

Catalytic Combustion of Benzene over Supported Metal Oxides Catalysts

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Abstract—Catalytic combustion of benzene over supported metal oxides has been investigated. The catalysts have been prepared by incipient wetness method and characterized by XRD, FT-Raman, ESR and TPR. Among supported metal oxides, CuO_x supported on TiO₂ is found to have the highest activity for benzene oxidation. In addition, among the catalysts of copper oxide supported on TiO₂, Al₂O₃ and SiO₂, titania-supported catalyst (CuO_x/TiO₂) gives the highest catalytic activity. CuO_x/TiO₂ (Cu loading 5.5 wt%) shows the total oxidation of benzene at about 250 °C. From the ESR and FT-Raman results, the CuO dispersed on the TiO₂ surface acts as an active site of CuO_x/TiO₂ catalysts on the oxidative decomposition of benzene. The catalytic activity gradually increases with an increase of Cu loading on TiO₂. When Cu loading reaches 5.5 wt%, the total conversion temperature is lowered to 300 °C. However, the catalytic activity considerably decreases at 7 wt% Cu loading. The catalytic activity increased with an increase of oxygen concentration but the concentration of benzene showed no difference in the benzene conversion. This result suggests that the rate determining step is the adsorption of oxygen.

Key words: CuO_x/TiO₂ Catalyst, Benzene, Catalytic Combustion, VOCs, TPR

INTRODUCTION

Volatile organic compounds (VOCs) include all organic compounds that exist in the gaseous state in ambient air. Offensive odours and toxic air emissions as well as the formation of ground-level ozone and petrochemical smog are environmental problems which are related to emissions of VOCs. To reduce the environmental impact of these emissions and be able to fulfil established goals regarding the reduction of VOCs, the legislation which already partly has been introduced will become more stringent and broader [Kim et al., 2001].

Benzene is a VOC emitted from different industries, such as petrochemical; paint and coating industries and steel manufacture [Cho et al., 1999; Ferreria et al., 2001]. Catalytic combustion of VOCs can operate at lower temperature. The major advantage of the catalytic combustion is that it can treat very dilute pollutants less than 1% efficiently which cannot be thermally combusted without additional fuel. It is more energy efficient, and therefore, has a distinct economic advantage. Hence, catalytic oxidation has a broad applicability for 'end of pipe' pollution clean up than does thermal oxidation [Hutchings et al., 1996].

Many different metal oxides are known to be active for the combustion of VOCs, e.g., CuO, Co₃O₄, Cr₂O₃, NiO, Fe₂O₃ and MnO₂ [Larsson and Andersson, 1998; Vass and Georgescu, 1996]. The oxide can be deposited on a support to increase its dispersion and, moreover, the specific activity can be increased due to a reaction or interaction with the support. TiO₂, which is a support widely used [Satterfield, 1991], is known in many cases to enhance the activity due to active phase-support interaction [Cordoba et al., 1998].

In the present work, we have investigated the results of the catalytic combustion of benzene over supported metal oxides. The catalysts were characterized using FT-Raman, X-ray diffraction (XRD),

electron spin resonance (ESR) and temperature-programmed reduction (TPR) in order to determine the nature of the copper species. In addition, their catalytic activity on benzene combustion in the presence of oxygen was also examined along with the effect of the type of supports, metal oxide, and copper loading ratio.

EXPERIMENTAL

All catalysts used in this experiment were prepared via incipient wetness method. The aqueous solutions of metal nitrates were used as precursors for metal oxides. TiO₂ (P-25), SiO₂ (Carbosil) and Al₂O₃ (γ -alumina) were impregnated with appropriate amounts of precursor solution to incipient wetness; followed by stirring continuously at 80 °C until the total evaporation of water. Finally, all samples were calcined at 500 °C for 12 h.

Reaction tests were carried out in a continuous flow fixed-bed reactor. The reactor was a quartz glass tube with 1 cm OD and 24 cm long, mounted in a tubular furnace. K-type thermocouple was in contact with the catalyst bed. The reaction was carried out at a range of 200-500 °C and a feed flow rate of 100 cm³/min (gas hourly space velocity GHSV=30,000 h⁻¹) controlled by a mass flow meter/controller (Tylan). The outlet gases were analyzed using on-line gas chromatography equipped with flame ionization and thermal conductivity detector. The analysis of benzene and CO/CO₂ were conducted through Carbowax and Hysep Dip columns, respectively.

