

5% Cr₂O₃/γ-Al₂O₃ Catalysts Synthesized as Research for Oxidation Activation of Trichloroethylene

Myung, So-Young¹ · Suh, Myung-Gyo² · Lee, Yong-Hee³

¹Materials and Science & Technology Division,

Korea Institute of Science and Technology(KIST), Korea

²Dept. of Medical Administration, Dongeui Institute of Technology, Korea.

³Research Institute of Basic Science, Dongeui University, Korea.

Abstract

The research addressed the ability of 5% Cr₂O₃/γ-Al₂O₃ to catalytically oxidize trichloroethylene(TCE). In order to determine which procedure gives the most active catalyst among the attempted several procedures, catalytic oxidation reaction of TCE was conducted to every catalysts synthesized according to different process in tubular reactor system, which had functional relationships with temperature and space velocity. The ratio of TCE conversion was analyzed by gas chromatography with electron capture detector.

Introduction

Volatile organic compounds (VOCs) emitted from industrial solvents used in paint, ink and adhesive manufacturing, and also from the petrochemical and chemical industries, are involved in environmentally damaging processes. This is a consequence of their toxicity to living things by direct reaction with living matter, or indirectly, through chemical reactions within the atmosphere which subsequently affect living matter. One of the most effective ways to assure complete destruction of VOCs present in gaseous emission is by incineration. Thermal incineration of VOCs is a widely used technology, and can be performed by direct-flame oxidation in a combustion chamber, at temperatures at 760°C or greater, depending upon the nature of the

VOCs. Halogenated organics are often more difficult to oxidize than unsubstituted organics. One technology which can help reduce costs and achieve complete oxidation is catalytic oxidation. The temperature needed for the catalytic oxidation reaction for the majority of VOCs is between 280°C and 600°C. Catalytic materials typically used for VOC incineration include platinum and palladium; other formulations are also used including transition metal oxide for emission streams containing chlorinated compounds. This study is to check the catalytic ability of Cr_2O_3 to decompose TCE and presents the results of an experimental investigation of the synthesis and operating parameters of a transition metal oxide, Cr_2O_3 , used as an oxidation catalysts.

Experiment

Table 1. Procedures tested in synthesizing 5% $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$.

catalyst procedure	A	B	C	D	E	F	G	H	I	J	K
presoaking with base	pH7.5	pH7.5	pH7.5	pH7.5	pH7.5	pH7.5	pH9	pH9	pH9	pH7.5	pH9
drying(100°C)	No	No	No	10hr	10hr	10hr	10hr	10hr	10hr	No	No
soak γ -alumina with $\text{Cr}(\text{NO}_3)_3(\text{aq})$ adjusted as pH 3.5	3/4V	3/4V	3/4V	V	V	V	V	V	V	1/2V	1/2V
drying(100°C)	4hr	10hr	10hr	4hr	10hr	10hr	4hr	10hr	10hr	4hr	4hr
precipitation by $\text{NH}_4\text{OH}(\text{aq})$	No	pH9 V	pH11 V	No	pH9 V	pH11 V	No	pH9 V	pH11 V	No	No
drying(100°C)	No	4hr	4hr	No	4hr	4hr	no	4hr	4hr	No	No
calcination(600°C) 6hr	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

The diversely attempted procedures to achieve proper $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ was evaluated by comparing the activities of catalytic oxidation of TCE over catalysts synthesized according to those procedures. For this diagnostic reaction, 100ppm TCE with balance air was flowed into top of the laboratory-scale tubular reactor (vertical type) that the each

synthesized catalyst (powder type) was located in the center of. The difference of TCE concentration between injected flow and outflow was regarded as the rate of conversion by each synthesized catalyst, and the concentrations were analyzed by GC-ECD after the bottom of reactor. Reaction temperature was controlled by furnace covering reactor from 100°C to 600°C, and space velocity was remained as 30,000v/v/hr.

