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Acetaldehyde yield and reaction products in the catalytic destruction of gaseous ethanol

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The catalytic destruction of ethanol (0.5% v/v) over a typical three-way catalyst (Pt/Rh/Ce) and two base catalysts (1% CuO and 10% CuO on γ-Al_2O_3) was studied in a continuous flow reactor, under atmospheric pressure. The effect of the temperature (100–500 °C) and of the oxygen concentration (0–10% v/v) on the operation of the tested catalysts and on the product profiles is presented. The formation of acetaldehyde during the catalytic destruction of ethanol, the main concern of ethanol addition to fuels, was extremely dependent on the oxygen concentration. It is noteworthy that more acetaldehyde was produced during the oxidation of ethanol in oxygen deficit conditions than during its decomposition in the absence of oxygen. Copper addition on γ-Al_2O_3 enhanced acetaldehyde formation, while less acetaldehyde amounts were produced over the noble metal catalyst.

KEY WORDS: three-way catalysts; copper catalysts

1. Introduction

Oxygenated compounds have been used as gasoline additives to compensate the knock behavior of lead since 1970. The concern about urban air quality has led to the idea of using these compounds in increased amounts in unleaded gasoline in order to reduce combustion-related pollution from vehicles by providing oxygen during the combustion process. Among the several possible oxygenated additives, methyl-*tert*-butyl ether (MTBE) and ethanol are the most frequently used ones. The use of oxygenated fuels generally decreases the total hydrocarbon (HC), carbon monoxide (CO) and nitrogen oxide (NO_x) emissions under moderate temperatures. They seem to produce, however, increased amounts of air pollutants such as aldehydes and peroxyacetyl nitrates, which are known toxics but not yet regulated [1,2].

The effect of MTBE addition to gasoline on the exhaust and evaporative emissions from cars has been extensively studied [3–6]. However, its use is accompanied by many problems owing to its potential for carcinogenicity and its high solubility in water. MTBE has been detected in vast portions of ground and surface water reservoirs, and leaking underground storage tank systems as well as faulty pipeline systems and accidental spills are thought to be the sources. Therefore, extensive consideration has been given to other oxygenated compounds, especially to ethanol since its use seems to be beneficial in terms of water contamination and there are no significant adverse impacts to public health or the environment from switching to ethanol [7].

Ethanol can be used either as supplemental blending stock or as a substitute for gasoline [8] and diesel [9]. Fewer studies are devoted to the exhaust emissions from internal combustion engines operating on ethanol-containing fuels. The most important disadvantage of ethanol addition to gasoline is the production of acetaldehyde [10,11].

Some research has been conducted on the catalytic combustion of ethanol. Catalysts containing noble metals (Pt, Pd, Rh, Ag) as well as base metal oxides (CuO, Cr_2O_3, Fe_2O_3, NiO, V_2O_3, Co_3O_4, Mn_2O_3) were tested for the oxidation of ethanol and acetaldehyde [12–23]. Excess oxygen conditions were used and acetaldehyde, CO, ethylene, diethylether and methane were detected in the reaction products. Pt from the first group and CuO from the second one were found to be the most active in ethanol oxidation. The influence of oxygen concentration on reaction product distribution and especially on acetaldehyde production through the partial oxidation of ethanol—the main drawback of ethanol addition to gasoline—is significant and should be further examined.

In the present study, the oxidation of ethanol on a commercial three-way catalyst and on two base-metal (CuO) laboratory catalysts is presented. Acetaldehyde and the other reaction products are detected under various oxygen concentrations, and temperature ranges are studied where these concentrations are the highest.

