Al_2O_3, and instead $^{13}CO_2$ formed at the same temperature as ^{13}CO. Moreover, CO and CO_2 formed at the same temperatures as the corresponding ^{13}C products, but in much smaller amounts. The ^{13}CO from ethanol

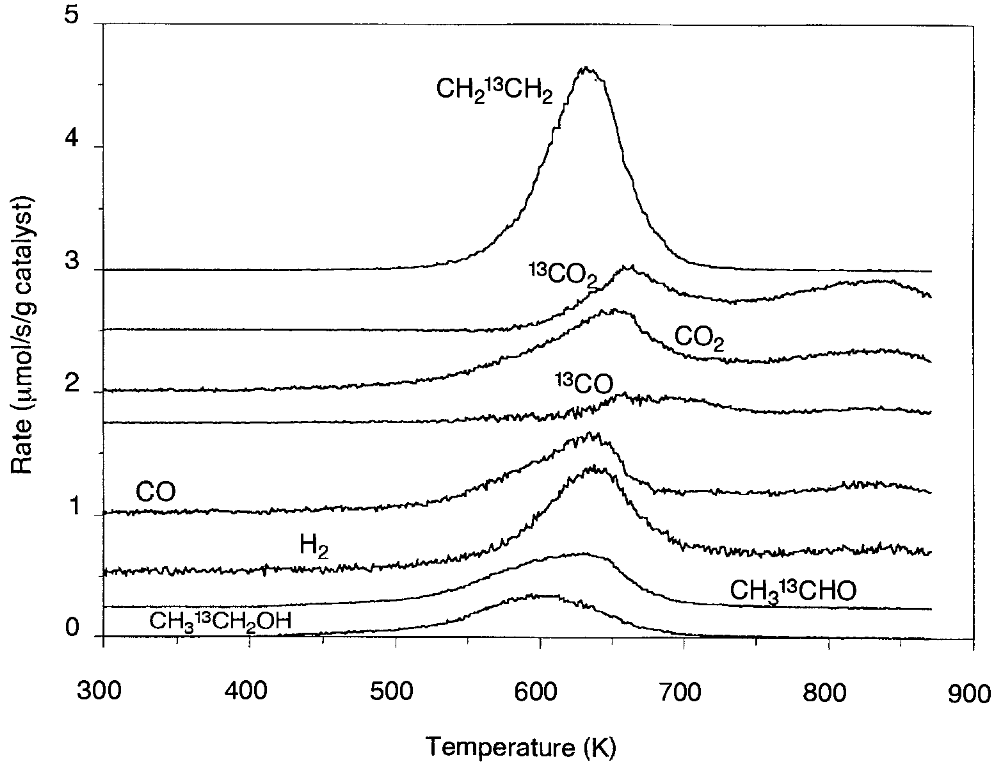

Fig. 2. TPD of $CH_3{}^{13}CH_2OH$ on Pd/Al_2O_3.

Table 1
Product amounts from TPD of $CH_3{}^{13}CH_2OH$ on Pd/Al_2O_3

Product	Amount (μmol/g catalyst)
H_2	447
CH_4	146
CO	–
^{13}CO	253
$CH_2{}^{13}CH_2$	12
$CH_3{}^{13}CHO$	31
CO_2	24
$^{13}CO_2$	40
$CH_3{}^{13}CH_2OH$	16
H_2O	detected
total ^{12}C	229
total ^{13}C	352

Table 2
Product amounts from TPD of $CH_3{}^{13}CH_2OH$ on PdO/Al_2O_3

Product	Amount (μmol/g catalyst)
H_2	196
CH_4	178
CO	57
^{13}CO	172
$CH_2{}^{13}CH_2$	–
$CH_3{}^{13}CHO$	17
CO_2	45
$^{13}CO_2$	110
$CH_3{}^{13}CH_2OH$	31
H_2O	detected
total ^{12}C	328
total ^{13}C	330

decomposition was more readily oxidized to $^{13}CO_2$ than was the CH_4. Both CO_2 and $^{13}CO_2$ were detected in peaks at high temperature in the same amounts and at the same temperature seen on Pd/Al_2O_3. The amounts of products on PdO/Al_2O_3 are shown in table 2.

A comparison of figs. 2 and 3 shows that reaction on PdO/Al_2O_3 was delayed to higher temperature relative to Pd/Al_2O_3 by the presence of lattice oxygen. Since CH_4 and ^{13}CO readily formed, the CO elimination reaction also took place on PdO, and the ^{13}CO and H_2 were able to extract lattice oxygen from PdO above 450 K. As the PdO was reduced to Pd and thus the oxygen supply was depleted, decomposition became similar to that on Pd/Al_2O_3. High temperature CO_2 formation, resulted from decomposition of a surface species that also formed during TPD on Pd/Al_2O_3.

