

Air Pollution Control by Oxidation of Aromatic Hydrocarbon over Supported Metal Oxide

Sompoch Pooperasupong^{a*}, Brigitte Caussat^b and Somsak Damronglerd^a

^a Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.

^b Laboratoire de Genie Chimique, ENSIACET/INP, Toulouse 31106 cedex 01, France.

* Corresponding author, E-mail: damronglerd_s@yahoo.co.th

Received 1 Aug 2007
Accepted 26 Nov 2007

ABSTRACT: The oxidation of styrene has been investigated over copper oxide and nickel oxide supported on commercial NaX zeolite. The catalyst screening illustrated that nickel oxide catalyst was the most active catalyst. The conversion of CO₂ became appreciable in the range of 220-280 °C. The reaction rate depended mainly on the styrene concentration and the reaction temperature. The apparent activation energies over copper oxide and nickel oxide were determined to be 251.3 and 273.1 cal/mole, respectively.

KEYWORDS: Oxidation of aromatic hydrocarbon; Catalytic oxidation; Supported metal oxide; VOCs.

INTRODUCTION

Volatile organic compounds (VOCs) are emitted from a variety of industrial and commercial processes, such as printing, oil supplying, dry cleaning, paint drying, metal degreasing, food processing, manufacturing of organic compounds and polymers. They are recognized as a major source of air pollution, either directly through their toxicity or malodorous nature, or indirectly as smog precursors, cause of acid rain and finally global warming¹. For this reason, legislation has been introduced in many countries to set very low emission limits for VOCs in process exhaust gases. A common way for reducing the emission of VOCs is catalytic oxidation. By incorporating suitable catalysts into the oxidation system, not only can the reaction be carried out at temperatures much lower than those required for thermal oxidation, but the energy requirement is dramatically reduced. More importantly, the production of NO_x, which is a toxic by-product, is significantly reduced.

Supported noble metals, such as Pt and Pd are well established as efficient catalysts for the VOCs oxidation. They possess high activities but are expensive. However, there is a potential for supported metal oxide catalysts, since they are cheaper, less sensitive to certain catalyst poison but less active²⁻⁴, compared with the noble metals. Furthermore, it is well known that supports play an important role in catalytic activity enhancement⁵. Large-pore zeolites are often chosen for their high specific surface area and acidic-basic properties, allowing high metal loading.

The main purpose of this work is to synthesize metal oxide catalysts supported on commercial NaX

zeolite and to investigate their catalytic activities for the combustion of aromatic hydrocarbon.

MATERIALS AND METHODS

Catalyst Preparation

The catalysts used in this research were copper oxide and nickel oxide, loading on commercial NaX molecular sieve. CuO and NiO were prepared by impregnation method using Cu(NO₃)₂·2.5H₂O and Ni(NO₃)₂·6H₂O as metal sources. NaX zeolite was soaked in solution and dried overnight at 110 °C then calcined in air at 400 °C for 2 hours. The theoretical loading of CuO and NiO were 0.8 wt%. Specific surface area and pore size of catalysts were determined by N₂ adsorption/desorption technique with a Micromeritics ASAP 2020 instrument. The catalysts were degassed at 90 °C in the vacuum tube prior to measurement of surface area. A standard procedure for determining the specific surface area was based on the adsorption of N₂ at liquid N₂ temperature.

Catalytic reactor

The reactors were made of stainless steel column with diameter of 5 cm, 1 m in height (packed with 0.8 kg of CuO catalyst) and a diameter of 10 cm, 1.5 m in height (packed with 6 kg of NiO catalyst). The reactor could be electrically heated by the heating coil with a temperature controller. A thermocouple was inserted into the reactor; then, connected to the temperature controller for measuring the reaction temperature. By adjusting the temperature controller, isothermal conditions could be achieved. The flow diagram and experimental

