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VOC Treatment by Catalytic Incineration

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ABSTRACT – Catalytic incineration of the most used VOCs in the chemical industries such as benzene, toluene, ethyl benzene, ethyl acetate and isopropanol have been investigated by using monolith supported metal oxide catalysts. CeO_2, Co_3O_4, Mn_2O_3, Cr_2O_3 and Cr_2O_3 – Co_3O_4 catalysts were prepared on ceramic monolith support and they were tested. The experimental studies were carried out at atmospheric pressure in a fixed-bed catalytic reactor with 500 to 850 % excess air. The prepared metal oxide catalysts showed excellent catalytic activity in the incineration of VOCs which were experienced. According to the experimental results, CeO_2 coated monolith catalysts was found to be suitable since it gave reproducible results, showed the highest mechanical stability and closely conversions for all experienced VOCs.

Keywords: air pollution, VOC treatment, incineration, monolith catalyst.

I. INTRODUCTION

Volatile organic compounds (VOCs) defined as hydrocarbons, including alcohols, alkenes and aromatics, are easily vaporized at ambient temperature and pressure and may pollute the atmosphere directly or indirectly as secondary pollutants [1]. These VOC contaminated gas streams are vented from a variety of industrial and commercial processes, such as printing, metal decorating, oil supplying, dry cleaning, paint drying, metal degreasing, manufacturing of organic compounds and polymers, and food processing, etc. [2]. VOC emissions should be limited and controlled to prevent air pollution, because they affect the change of climate, the growth and decay of plants and the health of human beings and all animals [3].

Several techniques, such as adsorption, absorption, thermal incineration and catalytic incineration, have been developed for the abatement of VOCs. Catalytic incineration is one of the most extended techniques used for the elimination of VOCs in environmental emission control, because catalytic incineration operates at temperatures much lower than those required for thermal incineration [4, 5, and 6].

The mechanism of catalytic incineration of VOCs depends on the type of catalyst used. In recent years, both precious metal and metal oxide catalysts have been used in incineration of VOCs. The noble metals platinum and palladium are recognized as the most typical species of precious metal catalysts. These catalysts are in general more active and also more tolerant to sulphur poisoning than metal oxides [7,8,9]. However, the base metal oxides are much cheaper, allowing a higher catalyst load. The use of a higher active surface area in the metal oxide bed also makes the catalyst less sensitive to no selective poisoning, which is common in stationary emission control [10, 11]. The catalytic activity of base metal oxide catalysts is inversely related to the strength of chemisorption of the VOC's and oxygen provided that adsorption is sufficiently strong for the VOC's and oxygen to achieve a high surface coverage. If the chemisorption are too strong, the catalyst will be quickly deactivated as active sites are irreversibly covered. This is one definition of poisoning. On the other hand chemisorption is too weak, only a small fraction of the surface is covered and catalytic activity is very low [5]. In many studies, MnO_2 , Cr_2O_3 , Co_3O_4 and CuO, were found to be the most active metal oxides for complete oxidation [10,12]. Ceria (CeO_2) is the commonly used catalyst in various catalytic converters due to its higher oxygen storage capacity. In recent decade, monolith supported CeO_2 catalysts were extensively used in the incineration of VOC's [13, 14].

Monoliths are one of the most innovating elements appeared in the last decades as the catalyst support. Thanks to its properties, its use has been extended in environmental applications, especially catalytic incineration. Monolithic catalysts are widely used due to their good attrition resistance and very low pressure drop in the high flows present in industrial emissions [15, 16].

The aim of this work is to compile the earlier experimental studies which are about the VOCs abatements with catalytic incineration and the performance of prepared monolith supported catalysts [17, 18, 19, and 20].

II. EXPERIMENTAL STUDY

The details of the preperation method of the mononolith supports and impregnation of the metal oxides on the catalysts have been reported elsewhere [17,18,19]. The list of the prepared catalysts and their metal oxide loading amount are given in Table 1.