Since reaction products were observed at similar temperatures during TPD on Pd/Al_2O_3 and PdO/Al_2O_3, the lattice oxygen oxidized the decomposition products and the decomposition rate was similar, whether or not the Pd was oxidized. Since less products were observed below 400 K on PdO/Al_2O_3, however, decomposition was delayed on PdO/Al_2O_3 until some lattice oxygen was extracted to form Pd metal. Hydrogen oxidized much faster than CO, and the ^{13}CO was more easily oxidized than the CH_3 species. Because some of the β-car-

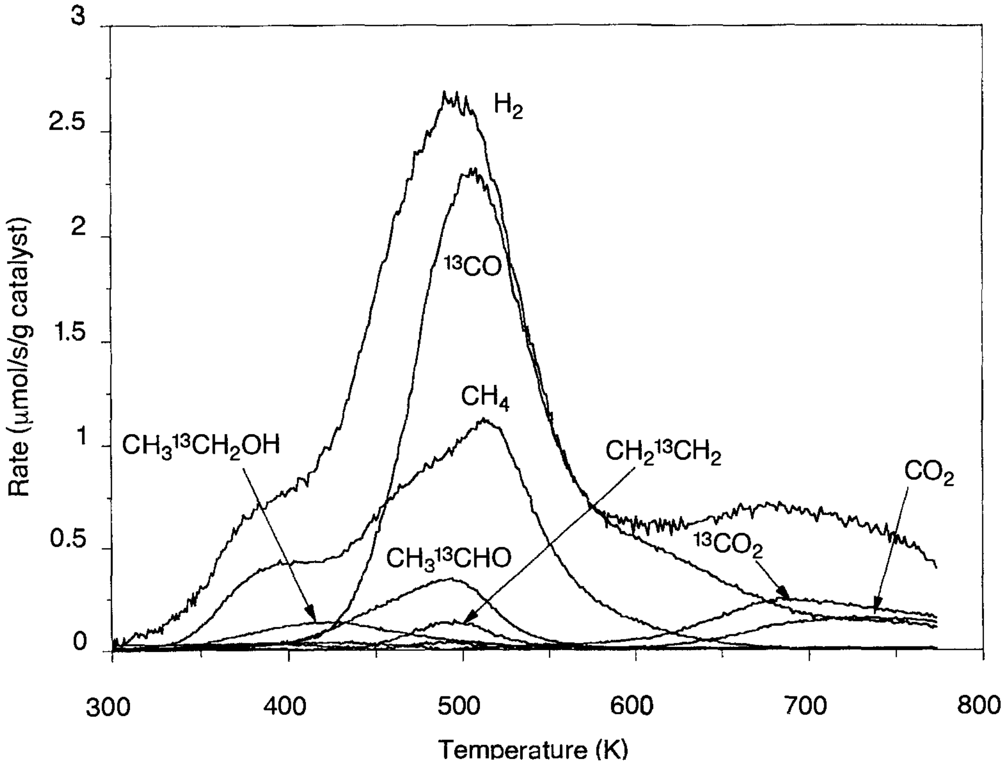

Fig. 3. TPD of $CH_3{}^{13}CH_2OH$ on PdO/Al_2O_3.

bon oxidized, less carbon (5% of total) remained on the surface by 773 K than on Pd/Al_2O_3. The ($CH_4 + CO_2 + CO$) amount was approximately equal to the ($^{13}CO + {}^{13}CO_2$) amount, showing that neither carbon in $CH_3{}^{13}CH_2OH$ was favored in formation of total gaseous products.

3.2. Temperature-programmed oxidation (TPO)

During TPO on Al_2O_3, dehydration to form ethylene was the dominant reaction, but dehydrogenation to acetaldehyde was also observed. The temperatures where reaction products formed (fig. 4) were similar to those seen during TPD. The amount of H_2 was much smaller, however, because the H_2 was oxidized to H_2O (not shown in the figure). Much more carbon monoxide and carbon dioxide were seen during TPO than TPD, indicating that Al_2O_3 was an ethanol oxidation catalyst above 550 K. More ^{12}C oxides formed than ^{13}C oxides, and the rate of ^{12}C oxide formation was faster at low temperature; that is, oxidation of the β-carbon in ethanol was favored on Al_2O_3.