The crystal structures of the prepared supported copper oxides were examined by powder X-ray diffraction (XRD) with Cu K α radiation (Rigaku Co. Model DMax). Temperature-programmed reduction (TPR) experiments were carried out using 20 mg catalysts under a gas flow (30 ml/min) of hydrogen (5%) and nitrogen (95%). The temperature of catalysts was linearly raised in a rate of 10 °C/min. A thermal conductivity detector was used to monitor the hydrogen consumed during TPR course. ESR measurement was carried out on a JEOL JEX-PX 2000 spectrometer working at the

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X-band frequency and 100-kHz field modulation. In addition, Raman spectra were recorded using a Bruker IFS 66/FRA-106/S spectrometer.

RESULTS AND DISCUSSION

1. Characterization of Catalysts

Fig. 1 shows the XRD patterns of the supported CuO_x catalysts calcined at 500 °C. In the case of $\text{CuO}_x/\text{Al}_2\text{O}_3$ and $\text{CuO}_x/\text{SiO}_2$ catalysts, CuO crystalline phase is observed at $2\theta=35.5^\circ$. In the $\text{CuO}_x/\text{TiO}_2$ catalyst, the major phase of the prepared particles was anatase and rutile of TiO_2 , while no reflection is observed at $2\theta=35.5^\circ$ corresponding to the most intense reflection of tenorite CuO. This means that if a part of copper exists in the form of CuO clusters, these are not large enough to be detected by XRD [Coq et al., 1995].

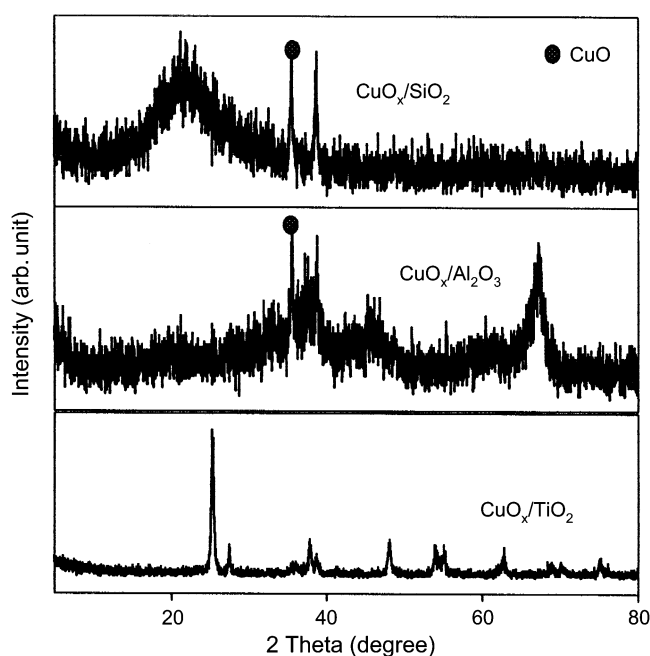


Fig. 1. XRD patterns of supported copper oxides.

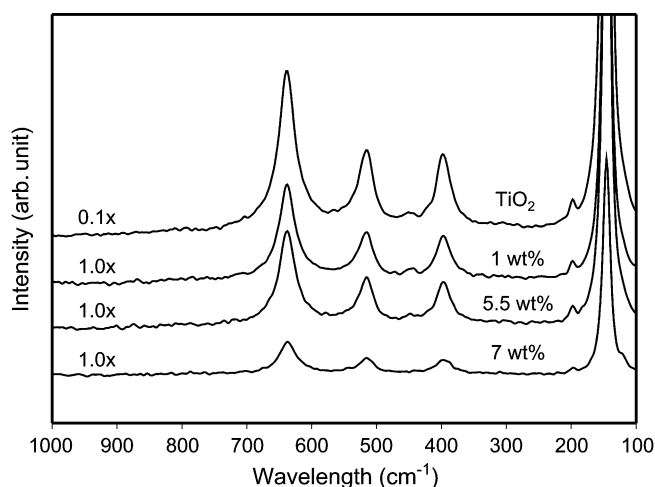


Fig. 2. Raman spectra for $\text{CuO}_x/\text{TiO}_2$ catalysts with different Cu loading.

This suggests that the TiO_2 support stabilizes the CuO phase in a highly dispersed state because of its small size compared to other support.

