Catalytic Combustion of Ethyl Acetate

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The catalytic combustion of ethyl acetate over prepared metal oxide catalysts was investigated. CeO, Co_2O_3, Mn_2O_3, Cr_2O_3, and CeO-Co_2O_3 catalysts were prepared on monolith supports and they were tested. Before conducting the catalyst experiments, we searched for the homogeneous gas phase combustion reaction of ethyl acetate. According to the homogeneous phase experimental results, 45% of ethyl acetate was converted at the maximum reactor temperature tested (350 °C). All the prepared catalysts were tested in order to find the best catalyst for the complete combustion of ethyl acetate. According to the results, all these catalysts produced higher conversion rates than that of the homogeneous experiment; however, none of the prepared catalysts resulted in complete combustion. The maximum conversion obtained with the CeO catalyst at 350 °C was 72%.

Key Words: Catalytic combustion, ethyl acetate, incineration, metal oxide catalysts, monolith.

Introduction

The emission of volatile organic compounds (VOCs) causes air pollution, either directly through their toxic or malodorous properties, or indirectly as ozone and smog precursors. Catalytic oxidation of VOCs present in low concentrations in industrial waste gas streams is an important technique for air pollution control.[1,2] The addition of a catalyst converts a homogeneous gas phase reaction into a heterogeneous phase in which oxidation takes place on the catalyst surface; thus, the activation energy required for a heterogeneous reaction is lower than that of the homogeneous case.[3,4]

The typical reactor-type catalytic combustion of VOCs consists of a monolith support that is characterized by low-pressure drop and a large external surface area.[5] The gas phase usually flows in the monolith channel in the laminar regime, and mass transfer between the gas phase and catalyst surface becomes the rate controlling step of the entire process.[6,7] The mechanism of the catalytic combustion of VOCs depends

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on the type of catalyst used. Precious metal catalysts are generally more active and more tolerant to sulfur poisoning than metal oxides; however, metal oxides are much cheaper, allowing a high catalyst load. The use of a large surface area in the metal oxide bed also makes the catalyst less sensitive to nonselective poisoning, which is common in stationary emission control.[8,9] Ethyl acetate, a key component in ink manufacturing, is oxidized to CO_2 using Pt and Pd supported on a γ-alumina catalyst operating at the temperature range of 220-320 °C.[10,11] However, base metal oxide catalysts may be an alternative due to the fact that these are cheaper than Pt and Pd, allowing a higher catalyst load.[11,12]

The aim of this study was to gain a better understanding of the fundamental phenomena involved in the catalytic combustion of ethyl acetate on prepared base metal oxide catalysts.

Experimental

The experimental study consisted of 3 parts. First we searched for the homogeneous gas phase oxidation reaction of ethyl acetate. A piece of uncoated monolith support was placed into the reactor and the reactor temperature was kept in the range of 100-350 °C at a constant feed flow rate of 0.025 mL/min.

In the second part, metal oxide catalysts were prepared on monolith supports in laboratory conditions. Catalysts were prepared in 2 consecutive steps. In the first step, a monolith support was corroded in an acid solution. In the second step, the corroded monolith support was coated with a chosen metal oxide. The composition of the prepared catalysts is given in the Table.

Table. Composition of the catalysts.

Catalyst	Composition (%)
CeO	11.8
Co_2O_3	21
Mn_2O_3	7.0
Cr_2O_3	6.0
CeO-Co_2O_3	3.5 CeO-5.7 Co_2O_3

The activity of these prepared catalysts was predetermined by light-off experiments. The test procedure was as follows:

1. Coated monoliths were placed in the reactor.

2. Air and nitrogen flow were directed to the reactor.

3. The pre-heater and reactor heater were switched on, and the reactor temperature was set to 300 °C.

4. Pumping of liquid VOCs began; when the temperature reached 300 °C, the reactor temperature was re-set to 400 °C.

5. From then on, heater and bed temperature were continuously recorded.

In the final part, all these prepared catalysts were tested in order to determine which was best for the complete oxidation of ethyl acetate.