Oxidation of ethanol was much faster on Pd/Al_2O_3 than on Al_2O_3; reaction started at room temperature and carbon dioxide and water were the only products seen. Nearly equal amounts of CO_2 and $^{13}CO_2$ formed on Pd/Al_2O_3 (fig. 5) and carbon dioxide formed in two peaks. More than half the carbon dioxide formed above 600 K. At 425 K, $^{13}CO_2$ formation was 50% faster than CO_2 formation, whereas at 750 K, CO_2 formation was 7% greater than $^{13}CO_2$ formation. Note that the signals are smaller in fig. 5 than during TPD (fig. 2) because less ethanol was used during TPO in order to avoid heat transfer problems. Since carbon dioxide formation was delayed to higher temperature during TPO relative to carbon-containing species that form during TPD, a partial oxidation product apparently formed that was less reactive than ethanol [3].

Carbon dioxide formation began at room temperature during TPO, but the rate of $^{13}CO_2$ formation was larger up to 475 K as the α-carbon oxidized faster. That is, the carbon with the higher oxidation state was preferentially oxidized at low temperature. The same peak temperatures for CO_2 and $^{13}CO_2$ for both peaks shows that the difference in oxidation rates of the two carbons on Pd/Al_2O_3 is not large. Ethanol reacted with oxygen adsorbed on Pd below 600 K, but PdO started to form above 600 K, as shown by O_2 uptake in the absence of adsorbed ethanol [3]. Thus, much of the carbon dioxide forms on PdO above 600 K in fig. 5.

The oxidation rate was much slower initially on PdO/Al_2O_3 than on Pd/Al_2O_3, and products did not form until 450 K. As seen in fig. 6, $^{13}CO_2$, CO_2, and CH_4, formed simultaneously with maxima near 530 K. Water also formed. At the peak maximum, the amount of $CO_2 + CH_4$ was approximately equal to the amount of $^{13}CO_2$. Above 600 K, CO_2 and $^{13}CO_2$ formed at similar rates, and oxidation was not complete at 773 K. During

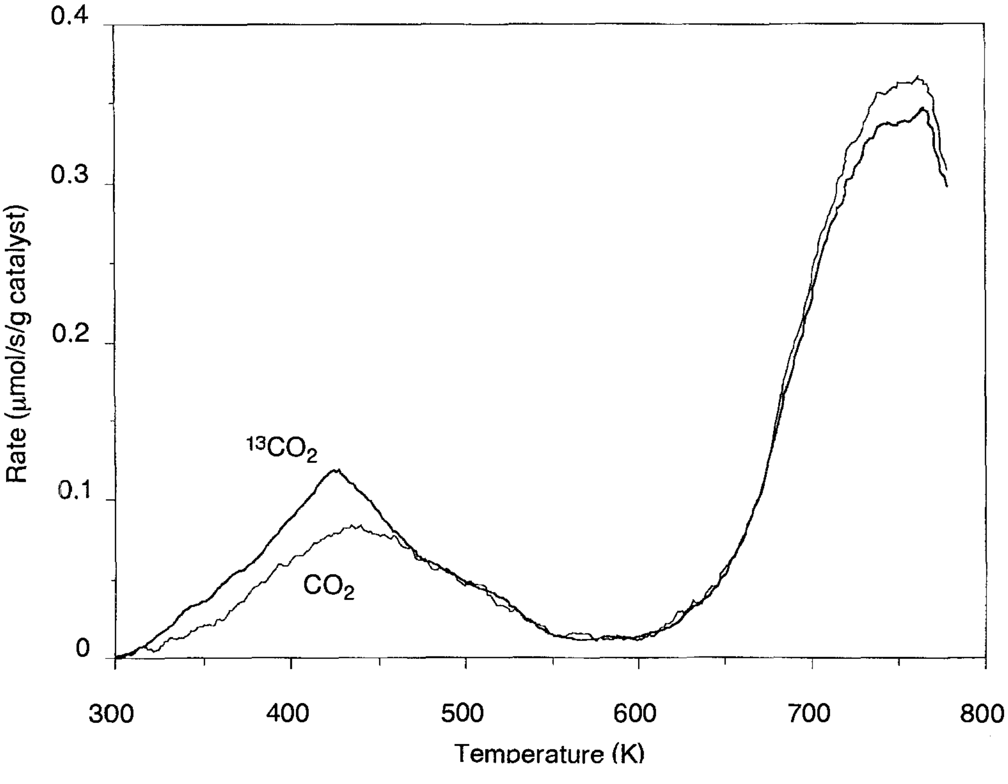

Fig. 4. TPO of $CH_3{}^{13}CH_2OH$ on Al_2O_3.