2. Materials and methods

2.1. Materials

Pt-Rh-Ce (Pt: 3.27×10^{-3} g g_{cat}^{-1}, Rh: 0.64×10^{-3} g g_{cat}^{-1}, Ce: 51.78×10^{-3} g g_{cat}^{-1}), a standard commercial three-way

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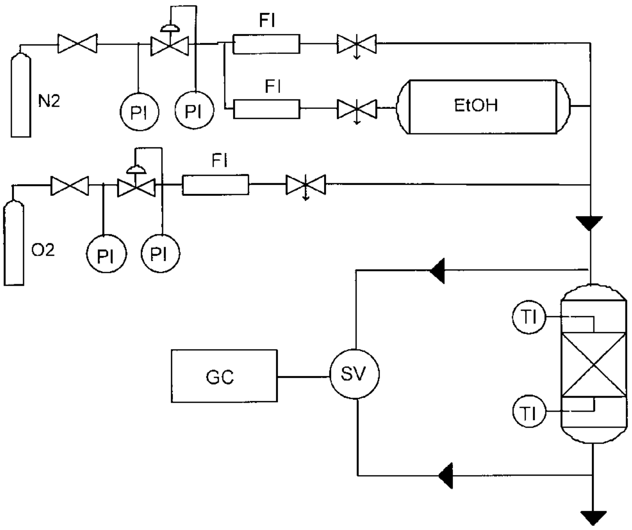

Figure 1. Experimental setup: PI, pressure indicator; FI, flow indicator; TI, temperature indicator; SV, sampling valve; GC, gas chromatograph.

catalyst, was supplied by Allied Signal Automotive Catalyst Company. The catalytic support consisted of ceramic monolith made of cordierite and the substrate of γ-Al_2O_3. The density of the monolith was 400 square cells in^{-2}. The CuO catalysts were prepared by wet impregnation of γ-Al_2O_3 particles with an aqueous copper nitrate solution. Catalysts containing 1% and 10% w/w CuO on γ-alumina were prepared. The γ-alumina used in this study had a specific surface area and specific pore volume of $176\,m^2\,g^{-1}$ and $0.61\,cm^3\,g^{-1}$, respectively. The metal salts used were analytical grade reagents. The catalysts were heated at 400 °C in hydrogen for 2 h prior to oxidation experiments to provide a clean catalyst surface.

2.2. *Experimental procedure*

The catalytic tests of ethanol oxidation were carried out in a quartz flow reactor and the experimental set-up is presented in figure 1. The catalytic bed contained 0.5 g of the catalyst. The feed composition was 0.5% ethanol and 0, 0.5 and 10% oxygen in nitrogen. All concentrations are expressed as a percentage of v/v. Inlet and outlet samples were analysed chromatographically for ethanol, acetaldehyde, ethylene, diethylether, methane, carbon monoxide and carbon dioxide. A Perkin–Elmer gas chromatograph equipped with a flame ionisation detector (FID) and a Hewlett-Packard gas chromatograph equipped with a thermal conductivity detector (TCD) were used. Experiments were conducted under atmospheric pressure at temperatures between 100 °C and 500 °C. The total volumetric flow of the reactants was $1200\,mL\,min^{-1}$ at 25 °C. The acceptable error in the steady-state carbon balance was ±7%.

3. Experimental results

3.1. *Ethanol conversion*

Unburned ethanol, acetaldehyde, carbon dioxide, ethylene, diethylether and methane in traces were detected in the reactor effluent. Acetic acid and carbon monoxide, possible reaction products, were not detected, which is in accordance with previous studies [15]. Since the system was about 90–99% N_2, it is reasonable to assume a constant overall density of the system at constant temperature and pressure. So, the conversion of ethanol, x_{EtOH}, and the yield of the product (i), y_i, can be defined as

$$x_{EtOH} = \frac{C_{EtOH,in} - C_{EtOH,out}}{C_{EtOH,in}} 100\%$$

and

$$y_i = \frac{C_{i,out}}{C_{EtOH,in}} \frac{1}{n} 100\%$$

respectively, where C_i is the concentration of species i, and n is the ratio of C atoms in ethanol to C atoms in compound i.

The effect of oxygen concentration on ethanol conversion over 1% CuO, 10% CuO and Pt/Rh/Ce is presented in figure 2(a), (b) and (c) respectively. Surprising though it may seem, 50% ethanol conversion was achieved at lower temperatures ($T_{50\%} = 240\,°C$) in the absence of oxygen in the case of 1% CuO. Oxygen concentration had no effect on $T_{50\%}$ (280 °C), whereas almost 100% ethanol destruction was achieved at 300 °C without oxygen and in the presence of 10% O_2, and at 350 °C in the presence of 0.5% O_2.