The experimental set-up included a vaporizer, a pre-heater, a monolithic reactor, a cooler, and an absorber. In the experiments, the reactor temperature ranged between 100 and 350 °C, with a constant ethyl acetate flow rate, and 500% of excess air was used at 1 atm. The pre-heater temperature was adjusted to 50 °C lower than the reactor temperature. Dry air was used for combustion and nitrogen was used as the carrier gas for ethyl acetate.

Results and Discussion

The results of the homogeneous oxidation reaction experiments with ethyl acetate are shown in Figure 1. It can be seen that the conversion of ethyl acetate slowly increased with temperature from 6% to 45%. Ethyl acetate is the most difficult organic compound to oxidize; therefore, the complete oxidation of ethyl acetate is limited in the homogeneous phase. At a reactor temperature of 350 °C, the maximum conversion obtained was only 45%.
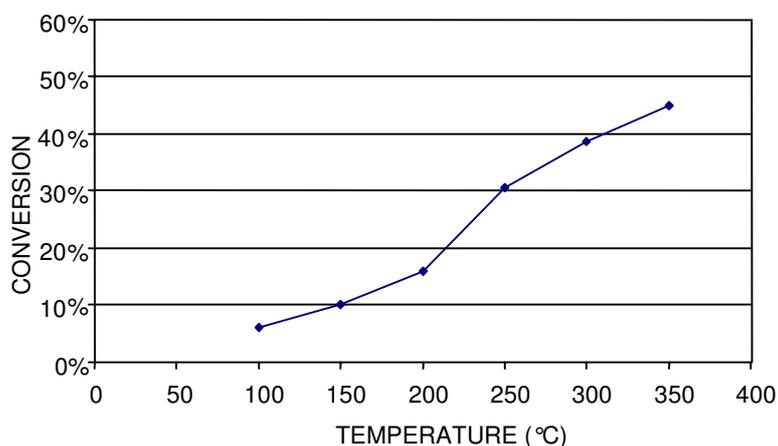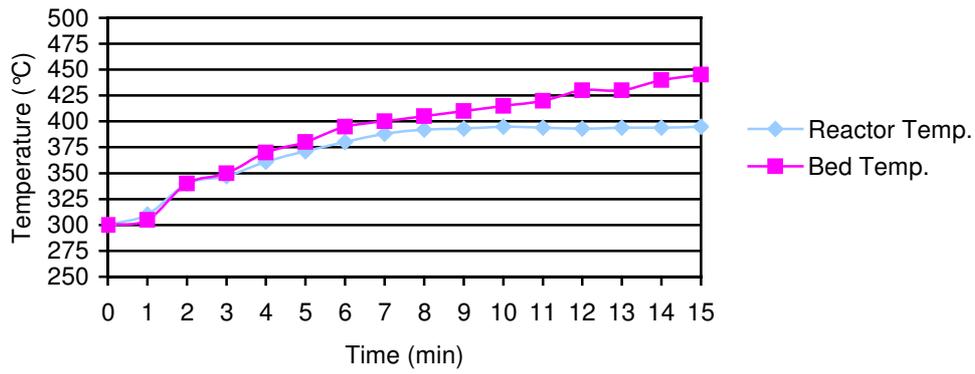

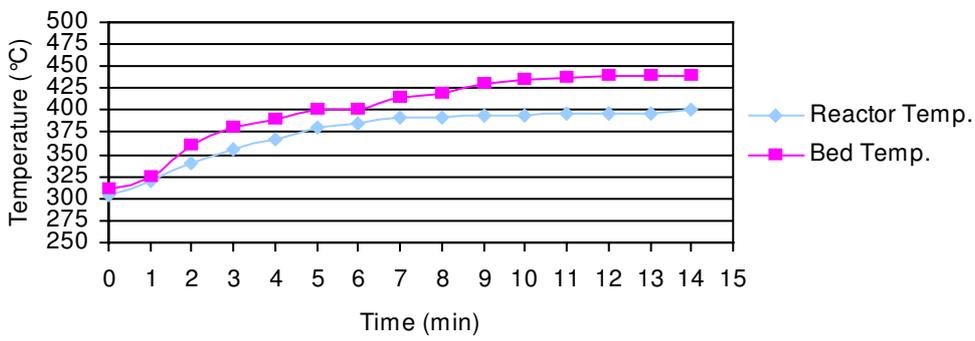**Figure 1.** Results of the homogeneous experiments with ethyl acetate.