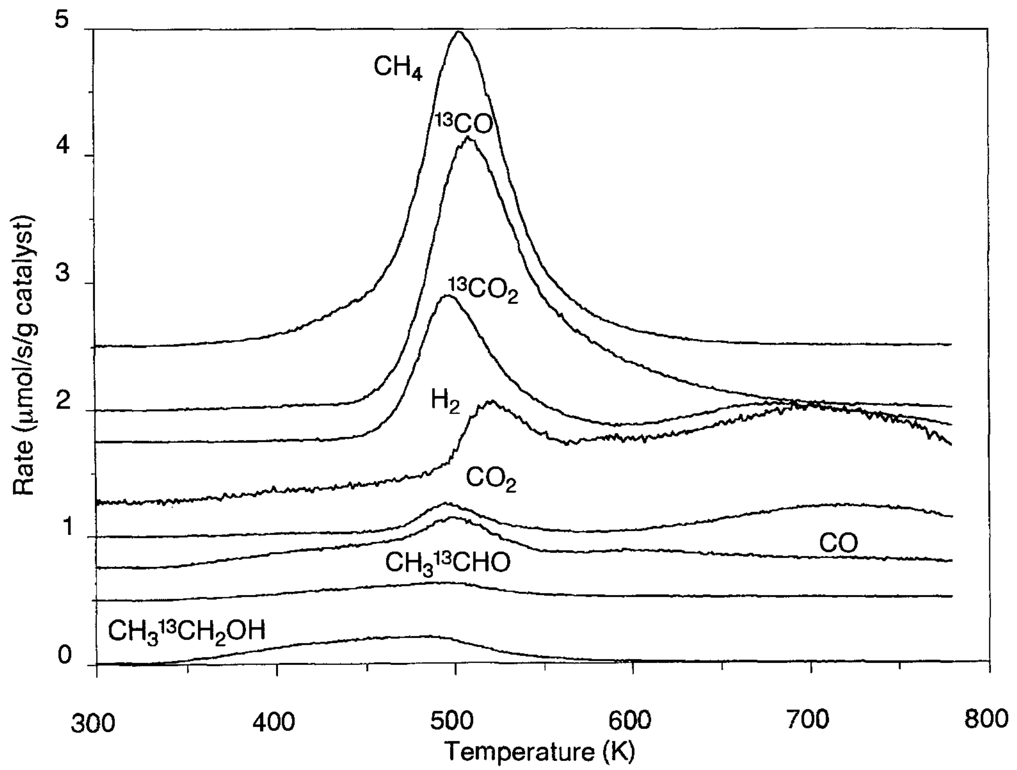

Fig. 5. TPO of $CH_3{}^{13}CH_2OH$ on Pd/Al_2O_3.