Fifty percent conversion of ethanol was also achieved at lower temperature (200 °C) in the absence of oxygen in

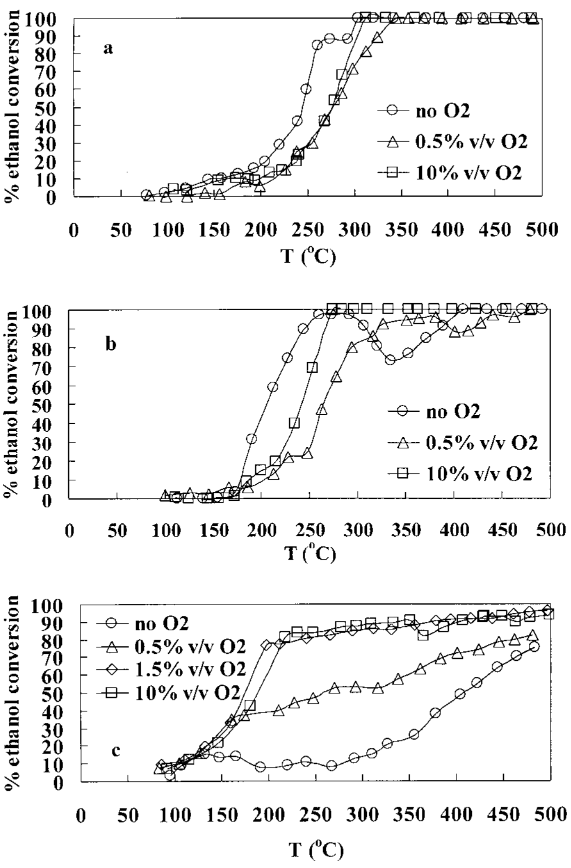

Figure 2. The effect of oxygen concentration on ethanol conversion over (a) 1% CuO; (b) 10% CuO; and (c) Pt/Rh/Ce.

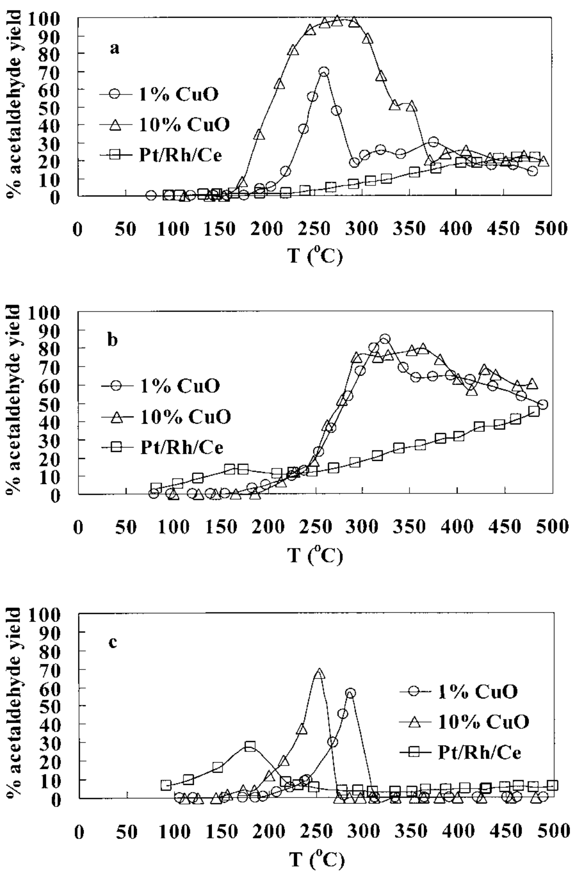

Figure 3. The acetaldehyde yield over the three catalysts in the presence of (a) 0% O_2; (b) 0.5% O_2; and (c) 10% O_2.

the case of 10% CuO, but 100% destruction was achieved only at 400 °C, whereas ethanol was totally oxidised at 270 °C in the presence of 10% oxygen.