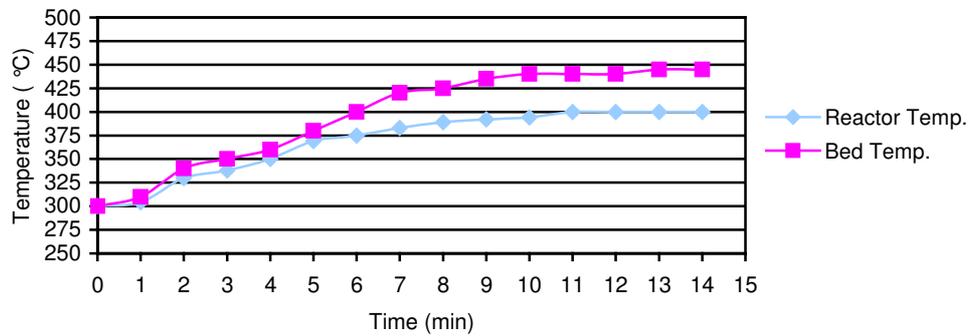Catalyst activity was predetermined by light-off experiments and the results can be seen in Figures 2-6.
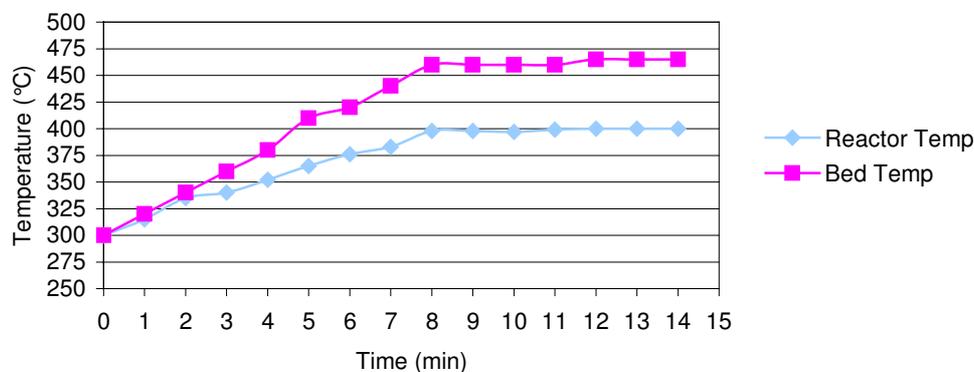
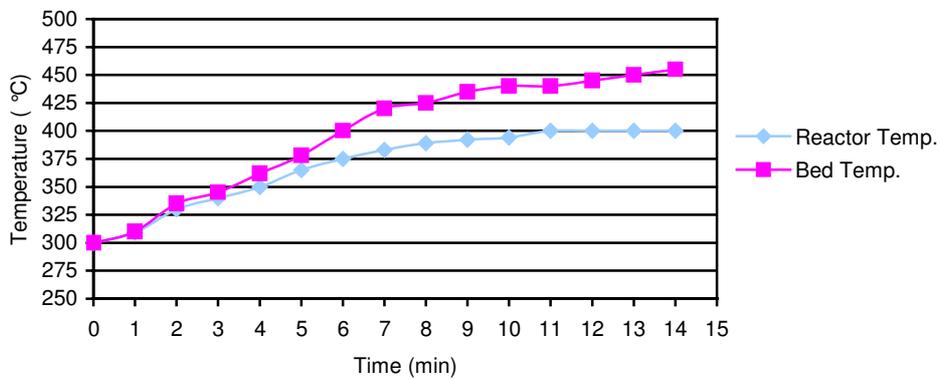**Figure 2.** Results of the light-off experiments with the CeO catalyst.

Figure 3. Results of the light-off experiments with the Co_2O_3 catalyst.

Figure 4. Results of the light-off experiments with the Mn_2O_3 catalyst.