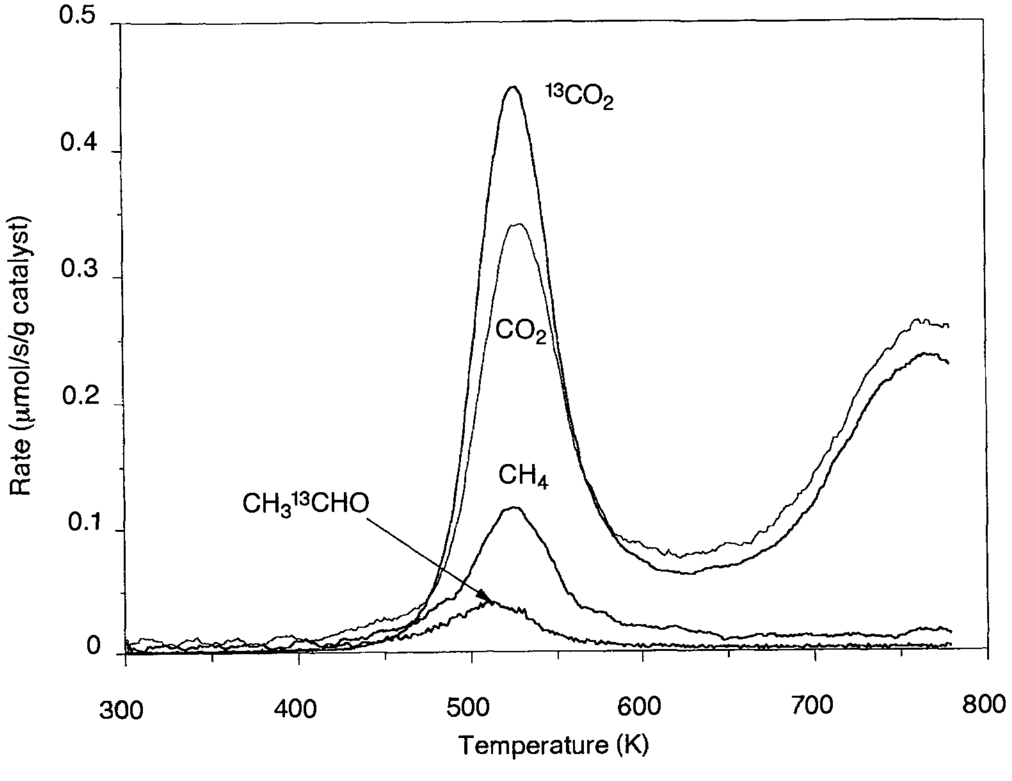

Fig. 6. TPO of $CH_3{}^{13}CH_2OH$ on PdO/Al_2O_3.

TPO on PdO/Al_2O_3, ethanol apparently decomposed and its products were oxidized, since the reaction temperatures were similar during both TPD and TPO.

During TPD, reaction was delayed on PdO/Al_2O_3 (relative to Pd/Al_2O_3) until oxygen was extracted from the PdO. Reduced Pd sites were created by extraction of lattice oxygen, and apparently some of the β-carbon was hydrogenated to CH_4 at these sites. During TPO, these Pd sites were occupied as O_2 adsorbed from the gas phase, and thus oxidation during TPO was at a higher temperature than during TPD. Because of the availability of more oxygen during TPO, however, the ethanol was more completely oxidized during TPO than during TPD.

Farrauto et al. [4] and Garbowski et al. [9] suggested that CH_4 oxidation on supported Pd proceeded through a Mars–van Krevelen mechanism, in which Pd particles cycled through oxidation by O_2 and reduction by CH_4. The same mechanism is expected during ethanol oxidation above 600 K, the temperature at which Pd oxidation began. The TPD experiments show that lattice oxygen can be extracted easily at lower temperatures. The formation of CO_2 at high temperatures during TPO on both Pd/Al_2O_3 and PdO/Al_2O_3 apparently results from formation of a partial oxidation product at lower temperature that is then oxidized completely at higher temperature on PdO, since Pd oxidizes above 600 K [3].

4. Conclusions

On Pd/Al_2O_3 and PdO/Al_2O_3, ethanol adsorbed on the Al_2O_3 support diffuses along the surface to Pd or PdO sites to react. Ethanol decomposes at a slower rate on Al_2O_3 and the main reaction is dehydration. On Pd/Al_2O_3, ethanol undergoes CO elimination to form CO, H_2, and CH_4, as seen on single crystal Pd. Carbon isotope labeling showed that the α-carbon forms CO whereas the β-carbon forms CH_4 and surface carbon. In the presence of O_2, Al_2O_3 catalyzes oxidation of the reaction products of ethanol decomposition, and the β-carbon oxidizes faster than the α-carbon. Palladium and PdO are much better oxidation catalysts, and complete oxidation of ethanol to CO_2 and H_2O was observed on Pd but not on PdO. The α-carbon more readily oxidizes, and a partial oxidation product forms that is only completely oxidized at high temperature. Ethanol decomposition products extract lattice oxygen from PdO and create Pd sites, which are more reactive than PdO for oxidation or decomposition.

Acknowledgement

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

References

[1] J.J. Spivey, Ind. Eng. Chem. Res. 26 (1987) 2165.
[2] E.C. Hsiao and J.L. Falconer, J. Catal. 132 (1991) 145.
[3] E.M. Cordi and J.L. Falconer, J. Catal., submitted (1995).
[4] R.J. Farrauto, M.C. Hobson, T. Kennelly and E.M. Waterman, Appl. Catal. 81 (1992) 227.
[5] T.E. Hoost and K. Otto, Appl. Catal. A 92 (1992) 39.
[6] S. Karski, Przemysl Chemiczny 71 (1992) 177.
[7] B. Chen and J.L. Falconer, J. Catal. 144 (1994) 214.
[8] J.L. Davis and M.A. Barteau, Surf. Sci. 187 (1987) 387.
[9] E. Garbowski, C. Feumi-Jantou, N. Mouaddib and M. Primet, Appl. Catal. A 109 (1994) 277.