Pt/Rh/Ce catalyst proved to be much more sensitive to oxygen concentration, and as a result the oxidation of ethanol in the presence of 1.5% O_2 was also studied in order to clarify the influence of oxygen on ethanol destruction. In the absence of oxygen, the conversion of ethanol exceeded 30% only above 370 °C. Ethanol was efficiently oxidised over Pt/Rh/Ce only at stoichiometric conditions of oxygen, although 100% ethanol destruction was not observed even at 500 °C, indicating strong mass transfer phenomena.

Comparing the tested catalysts, Pt/Rh/Ce was superior to copper catalysts on ethanol oxidation only when oxygen was in excess, whereas 10% CuO was more effective than 1% CuO in most cases.

3.2. Acetaldehyde yield

The results obtained indicate that in the absence of oxygen or under oxygen deficit, acetaldehyde was formed, either as a dehydration product or as the intermediate oxidation product, and acetaldehyde was present in the reaction products even at the high temperatures tested (figure 3). On the other hand, in oxygen excess, its production went through a maximum within a limited temperature range and decreased abruptly as it was oxidised further, in accordance with the mechanism proposed in the literature [12,17,20].

The commercial catalyst was by far the best since less acetaldehyde amounts were produced compared to copper catalysts. It is noteworthy that more acetaldehyde was produced under oxygen deficit than in the absence of oxygen, which confirms the dependence of catalyst operation on the oxygen to ethanol ratio (figure 4).

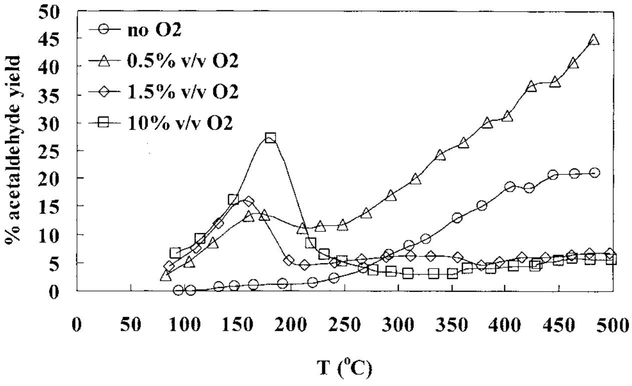

Figure 4. The effect of oxygen concentration on acetaldehyde yield over Pt/Rh/Ce.

The greatest acetaldehyde emissions were observed in the case of 10% CuO, and especially in the absence of oxygen ethanol was almost totally converted to acetaldehyde in the temperature range of 250–300 °C over this catalyst.

3.3. Reaction products

The products of the conversion of ethanol are acetaldehyde, carbon dioxide, ethylene, diethylether and methane. Acetic acid, a possible reaction product, was not detected during the experimental runs.

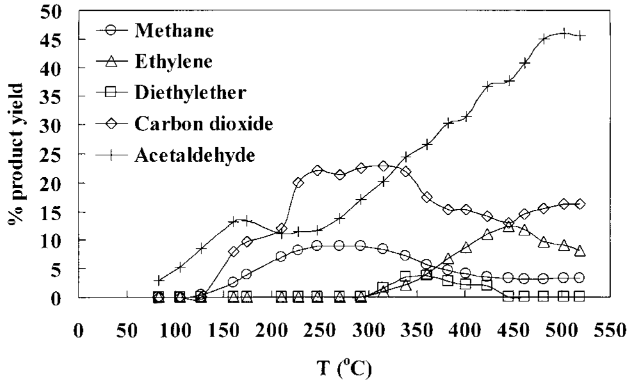

Figure 5. By-product yields of ethanol oxidation over Pt/Rh/Ce in the presence of 0.5% O_2.