The catalytic test performed in a fixed bed monolithic reactor in the temperature range of 100- 350 °C in a feed consists of 2100-3500 ppm VOC in inlet gas stream at atmospheric pressure. Dry air was used for incineration and nitrogen was used as carrier gas. The experimental system included mainly a vaporizer, a preheater, a monolithic reactor, a cooler and an absorber. The scheme of the experimental system and detailed explanation of apparatus have been given in previous studies [17]. Hewlett Packard (HP) 5890 Series II Gas Chromatograph (GC) equipped with flame ionisation detector and HP integrator was used for analysis of the exit gas stream.

TABLE. 1. The list of the prepared catalysts and metal oxide loading

Metal Oxide	Loading weight %
CeO_2	10-12
Co_3O_4	8-9
Mn_2O_3	8-9
Cr_2O_3	6-9

The specific surface areas (BET) of metal oxide coated monolith catalyst were characterized by multipoint physical adsorption of N_2 by using a Micrometrics ASAP 2010 instrument at 77 K.

III. RESULTS AND DISCUSSION

The BET results of the monolith catalysts used are as shown in Table 2. N_2 adsorption-desorption isotherms reveal the mesoporous character of the all catalysts.

TABLE. 2. The BET results of the catalysts

	Co_3O_4	Mn_2O_3	CeO_2	Cr_2O_3
S_{BET} (m^2/g)	8.4652	7.5255	9.4136	9.2735
Micro pore Volume (cm^3/g)	0.00236	0.00197	0.00187	0.00217
Average Pore Diameter (Å)	71.32	84.273	56.0971	82.329

The metal oxide coating increases significantly the surface area of the corroded monoliths and while metal oxide loading amount on the monolith support enhance the BET surface areas also enhance.

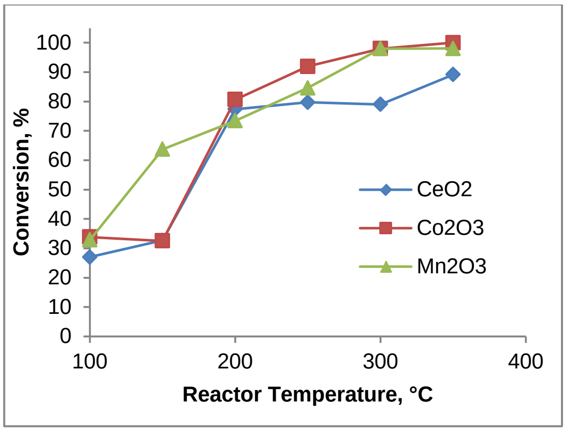


Fig. 1. Conversions of Isopropanol as a function of temperature on various metal oxide catalysts

Figure 1 shows the experimental results of the catalytic oxidation of isopropanol on CeO_2, Co_3O_4, and Mn_2O_3 catalysts. When the reactor temperature increased, the conversion of isopropanol also increased as expected. With CeO_2 catalyst, below 150°C, the conversion was limited to almost 30%. But after that the conversion sharply raised to 77%. The effect of the catalyst was seen when the reactor temperature exceeds 150°C. But the same increase did not continue with the temperature above 200 °C. Maximum 89 % conversion was obtained on the CeO_2 catalyst at 350°C. The complete combustion of IPA did not occur with this catalyst. With Co_3O_4 catalyst, at 200°C, 81% conversion was obtained. This value is higher than the conversion obtained at the same temperature with the other experienced catalysts. The conversion increased with increasing temperature and reached complete combustion above 300 °C with Co_3O_4 catalyst. In the results of the Mn_2O_3 catalyst experiments, the effect of the catalyst was seen up to 300 °C with a 64 % conversion at 150°C and with 98 % conversion at 300 °C, after then conversion remains constant.

In Figure 2 the results of the catalytic oxidation of ethyl acetate on the prepared catalysts is reported. With none of the four experienced catalysts, the complete combustion of ethyl acetate can be achieved. With CeO_2 catalyst, 21% conversion was recorded at 100°C. Conversion increased steadily to 39% at 200°C, and with a sharp rise to 61% at 250°C. After this a steady increase to 72% conversion at 350°C was observed. With Co_3O_4 catalyst, the maximum conversion obtained was 63% at 350 °C. Unexpected results were recorded with Mn_2O_3 catalyst. For example, at the maximum temperature of 350°C, the conversion was only 55%. As it is seen from the figure Cr_2O_3 catalyst also gives lower conversions like Mn_2O_3 catalyst. The maximum conversion is limited to 52.6%, at 350°C [18].