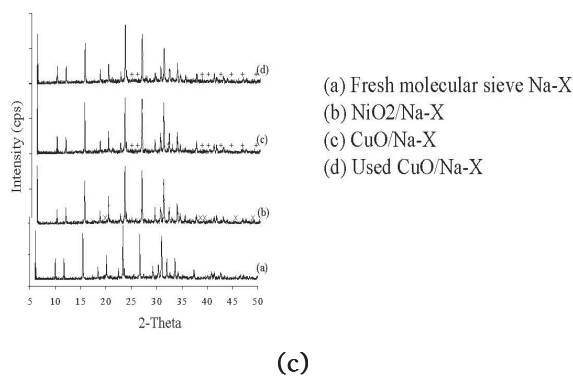
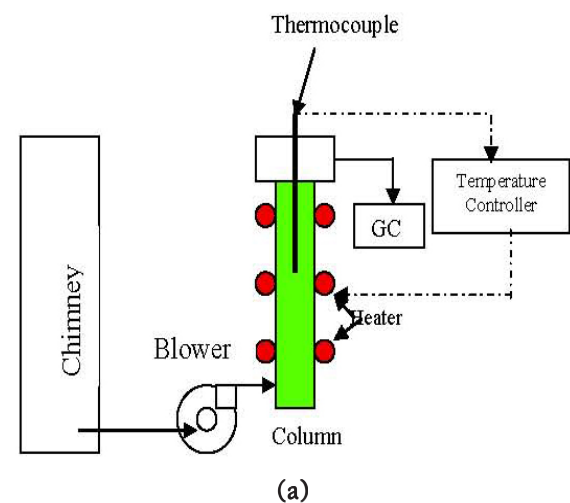


Fig 1. (a) Flow diagram and experiment equipments. (b) Flow diagram and experiment equipments. (c) XRD of fresh catalysts and used catalyst.

equipments were shown in Figure 1, (a) and (b).

Activity measurement

The catalytic activity was tested using styrene oxidation as the model reaction. The concentration of the styrene used was 3.55 mole% in air. The catalytic activity of all catalysts was measured in terms of “light-off temperature”. In the experiment, two types of catalyst were prepared in the spherical form and then were placed in the reactor column. The experiments were carried out by running the steady state oxidation in a fixed bed reactor with various inlet gas flow rates. The temperature of the catalyst bed was increased continuously from 40 to 280 °C. The product sampling began after the reactant gas had passed through the catalyst bed for 5 minutes to allow the system to reach the steady state. The product gas was analyzed with a gas chromatograph to find the conversion. The reaction-temperature plotting of conversion was represented by the activity curves. These activities were measured in terms of the temperature corresponding to 50% conversion. The kinetic parameters would also be evaluated by taking the reaction over the catalyst in order to establish the kinetic model.

RESULTS AND DISCUSSION

Catalyst Characterization

The specific surface area measurements and average pore sizes of the catalysts are summarized in Table 1. The specific surface area and average pore size of copper oxide catalyst are 488.0 m²/g and 24.7 Å, respectively. The specific surface area and average pore size of nickel oxide catalyst are not different from that of copper oxide catalyst, being 484.6 m²/g and 25.2 Å, respectively.

Catalyst Activity

The catalyst screening was achieved by comparing the catalytic activity over the oxidation reaction in term of light-off temperature. The conversion as a function of reaction temperature is illustrated in Fig. 2 and 3 for copper oxide and nickel oxide catalysts respectively. As shown in Fig. 2, at the flow rate of 86 liter/hr 0.8 kg CuO/NaX catalyst ($W/F_{cat} = 5.84 \text{ kg}_{cat} \cdot \text{hr}/\text{mole}$), the light-off temperature at 50% conversion was 190 °C. When the flow rate increased to 428 liter/hr ($W/F_{cat} = 1.18 \text{ kg}_{cat} \cdot \text{hr}/\text{mole}$), the light-off temperature at 50% conversion increased to 207 °C. The explanation for this result could be that due to the decrease in residence time, the higher reaction temperature was required to reach the same removal efficiency. In the case of NiO/NaX catalyst, at the flow rate of 2,897 liter/hr 3 kg catalyst ($W/F_{cat} = 0.65 \text{ kg}_{cat} \cdot \text{hr}/\text{mole}$) and the flow rate of 5,973 liter/hr 3 kg catalyst ($W/F_{cat} = 0.33 \text{ kg}_{cat} \cdot \text{hr}/\text{mole}$), the light-off temperature at

50% conversion was 181 and 197 °C respectively.

It could be seen that the nickel oxide catalyst was more suitable than the copper oxide catalyst for catalytic oxidation because of the lower light-off temperature at 50% conversion and the higher removal efficiency in high temperature region. The light-off temperatures and the removal efficiencies for two catalysts are presented in table 2.