In figure 5, the typical evolution of methane, ethylene, diethylether, carbon dioxide and acetaldehyde over the commercial catalyst in the presence of 0.5% O_2 is

Table 1
Temperature range for maximum product formation and respective yield in the absence of oxygen

Product	Pt-Rh-Ce	1% CuO/γ-Al_2O_3	10% CuO/γ-Al_2O_3
Acetaldehyde	Appears after 300 °C, increasing until 440 °C, then stable at 20%	Appears after 100 °C, max. at 260 °C, 77%	Max. at 270 °C, 97%
Diethylether	Appears after 200 °C, increasing until 380 °C, then stable at 10%	Appears after 200 °C, max. 200–300 °C, 37% disappears at 400 °C	Appears after 370 °C, max. at 370 °C, 15%
Ethylene	Appears after 300 °C, max. at 510 °C, 46%	Appears after 200 °C, increasing until 410 °C, then stable at 64%	Appears after 300 °C, max. at 440 °C 56%
Methane	270 °C, 2%	Appears after 400 °C, max. at 500 °C, 1%	Not detected
Carbon dioxide	Appears after 400 °C, max. at 510 °C, 12%	Appears after 300 °C max. at 500 °C, 35%	Appears after 300 °C max. at 520 °C, 35%

Table 2
Temperature range for maximum product formation and respective yield in the presence of 0.5% oxygen

Compound	Pt-Rh-Ce	1% CuO/γ-Al_2O_3	10% CuO/γ-Al_2O_3
Acetaldehyde	Increasing up to 520 °C, 52%	Increasing up to 340 °C, then stable at 75%	Appears after 200 °C, stable after 440 °C, 93%
Diethylether	Appears after 300 °C, max. at 360 °C, 4%	Appears only between 200 and 300 °C, 4%	Not detected
Ethylene	Appears after 300 °C, max. at 460 °C, 13%	Appears after 200 °C, max. at 510 °C, 6%	Appears after 200 °C, max. at 520 °C, 8%
Methane	Max. at 270 °C, 2%	Appears after 400 °C, max. at 500 °C, 1%	Not detected
Carbon dioxide	Stable between 200–520 °C, 22%	Appears after 200 °C, stable after 300 °C, 45%	Appears after 200 °C, stable after 380 °C, 35%

Table 3
Temperature range for maximum product formation and respective yield in the presence of 10% oxygen

Compound	Pt-Rh-Ce	1% CuO/γ-Al_2O_3	10% CuO/γ-Al_2O_3
Acetaldehyde	Max. at 180 °C, 31%	Max. at 290 °C, 48% disappears after 300 °C	Max. at 250 °C, 68% disappears after 300 °C
Diethylether	Not detected	Max. at 270 °C, 3.5% present only between 200–300 °C	Not detected
Ethylene	Not detected	Max. at 330 °C, 2.4%	Not detected
Methane	Max. at 220 °C, 1.4%	Appears after 400 °C, max. at 450 °C, 1%	Not detected
Carbon dioxide	Stable between 200–520 °C, 88%	Stable between 300–520 °C, 98%	Stable between 200–520 °C, 100%

presented. Similar results were obtained over the CuO catalysts. The results obtained show that the catalytic system performance depends on the ratio of oxygen to ethanol for all catalysts studied: without oxygen the major products were ethylene, diethylether and acetaldehyde for all catalysts tested, while traces of methane were also formed. Ethylene, diethylether and methane production decreased with increasing oxygen concentration in all cases. Finally, with excess oxygen, carbon dioxide appeared at 180 °C over the commercial catalyst, while higher temperatures (up to 280 °C) were required for the CuO catalysts.

The exhaust gas temperature may be quite low, occasionally below 200 °C, due to the driving pattern in the inner city. So, the temperature ranges where each by-product is present are of great importance. In tables 1–3 the maximum yield and the temperature where each by-product appeared are reported for all catalysts tested.

The superiority of the commercial catalyst with excess oxygen is evidenced by the lower temperature where maximum acetaldehyde yield occurred and in accordance with the lower temperature where carbon dioxide production begun. Under oxygen deficit however all catalysts produced various amounts of intermediate products, namely diethylether and ethylene, while traces of methane were also detected.