Figure 5. Results of the light-off experiments with the Cr_2O_3 catalyst.


Figure 6. Results of the light-off experiments with the $CeO-Co_2O_3$ mixed catalyst.

The difference between bed and heater temperature was an indicator of the oxidation reaction on the catalyst. Therefore, by recording these temperatures and observing the temperature difference, the activity of the catalyst was determined.

According to light-off experiment results of all the catalysts, the temperature difference of the CeO catalyst was the highest.

The experimental results of the catalytic combustion of ethyl acetate with the 5 prepared catalysts are given in Figure 7.
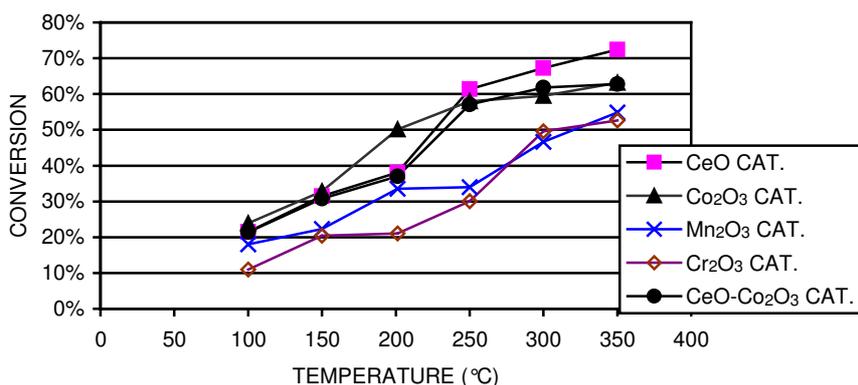
Figure 7. Catalytic oxidation reaction results with the prepared catalysts.

It follows from Figure 7 that the conversion rate of ethyl acetate on the CeO catalyst increased with increasing temperature. At 100 °C the conversion rate was 21%, which increased steadily to 39% at 200 °C. After that a sharp rise to 61% conversion occurred at 250 °C, followed again by a steady increase to 72% conversion at 350 °C. However, complete conversion was not obtained with this catalyst. The effect of the CeO catalyst cannot be seen above these reactor temperatures.

After comparing the results of the homogeneous and catalytic reactions on the CeO catalyst, it was seen that the CeO catalyst increased the conversion rate considerably. For example, at 250 °C the conversion rate with the catalyst was 61%, while it was only 31% in the homogeneous reaction.

As can be seen from Figure 7, reaction with the Co_2O_3 catalyst at reactor temperatures below 200 °C caused the conversion rate to sharply increase with increasing temperature. At 200 °C 50% of ethyl acetate was destroyed; however, above this temperature the increase in the rate of conversion was slow. Maximum conversion was 63%, at 350 °C. Total combustion did not occur with this catalyst either.

Unexpected results were obtained with the Mn_2O_3 and Cr_2O_3 catalysts. The conversion rates with these catalysts were not as high as expected in comparison to those obtained with the homogeneous reactions. For example, at the maximum temperature of 350 °C, the conversion rate was only 55% with Mn_2O_3 and 53% with Cr_2O_3, while it was almost 45% in the homogeneous experiment.

Unfortunately, on the mixed metal oxide catalyst, the synergetic effect of CeO and Co_2O_3 could not be seen. Only 21% conversion was obtained at 100 °C. Conversion increased steadily to 37% at 200 °C, after which a sharp rise to 57% conversion at 250 °C was observed, as with the CeO catalyst. From this point on a very small increase to 63% conversion at 350 °C was obtained, whereas it was 72% with the CeO catalyst alone.

Conclusion

For the oxidation of ethyl acetate, all 5 catalysts tested gave higher conversions than the homogeneous reactions; however, none of the 5 catalysts resulted in the complete combustion of ethyl acetate. At low reactor temperatures the conversion rates obtained with CeO and Co_2O_3 catalysts were almost the same, but at elevated temperatures the conversion rates with CeO were higher than those with Co_2O_3. For example, at 350 °C the difference was about 10%. The CeO catalyst may be further developed for the complete combustion of ethyl acetate in future studies.

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