Table 1. Specific surface area and average pore size of two catalysts used.

| Catalyst | Specific surface area m ² /g) | Average pore size (Å) |
|----------|---|--------------------------|
| CuO/NaX | 488.0 | 24.7 |
| NiO/NaX | 484.6 | 25.2 |

Table 2. Activity in term of light-off temperatures and removal efficiency at 270 °C.

| Type of Catalyst | W/F ₀ (kg•hr/mole) | Light-off temperature at 50% conversion (°C) | %conversion at 270 °C |
|------------------|----------------------------------|--|-----------------------|
| CuO/NaX | 5.84 | 190 | 74.2 |
| | 1.18 | 207 | 62.0 |
| NiO/NaX | 0.65 | 181 | 76.8 |
| | 0.33 | 197 | 54.0 |

Kinetic Study

In kinetic measurements, the rate of reaction can be determined in terms of initial reaction rate, which is measured by the integral method according to equation (1):

$$r = \frac{dX}{d(W / Fo)} \tag{1}$$

- Where r = reaction rate, mole•hr⁻¹•kg⁻¹cat
- X = the conversion of reaction
- W = the catalyst weight, kg
- F₀ = the molar flow rate, mole•hr⁻¹

For kinetic model, the effect of reactant concentration on the reaction rate was investigated at 280 °C. Fig. 4 shows the relationship between the reaction rate at a given temperature and reactant concentration. The reaction order was found to be 2 with respect to styrene concentration. The effect of temperature on the reaction rate was studied in the temperature range of 210 to 260 °C at the atmospheric pressure. The Arrhenius plots of the reaction rate as a function of the reciprocal absolute temperature are depicted in Fig. 5 and 6 for copper oxide and nickel oxide catalyst respectively. These figures show the linear line whose slopes represent the apparent activation

energies. From these figures, the apparent activation energies were obtained at 251.3 and 272.1 cal/mole for CuO and NiO catalyst respectively.

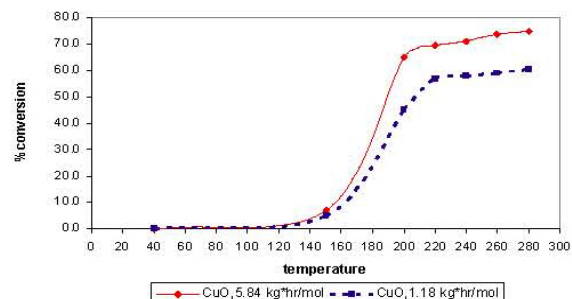


Fig 2. The oxidation activity data for CuO catalyst.

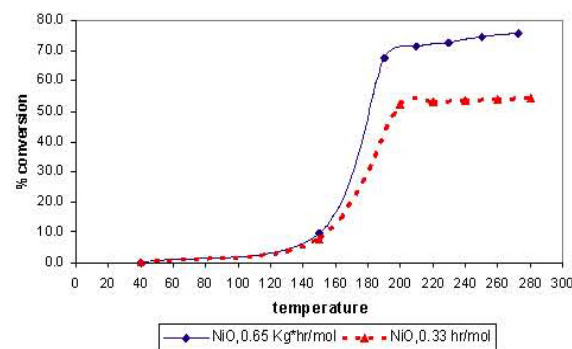


Fig 3. The oxidation activity data for NiO catalyst.

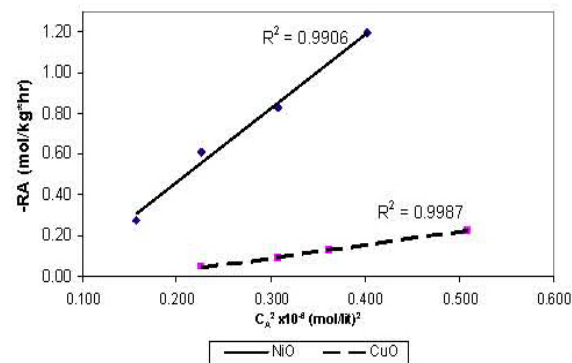


Fig 4. The reaction rate as a function of concentrations.

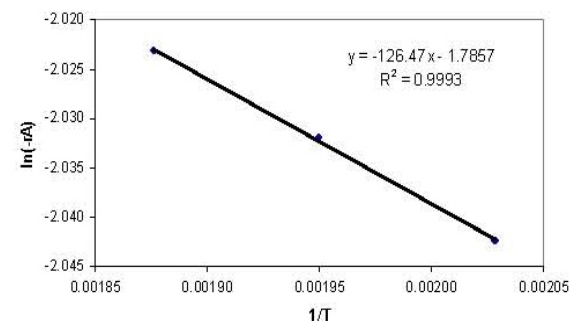


Fig 5. Plot for determining Ea over the CuO catalyst (0.8 kg catalyst and flow rate of 428 liter/hr).