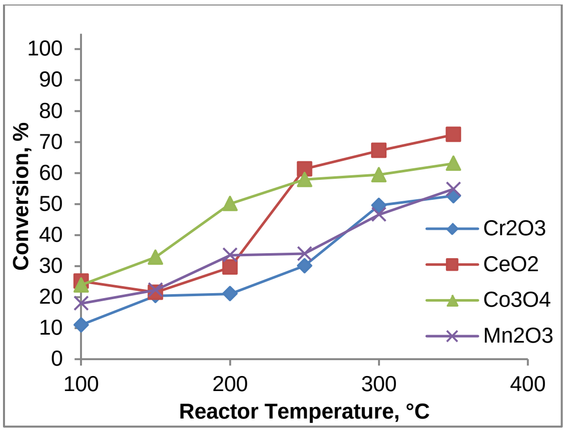


Fig. 2. Ethylacetate conversions as a function of temperature on various metal oxide catalysts

It can be seen from the Figure 3, at 150 °C, approximately 40% to 50% of ethyl benzene in the inlet gas stream was destroyed with all three tested catalysts. Above this temperature, with Cr_2O_3 catalyst the conversion values were obtained slightly higher than the other catalysts. Unfortunately, on mixed metal oxide catalyst the synergetic effect of Cr_2O_3 and Co_3O_4 was not seen. Only 73% conversion was obtained at 400°C, whereas it was 76 % with Cr_2O_3, and 74% with Co_3O_4 catalysts. However complete conversion was not obtained with these three catalysts [19].

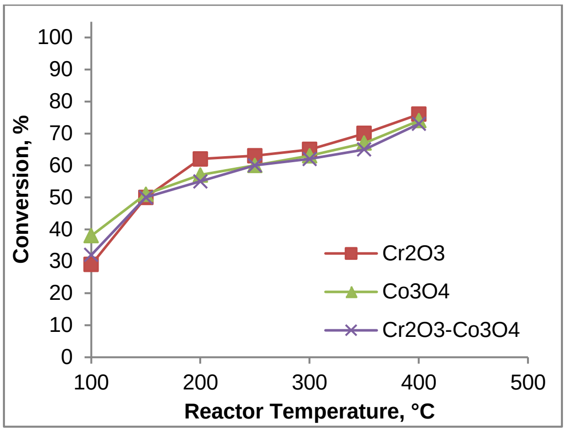


Fig. 3. Ethyl bnzene conversions as a function of temperature on various metal oxide catalysts

In Figure 4, the results of benzene incineration by using Cr_2O_3 and CeO_2 catalysts are shown. The incineration performances of the both catalysts were closely each other. With CeO_2 catalyst, 28% conversion was recorded at 150°C and then the conversion increased steadily to 60% at 250°C. At the maximum studied temperature (350°C), 72% of the inlet benzene was disposed of. By using Cr_2O_3 catalyst, below the reactor temperature 300 °C, obtained conversions are approximately 2 % higher than by using CeO_2 catalyst. The maximum conversion obtained was 70% at 350°C with Cr_2O_3 catalyst.

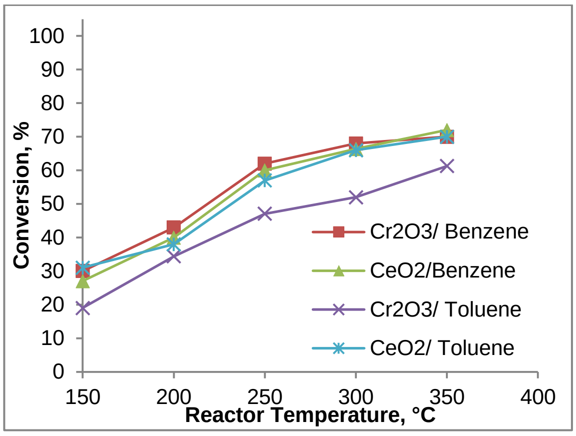
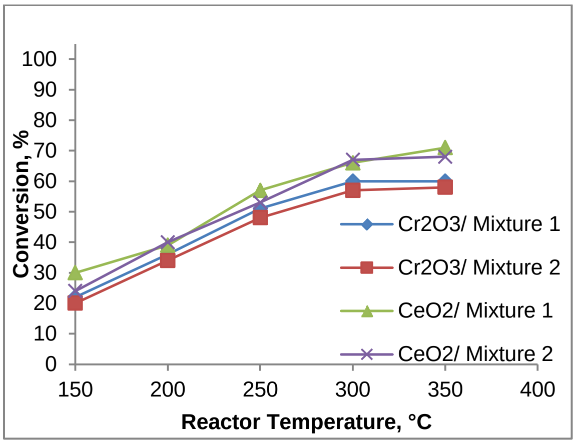