Fig. 2 shows the Raman spectra for pure TiO_2 and TiO_2 loaded with different amount of CuO_x . As shown in Fig. 2, the four typical bands of TiO_2 anatase [Larsson and Andersson, 1998] at 150, 395, 516 and 640 cm^{-1} can be seen for all catalysts containing TiO_2 . It is well known that pure CuO has one strong band at 296 cm^{-1} and two weak band at 345 and 631 cm^{-1} [Reimann and Syassen, 1990]. However, for the $\text{CuO}_x/\text{TiO}_2$ catalyst, no band for CuO is observed and only the bands from TiO_2 anatase are present. In addition, the intensity of the TiO_2 bands strongly decreases with an increase of CuO_x loading. This indicates that the Raman technique is sensitive to the coverage of the support [Sanati et al., 1993]. Less than 10% of the intensity of the TiO_2 support band remains in the spectra for the $\text{CuO}_x/\text{TiO}_2$ catalysts and there are no bands from CuO. This also indicates that the CuO_x species are well dispersed on the surface of the support.

Fig. 3 shows the ESR spectra for TiO_2 loaded with different amount of CuO_x . These spectral parameters has been interpreted as arising from distorted octahedrally coordinated Cu^{2+} ions [Dow et al., 1996]. The hyperfine splittings indicate that there are isolated Cu^{2+} ions on the TiO_2 surface [Berger and Roth, 1967].

When the copper contents are increased, a poorly resolved hyperfine structure is observed and the signal intensities of ESR spectra also significantly decrease. These are due to dipolar coupling arising from the strong interaction of near-neighbor copper atoms and the cluster formation experiencing antiferromagnetic coupling, which make them undetectable by ESR [Berger and Roth, 1967]. These also imply that a great part of these isolated Cu^{2+} ions are buried in multilayered crystallite whose spatial structure approaches that of a normal CuO lattice. Nevertheless, the hyperfine structure can still be observed in the ESR spectrum of 7 wt% $\text{CuO}_x/\text{TiO}_2$ catalyst. Similar results were also found by Dow et al. over $\text{CuO}/\gamma\text{-alumina}$ catalysts [Dow et al., 1996].

These results strongly suggest that the CuO dispersed on the TiO_2

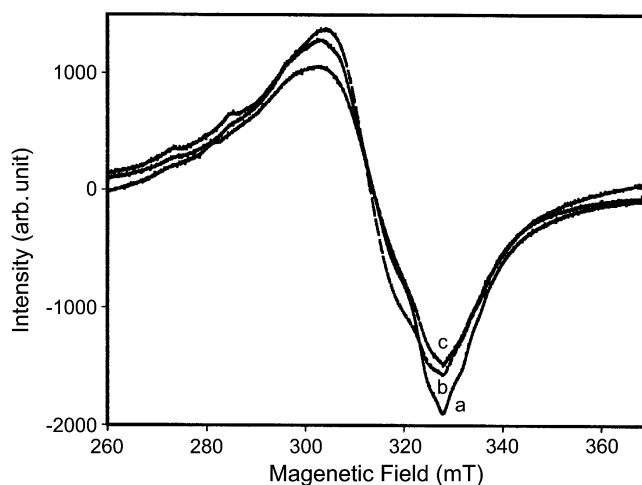


Fig. 3. ESR spectra at 77 K of $\text{CuO}_x/\text{TiO}_2$ catalysts with different Cu loading.

(a) 1 wt% $\text{CuO}_x/\text{TiO}_2$, (b) 5.5 wt% $\text{CuO}_x/\text{TiO}_2$, (c) 7 wt% $\text{CuO}_x/\text{TiO}_2$

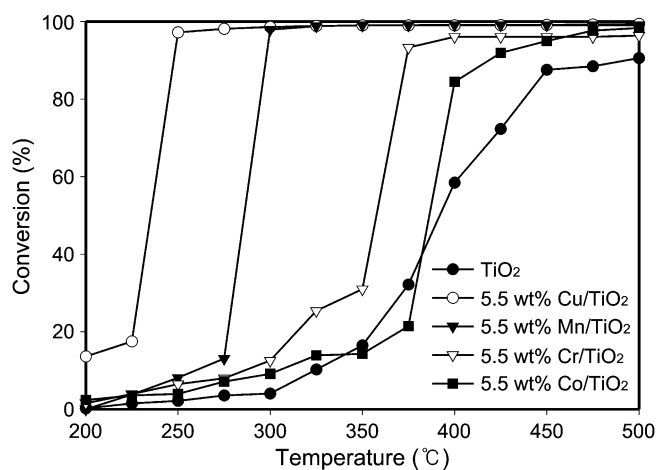


Fig. 4. Comparison of benzene conversion for different metal oxide supported on TiO_2 catalysts: benzene=1%, O_2 =20%, GHSV=30,000 h^{-1} .