4. Discussion

On the basis of the products detected during these experiments, the decomposition or oxidation of ethanol over the catalysts tested involves one or more of the following reactions:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \quad (1)$$

$$C_2H_5OH + 0.5O_2 \rightarrow CH_3CHO + H_2O \quad (2)$$

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \quad (3)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (4)$$

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \quad (5)$$

$$C_2H_5OH \rightarrow 2CH_4 + 0.5O_2 \quad (6)$$

Ethanol oxidation over pure γ-Al_2O_3 resulted in dehydration products, namely ethylene and diethylether through reactions (4) and (5). Alumina contains Lewis acid sites (Al^{3+} cations), which are involved in reactions of alcohols to ethers. Alumina also contains Brønsted acid sites, which promote dissociation of the alcohol hydroxyl group during olefin formation [22]. Consequently, the formation of significant amounts of ethylene and diethylether over the catalysts tested, especially in the absence of oxygen, is attributed to the alumina support. Since the alumina content is greater in the case of CuO catalysts, the concentrations of the dehydration products are higher for CuO catalysts than for Pt/Rh/Ce. The amounts of ethylene and mainly of diethylether produced over the 10% CuO were less than those over the 1% CuO, which in turn were less than those over the γ-Al_2O_3 alone, due to the blocking of the acid sites on alumina from the base metal.

At low temperatures, higher conversions of ethanol were observed in the absence of oxygen than in its presence, in the case of CuO catalysts. At these conditions, ethanol was almost entirely converted to acetaldehyde, particularly over 10% CuO. According to Ismagilov *et al.* [21], at the first step ethanol is converted to acetaldehyde over CuO following the reaction (3). The more the CuO content in the catalyst, the more the acetaldehyde produced. The adsorption of oxygen inhibits this reaction, since the temperature is not sufficient to start oxidation reactions. On the other hand, the lack of oxygen is critical in the case of Pt/Rh/Ce. Oxidation reactions do not take place on noble metals and dehydration products are only formed on the γ-Al_2O_3 support on the monolith. However, this is beneficial in terms of air pollution because acetaldehyde is a very toxic compound and very active in photochemical smog formation.

In the presence of oxygen, acetaldehyde and carbon dioxide are the main compounds produced. The Pt/Rh/Ce catalyst shows high selectivity to carbon dioxide. The formation of carbon dioxide over CuO follows a consecutive scheme through the oxidation of acetaldehyde:

$$C_2H_5OH \rightarrow CH_3CHO \rightarrow CO_2$$

The higher conversions of ethanol to carbon dioxide over the Pt/Rh/Ce are due to the combined effect of the above scheme and a direct oxidation path to CO_2 [15,17,22,23]. Moreover, the differences between temperatures for 50% conversion of ethanol over the CuO/γ-Al_2O_3 and Pt/Rh/Ce catalysts may be associated with different stabilities of surface ethoxide species formed as intermediates during ethanol oxidation. These species are more readily decomposed on oxygen pre-covered Pt than Cu [12].

5. Conclusions

In this study, the destruction and the oxidation of ethanol over a commercial three-way catalyst (Pt/Rh/Ce) and two laboratory-prepared copper catalysts on alumina (1% and 10% CuO) were studied. The main points of this work are:

(a) In the absence of oxygen or under oxygen deficit, considerable amounts of acetaldehyde were present in the reaction products even at high temperatures. On the other hand, with excess oxygen, its yield passed through a maximum within a limited temperature range and then decreased rapidly.

(b) With excess oxygen, the commercial catalyst was superior to copper catalysts, producing less acetaldehyde and having the lowest $T_{50\%}$ for ethanol. Under oxygen deficit however, while producing less acetaldehyde, the commercial catalyst exhibited higher $T_{50\%}$ for ethanol, being thus more sensitive to oxygen concentration than CuO. The superiority of the commercial catalyst with excess oxygen was also evidenced through the lower temperature where carbon dioxide formation was observed.

(c) Under oxygen deficit all catalysts produced various amounts of intermediate products, namely diethylether and ethylene, while traces of methane were also detected. Ethylene, diethylether and methane production decreased with increasing oxygen concentration in all cases.

(d) The catalyst operation depended on the temperature and oxygen concentration, especially in the case of Pt/Rh/Ce catalyst.

Acknowledgments

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