Result

The oxidation of 100 ppm TCE at a space velocity of 30,000 v/v/hr, and in the temperature range 200°C to 600°C was used as a diagnostic reaction to determine the most active catalyst among those synthesizes. Fig. 1 shows the typical TCE conversion curve. This type of curve was obtained for each of the 11 synthesized catalysts. The best catalysts were those that were shifted to the left, i.e., the same conversion was achieved at a lower temperature. Since all synthesized catalysts showed that the percent conversion is relatively high at temperature 250°C and 350°C, the conversion percentage of each synthesized 5% Cr₂O₃/γ-Al₂O₃ was compared at 300°C. The result of this activity test is compared as a bar graph at Fig. 2. In this bar graph, it can be seen that the most active synthesized 5% Cr₂O₃/γ-Al₂O₃ catalyst was the one developed using procedure C as listed in Table 1. This catalyst shows 67.2% TCE conversion at 300°C. The procedure used to synthesize this catalyst is summarized as follows; First, γ-Al₂O₃ is soaked in a quarter of the total volume needed to fill its pores with 0.01N NH₄OH, The resulting pH is 9. Then this presoaked γ-Al₂O₃ is soaked with the remaining three quarters of volume with chromium nitrate aqueous solution whose pH was adjusted with NH₄OH to about 3.5. This γ-Al₂O₃ containing the precursor of active catalytic material is then dried. Cr(OH)₃ precipitate is formed by soaking in pH=11 NH₄OH solution equal to the total pore volume of γ-Al₂O₃. Finally the product is calcined 600°C for 6hours. In the course of the research to modify the incipient wetness method to prepare active 5% Cr₂O₃/γ-Al₂O₃ for TCE catalytic oxidation, and to compare the activity of catalysts prepared by different synthetic methods, several interesting observations were noted and investigated. It was observed that the γ-Al₂O₃ presoaked in 0.01N NH₄OH, the resulting pH is 9, seems to give a

more active catalysts than that soaked in 0.01N NH_4OH , the resulting pH is 11. Catalysts A, B, C, D, E, F and J which were synthesized using a presoak of pH 9 NH_4OH showed generally higher activity than catalysts G, H, I and K which were presoaked in pH=11 NH_4OH . This is most apparent when we see catalysts, catalyst J has higher activity than catalyst K. Catalyst J and K were both synthesized using same procedure except that the J catalyst was presoaked in pH=9 NH_4OH and K was presoaked in pH=11 NH_4OH . It was also observed that the procedure that included a $\text{Cr}(\text{OH})_3$ precipitation step obtains a more active catalyst. Catalyst A and B were produced following same procedure except that the Cr_2O_3 in catalyst A was formed by removing the nitrate in $\text{Cr}(\text{NO}_3)_3$, while Cr_2O_3 in catalyst B was obtained after Cr^{3+} is precipitated by NH_4OH . The differences between catalyst D and E, and G, H are the same as the differences between catalyst A and B. The B, E and H synthetic procedure involving a precipitation step produced catalysts with higher activity than A, D and G catalysts. It was also noted from the activity comparison that formed from the conversion of $\text{Cr}(\text{OH})_3$ produced using pH=11 NH_4OH is more active than the Cr_2O_3 from $\text{Cr}(\text{OH})_3$ formed at pH=9. In the case of catalysts B and C, these catalysts were synthesized using same procedure, except that $\text{Cr}(\text{OH})_3$ is formed using different pH. The comparison of E and F, and catalysts H and I follows that described for B and C. In each case, precipitation at pH=11 NH_4OH produces a slightly more active Cr_2O_3 on $\gamma\text{-Al}_2\text{O}_3$ than was found for pH=9.

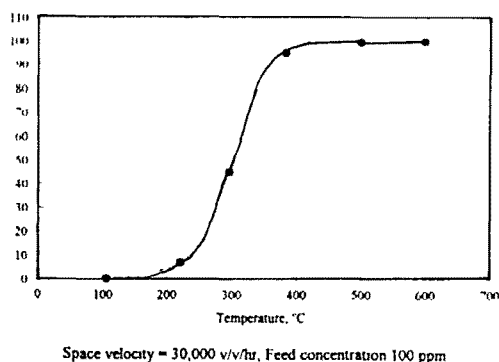


Fig. 1. Typical temperature dependent of TCE conversion.

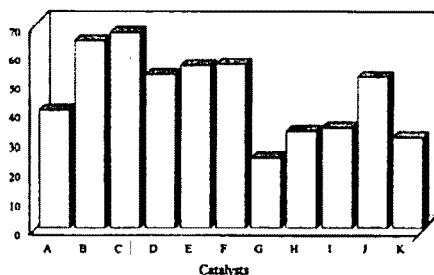


Fig. 2. Activity comparison of 5% $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts synthesized by different procedures.

Conclusion

Modifications to the incipient wetness method used in the preparation 5% $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts for TCE oxidation give conversions in the range of 20% to 67% at 300 °C and 30,000v/v/hr. The main products from the catalytic oxidation of TCE over synthesized 5% $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ are CO, CO_2 , chlorine and hydrogen chloride.

References

1. Bretschneider, B. and Kurfurst, J. *Air Pollution Control Technology*, Fundamental aspects of pollution control and environmental science series 8, New York, pp. 170–173, 1987.
2. Lawton, T. J. and Gower, R. Catalysis aid cleaner environment thermal incineration process enhanced by platinum-based catalyst, *platinum metals review* edited by Johnson matthey, environmental products catalytic systems division, Royston, vol. 38, No. 4, pp. 160–162, 1994.
3. Syracuse Research Corp. *Toxicological profile for trichloroethylene*, oak ridge national laboratory under DOC interagency agreement No. 1857-BO26-AL, 1989.