surface acts as an active site of $\text{CuO}_x/\text{TiO}_2$ catalysts on the oxidative decomposition of benzene.

2. The Catalytic Activity of Supported Metal Oxides

The conversion of benzene over various metal oxide catalysts (5.5 wt% metal loading) supported on TiO_2 is shown in Fig. 4 as a function of reaction temperature.

Fig. 4 shows typical S-shaped dependences for the conversion as a function of temperature. The steep rise in conversion shows similar results that are observed many other oxidation reactions [Larsen et al., 1996; Liu et al., 2001]. In a blank experiment, the empty quartz glass tube gives only 2% benzene conversion at 500 °C. All the catalysts studied in the experiment produce carbon oxides and no detectable C-containing by-products are found.

As shown in Fig. 4, among supported the metal oxides, CuO_x supported on TiO_2 is found to have the highest activity for benzene oxidation. The conversion of benzene oxidation on $\text{CuO}_x/\text{TiO}_2$ catalyst reaches 100% at about 250 °C. The activity is shown in the order of $\text{CuO}_x > \text{MnO}_x > \text{CrO}_x > \text{CoO}_x$ and the pure TiO_2 shows very

low activity for benzene oxidation. For pure TiO_2 catalyst, the temperature for 90% conversion of benzene requires at least 500 °C, which is 250 °C higher than that for $\text{CuO}_x/\text{TiO}_2$ catalyst. This result indicates that metal oxides supported on TiO_2 play an important role and have an influence on the catalytic activity of benzene oxidation.

Fig. 5 shows the reduction behaviors of these catalysts. For $\text{CuO}_x/\text{TiO}_2$ catalyst, there are reduction peaks at 190 °C and 270 °C, and the peaks appear at the lowest temperature among the all catalysts. In addition, the catalytic activity increases with a decrease of reduction peak temperature. Thus, for the $\text{CuO}_x/\text{TiO}_2$ catalyst, more oxygen can be used in the redox cycle. This is likely owing to highly dispersed CuO_x on TiO_2 [Gallardo-Amores et al., 1999]. However, the higher reduction temperature peak for $\text{CoO}_x/\text{TiO}_2$ catalyst is possibly attributed to the low dispersion of CoO_x on TiO_2 . This result suggests that the $\text{CuO}_x/\text{TiO}_2$ catalyst has the best redox property, which must be one of reasons for the highest activity for the catalytic combustion of benzene.

The conversion of benzene oxidation over CuO_x catalysts (5.5 wt% Cu loading) supported on Al_2O_3 , SiO_2 and TiO_2 is shown in Fig. 6 as a function of temperature. As shown in Fig. 6, among Al_2O_3 , SiO_2 and TiO_2 supports, copper oxide supported on TiO_2 is found to have the highest activity for benzene oxidation. The conversion of benzene oxidation reaches almost 100% at 250 °C. At this temperature, benzene conversion for $\text{CuO}_x/\text{Al}_2\text{O}_3$ catalyst is about 25%, and is about 10% for $\text{CuO}_x/\text{SiO}_2$. For $\text{CuO}_x/\text{Al}_2\text{O}_3$ catalyst, the temperature for complete conversion of benzene requires at least 400 °C, which is 150 °C higher than that for $\text{CuO}_x/\text{TiO}_2$ catalyst.