CONCLUSION

Catalytic oxidation of styrene in excess oxygen is carried out over two catalysts. The activities of all catalysts are investigated in terms of light-off temperature at 50% conversion. The reaction is operated in the range of 40 to 280 °C. The complete combustion product such as CO₂ and water are obtained as the major products within this temperature range. Among the two catalysts studied, NiO loading on NaX catalyst is suitable for complete oxidation; as a result, CO₂ is apparently produced as primary product, indicating the efficiency of nickel in promoting the destruction of the C-C bond to complete combustion products. In this study, NO_x is not found to be a product from the catalytic oxidation due to the low reaction temperature. The reactions over copper and nickel oxide catalysts at 280 °C show a second order dependence on VOCs concentration. The Arrhenius plots show the apparent activation energies of reaction over copper and nickel catalysts to be 251.3 and 272.1 cal/mole, respectively.

ACKNOWLEDGEMENTS

Financial support from the Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program (Grant No. PHD/0125 /2547) to Sompoch Pooperasupong and Somsak Damronglerd is acknowledged.

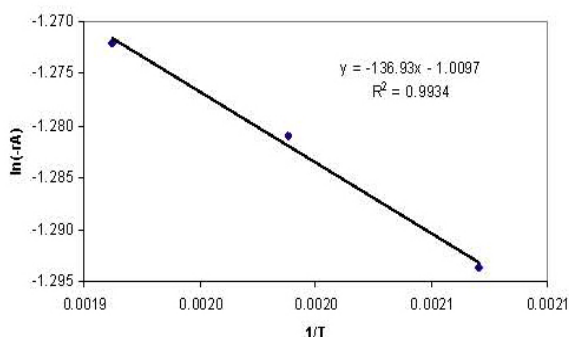


Fig 6. Plot for determining Ea over the NiO catalyst (3 kg catalyst and flow rate of 2,897 liter/hr).

REFERENCES

1. P. Papaethimiou, T. Ioanides, X.E. Verykios, Combustion of non-halogenated volatile organic compounds over group VIII metal catalysts, *Applied Catalysis B: Environmental* **13** (1997)
2. P.O. Larsson, H. Berggren, A. Andersson, O. Augustsson, Supported metal oxides for catalytic combustion of CO and VOCs emissions: preparation of titania overlayers on a macroporous support, *Catalysis Today* **35** (1997) 137-44.
3. I.E. Sungkono, H. Kameyama, T. Koya, Development of catalytic combustion technology of VOC materials by anodic

- oxidation catalyst, *Applied Surface Science* **121/122** (1997) 425-8.
4. J. I. Gutiérrez-Ortiz, Beatriz de Rivas, R. López-Fonseca, J.R. González-Velasco, Catalytic purification of waste gases containing VOC mixtures with Ce/Zr solid solutions, *Applied Catalysis B: Environmental* **65** (2006) 191-200.
5. H.L. Tidahy, S. Siffert, F. Wyrwalski, J.-F. Lamonier, A. Aboukais, Catalytic activity of copper and palladium based catalysts for toluene total oxidation, *Catalysis Today* **119** (2007) 317-20.
6. L. Pinard, P. Magnoux, P. Ayrault, M. Guisnet, Oxidation of chlorinated hydrocarbons over zeolite catalysts 2. Comparative study of dichloromethane transformation over NaX and NaY zeolites, *Journal of Catalysis* **221** (2004) 662-5.
7. S.C.Kim, The catalytic oxidation of aromatic hydrocarbons over supported metal oxide, *Journal of Hazardous Materials* **B91** (2002) 285-99.
8. Q. H. Xia, K. Hidajat, S. Kawi, Adsorption and catalytic combustion of aromatics on platinum-supported MCM-41 materials, *Catalysis Today* **68** (2001) 255-62.
9. S.F. Tahir, C.A. Koh, Catalytic destruction of volatile organic compound emissions by platinum based catalyst, *Chemosphere* **38** (1999) 2109-16.
10. C.N. Satterfield, *Heterogeneous Catalysis in Industrial Practice*, McGraw-Hill, New York, 1991.
11. E. Noordally, J.R. Richmond, S.F. Tahir, Destruction of volatile organic compounds by catalytic oxidation, *Catalysis Today* **17** (1993) 359-66.
12. D.R. Van der Vaart, W.M. Vatvuk, A.H. Wehe, Thermal and catalytic incinerators for the control of VOCs, *Journal of Air and Waste Management Association* **41** (1991) 92-8.
13. J.H. Lee, D.L. Trimm, Catalytic combustion of methane, *Fuel Processing Technology* **42** (1995) 339-59.