Fig. 4. Benzene and Toluene conversions as a function of temperature on various metal oxide catalysts.

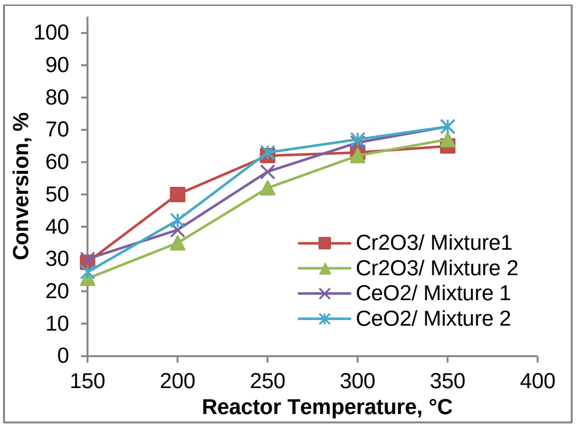
Figure 5 shows the experimental results of the catalytic oxidation of toluene. The comparing two catalysts the CeO_2 catalyst is seen more effective and observed conversions are approximately 10% higher than with Cr_2O_3 catalyst. The maximum conversions were obtained as 61% by using Cr_2O_3 catalyst and 70% by using CeO_2 catalyst at 350°C.

The conversions of Benzene and Toluene in the tested two mixtures are given in Figure 6. According to the experimental results on the Cr_2O_3 catalyst, below the reactor temperature at 250°C, there is no significant difference between toluene and benzene conversions, for both tested benzene-toluene mixtures. However at the temperature above this value, conversion of benzene is higher than toluene's. At 350°C, toluene conversions are 58% for mixture 1 (25% benzene-75 % toluene by mole) and 60% for mixture 2 (50% benzene-50 % toluene by mole) but benzene conversions are 70% for mixture 1 and 67% for mixture 2. With the CeO_2 catalyst, there are no considerable differences between benzene and toluene conversions for both mixtures. At 350°C, conversions obtained with CeO_2 catalyst are 71% for toluene and 74% for benzene at mixture 1. At the same temperature, 68% of toluene and 70% of benzene conversions are obtained for mixture 2.

The composition of the benzene-toluene mixture has no recordable effect on the conversions of the VOCs. By comparing the experimental results of CeO_2 catalyst and Cr_2O_3 catalyst, it can be seen that CeO_2 catalyst showed higher conversion values than Cr_2O_3 catalyst in both mixtures [20].



a. Toluene conversions in the mixture



b. Benzene conversions in the mixture

Fig. 5. Benzene – Toluene mixtures conversions as a function of temperature on various metal oxide catalysts

IV. CONCLUSION

From the all experimental results, it can be said that the performance of a catalyst is different for each VOCs. For example; 98% conversion was obtained at 350^{o}C for isopropanol incineration, but at same temperature only 55 % conversion was obtained with Mn_2O_3 catalyst. According to the results isopropanol was destroyed more easily than benzene, toluene and ethyl acetate with all tested metal oxide catalysts.

CeO_2 catalyst was found most stable and active within the all prepared catalysts for tested VOCs. Approximately 70% conversions were obtained for isopropanol, ethyl acetate, benzene, toluene and both benzene/toluene mixtures. CeO_2 catalyst is also known as a key component in the automobile three-way catalysts primarily for its role in oxygen storage, taking up oxygen under oxidizing conditions and releasing it [21].

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