Fig. 7 shows TPR profiles of these catalysts. For $\text{CuO}_x/\text{TiO}_2$ catalyst, there are reduction peaks at 190 °C and 270 °C. $\text{CuO}_x/\text{Al}_2\text{O}_3$ catalyst gives the reduction peaks at 250 °C and 300 °C and $\text{CuO}_x/\text{SiO}_2$ catalyst does the reduction peak at 310 °C. When copper oxide is supported on TiO_2 and Al_2O_3 , two TPR peaks are observed. It is thought that the peak at low temperature is attributed to the reduction of highly dispersed copper oxide species and the peak at high temperature is ascribed to the reduction of bulk CuO . This result can be confirmed by that the peak at high temperature increases with an increase of CuO_x loading (Fig. 9). Thus, the higher reduc-

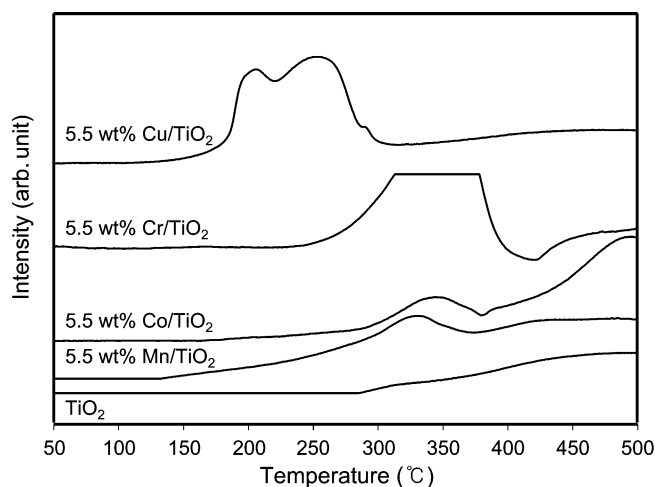


Fig. 5. TPR profiles measured for different metal oxide supported on TiO_2 catalysts: heating rate=10 K/min, gas mixture=7.5% H_2/N_2 .

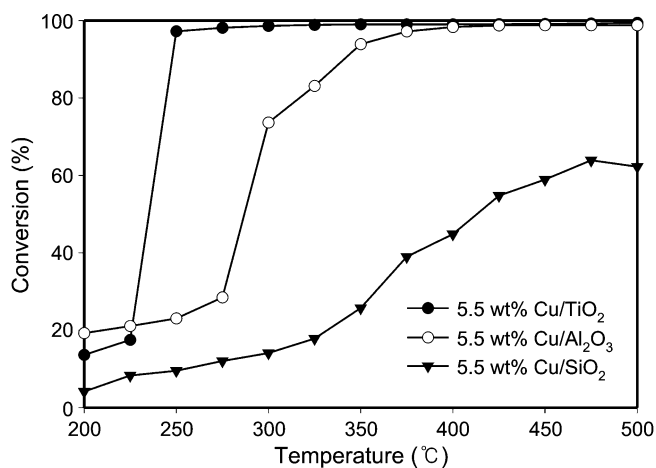


Fig. 6. Comparison of benzene conversion for CuO_x catalysts supported on TiO_2 , Al_2O_3 and SiO_2 : benzene=1%, O_2 =20%, GHSV=30,000 h^{-1} .

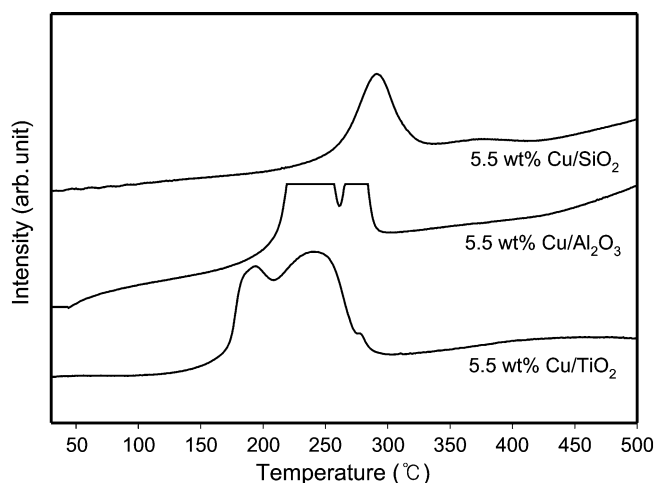


Fig. 7. TPR profiles measured for CuO_x catalysts supported on TiO₂, Al₂O₃ and SiO₂; heating rate=10 K/min, gas mixture=7.5% H₂/N₂.

tion temperature peak for CuO_x/SiO₂ is possibly attributed to the low dispersion of CuO_x on SiO₂. Therefore, the CuO_x/TiO₂ catalyst shows the best redox property and the highest activity for the catalytic oxidation of benzene.

3. The Catalytic Activity of CuO_x/TiO₂ with Different Cu Loadings

To make further investigation, a series of TiO₂-supported copper oxide catalysts were prepared with different Cu loadings. Their catalytic activities are shown in Fig. 8 as a function of reaction temperature. The pure TiO₂ catalyst shows very poor catalytic activity compared with CuO_x/TiO₂ catalysts. This result indicates that the CuO_x acts as an active site on the combustion of benzene. In addition, the catalytic activity gradually increases with an increase in Cu loading on TiO₂. When Cu loading reaches 5.5 wt%, the total conversion temperature is lowered to 300 °C. However, the catalytic activity considerably decreases at 7 wt% Cu loading. This result indicates that the high dispersion of Cu on TiO₂ is achieved at lower than 5.5 wt% Cu loading.

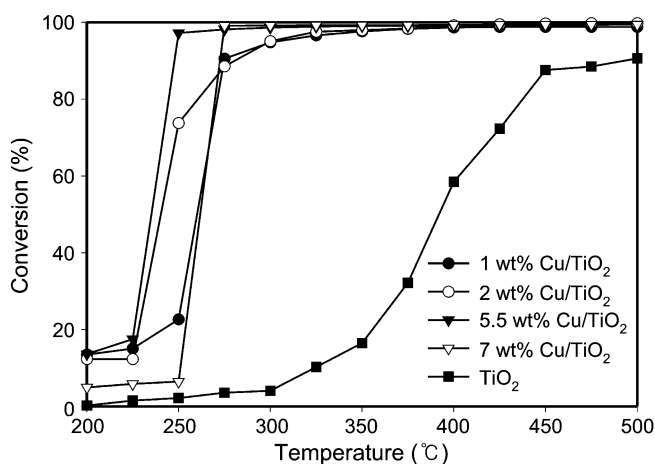


Fig. 8. Comparison of benzene conversion for CuO_x/TiO₂ catalysts with different Cu loadings: benzene=1%, O₂=20%, GHSV=30,000 h⁻¹.

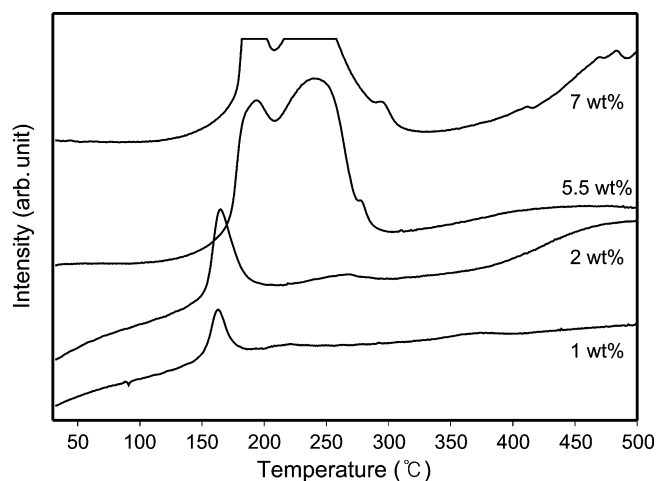


Fig. 9. TPR profiles measured for CuO_x/TiO₂ catalysts with different Cu loadings: heating rate=10 K/min, gas mixture=7.5% H₂/N₂.

TPR profiles for a series of CuO_x/TiO₂ catalysts with Cu loadings from 1 to 7 wt% are shown in Fig. 9. At the lower Cu loadings, only one reduction peak appears at about 170 °C. Along with the increase of Cu loadings, another reduction peak emerges at 270 °C, which is close to the reduction peak of bulk CuO at 300 °C. As before-mentioned, the reduction peak at higher temperature (~270 °C) is attributed to the reduction of bulk phase of copper oxide and that at lower temperature (~170 °C) belongs to the reduction of highly dispersed copper oxide. When Cu loading reaches at 7 wt%, the reduction peak at 270 °C becomes much stronger, suggesting that more aggregated copper oxide particles are formed. These shows the similar tendency with other results [Larsson et al., 1996; Liu et al., 2001].

Correlated with catalytic activity results shown in Fig. 8, the catalytic activity no longer increase evidently when Cu loadings are equal or higher than 5.5 wt%, it can be concluded that the oxidation activity are mainly contributed to the highly dispersed CuO_x.

4. The Effect of Reactant Concentrations

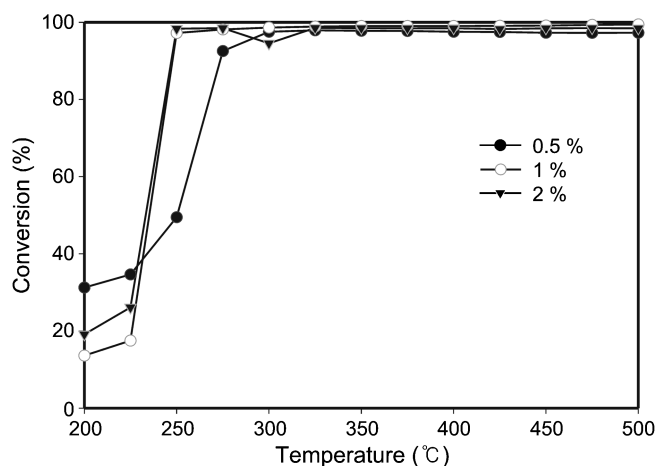


Fig. 10. The effect of benzene concentration on the benzene conversion over 5.5 wt% CuO_x/TiO₂ catalyst: O₂=20%, GHSV=30,000 h⁻¹.

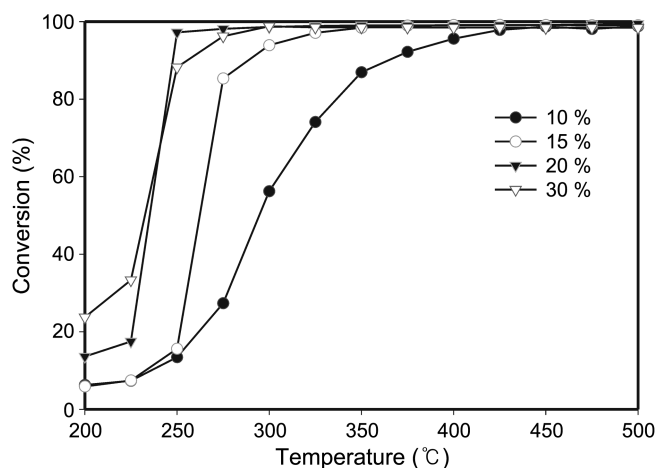


Fig. 11. The effect of oxygen concentration on the benzene conversion over 5.5 wt% $\text{CuO}_x/\text{TiO}_2$ catalyst: benzene=1%, GHSV=30,000 h^{-1} .

The effect of benzene concentration on catalytic properties has been investigated and the result is shown in Fig. 10. The concentration of benzene shows not so much difference on the conversion of benzene. The complete conversion temperature is relatively constant (270 °C) for benzene concentration ranges from 0.5 to 2 mole%. This result suggests that this catalyst can be used as an industrial catalyst, because the concentration of pollutants under actual working condition is usually changeable.

Fig. 11 shows the effect of oxygen concentration on the catalytic activity. The conversion of benzene increases with an increase of oxygen concentration. The complete conversion temperature appears at 250 °C in case of 20 mole% oxygen concentration.

From these results, the catalytic activity increased with increasing oxygen concentration but the concentration of benzene showed no difference in the benzene conversion.

CONCLUSIONS

In the present work, we have investigated the catalytic combustion of benzene over supported metal oxides. Among the supported metal oxides, CuO_x supported on TiO_2 is found to have the highest activity for benzene oxidation. In addition, among the catalysts of copper oxide supported on TiO_2 , Al_2O_3 and SiO_2 , titania-supported catalyst ($\text{CuO}_x/\text{TiO}_2$) gives the highest catalytic activity. $\text{CuO}_x/\text{TiO}_2$ (Cu loading 5.5 wt%) shows the total oxidation of benzene at about 250 °C. From the ESR and FT-Raman results, the CuO dispersed on the TiO_2 surface acts as an active site of $\text{CuO}_x/\text{TiO}_2$ catalysts on the oxidative decomposition of benzene. The catalytic activity gradually increases with an increase of Cu loading on TiO_2 . When Cu loading reaches 5.5 wt%, the total conversion temperature is lowered to 300 °C. However, the catalytic activity considerably decreases at 7 wt% Cu loading. The catalytic activity increased with an increase of oxygen concentration but the concentration of benzene showed no difference in the benzene conversion.

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