

## CATALYTIC PERFORMANCE OF ZrO<sub>2</sub> AND TiO<sub>2</sub> SUPPORTED COPPER CATALYSTS FOR NO<sub>x</sub> REDUCTION IN THE PRESENCE OF OXYGEN

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### ABSTRACT

The catalytic reduction of NO<sub>x</sub> using copper modified zirconia (ZrO<sub>2</sub>) and titania (TiO<sub>2</sub>) catalysts was studied under lean conditions using propene as a reducing agent. All supported copper based catalysts were synthesized using the conventional impregnation method. X-ray diffraction analysis was applied to examine the crystalline structure of each synthesized catalyst. The x-ray diffraction patterns showed evidence that coppers were well dispersed on the surface of the catalyst support. The crystalline CuO phase was the major crystallite traced by x-ray diffraction analysis in both catalysts. The ZrO<sub>2</sub> has a lower tendency than TiO<sub>2</sub> to form crystalline CuO under the same preparation mode. The catalytic performance test using a micro packed bed reactor was conducted for both synthesized catalysts at 1 atm and 300°C. The CuZrO<sub>2</sub> catalyst showed a better NO<sub>x</sub> conversion than CuTiO<sub>2</sub>. This is particularly due to more crystalline CuO phase formed in CuTiO<sub>2</sub> which suppressed the catalytic reduction of NO<sub>x</sub> by propene. In this study, it may be concluded that ZrO<sub>2</sub> is a good catalyst support for copper loading in the catalytic reduction of NO<sub>x</sub> by propene.

**Keywords:** Zirconia; Titania; NO<sub>x</sub> reduction; Propene; CuO

### INTRODUCTION

The stringent emission standards in several developed nations such as Japan and Europe have fostered the development of new pollutant abatement technologies for vehicles, ranging from pretreatment to end of pipe treatment. The discovery of lean-burning engines by automobile industries has minimized the emissions of CO<sub>x</sub> and hydrocarbons due to excess oxygen level. However, the presence of excess oxygen in a lean-burning engine causes the rapid formation of NO<sub>x</sub>, and also hinders the catalytic removal of NO<sub>x</sub> by a conventional three-way catalytic converter [1]. The lack of reliable long term supplies of precious metals such as Pt, Pd and Rh [2] causes the big price fluctuation of three-way catalytic converters. In addition, the selective catalytic reduction with ammonia or hydrogen as reducing agents is hard to handle in mobile NO<sub>x</sub> control. The extraordinary properties of metal oxide catalysts such as higher thermal stability and a great extent of composition variation have attracted many technologists to investigate the application of these catalysts under lean conditions. Combination of copper with zirconia was the first oxide reported to show effective lean NO<sub>x</sub> reduction comparable to CuZSM-5 [3]. Several copper supported catalytic systems have been investigated, which mainly focused on the effect of oxide support [4, 5], role of oxygen [6] and type of reducing agents [7]. The kind of copper oxide species formed is an essential factor that exerts significant influence on the catalytic conversion of NO<sub>x</sub> by hydrocarbons [6]. Thus, the effect of catalyst support specifically the formation of copper oxide species has been studied over CuZrO<sub>2</sub> and CuTiO<sub>2</sub> in this work. The catalytic activities of the CuZrO<sub>2</sub> and CuTiO<sub>2</sub> in the NO<sub>x</sub> + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> at 300°C were investigated. The results proved that the performance of the catalysts in terms of NO<sub>x</sub> and C<sub>3</sub>H<sub>6</sub> conversion are strongly affected by copper oxide either as a surface-dispersed species or as a crystalline phase.

### EXPERIMENTAL

#### Catalyst Preparation

Titanium (IV) oxide (TiO<sub>2</sub>) and zirconium (IV) oxide (ZrO<sub>2</sub>) purchased from Merck and Riedel-deHaën were used as catalyst supports. 3 wt.% of copper were loaded on the ZrO<sub>2</sub> and TiO<sub>2</sub> using the conventional impregnation method at room conditions. Then, the catalysts were washed and filtered to remove any contaminants. The catalysts were dried overnight in an oven at 110°C. Finally, the dried

catalysts were calcined in a furnace at 550°C for 5 hours. The synthesized catalysts were denoted as CuZrO<sub>2</sub> and CuTiO<sub>2</sub>.

#### Catalyst Characterization

The crystalline phases and structure of CuZrO<sub>2</sub> and CuTiO<sub>2</sub> were traced using X-ray Diffraction (XRD). The XRD patterns were obtained with a Siemen D5000 employing Cu-K $\alpha$  radiation. The X-ray tube was operated at 40 kV and 30 mA with 2 $\theta$  ranging from 5–80°. The scanning speed applied in this analysis was 3°/min.

#### Catalytic Performance Test

The catalytic behaviour of both synthesized catalysts in NO<sub>x</sub> reduction by propene under lean conditions was conducted using a lab scale fixed bed reactor (SS316, length = 30 cm and OD = 10 mm) at 1 atm and 300°C. The catalyst bed in the reactor was preheated for an hour under He flow at 220 ml/min. A simplified synthetic exhaust gas consists of 1000 ppm NO, 1000 ppm C<sub>3</sub>H<sub>6</sub> and 3% O<sub>2</sub> with balance of He was fed into the reactor at 13020 ml/(g-cat.hr) after an hour preheating period. The NO<sub>x</sub> concentration from the reactor was measured by a Bacharach® emission analyzer. A gas analyzer (Kane-May 900) was used to detect the oxygen and CO<sub>x</sub> level in the reactor outlet gas stream of reactor furnace. A gas chromatography (Perkin-Elmer) equipped with a FID detector was utilized to measure the concentration of propene using a HP-1 capillary column.

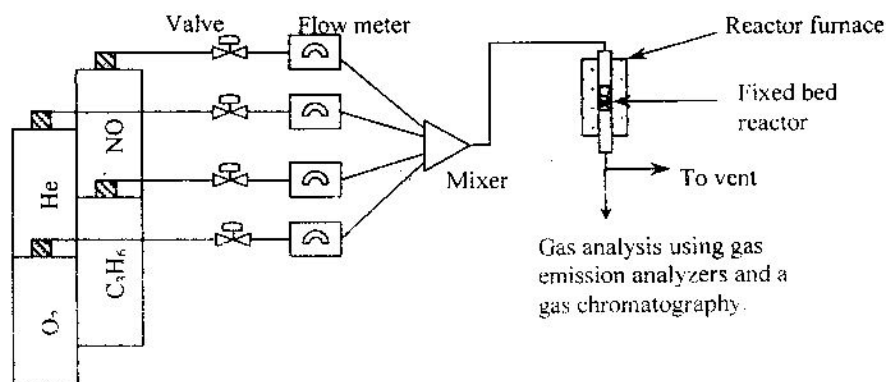


Figure 1: A schematic diagram showing the experimental rig setup for catalytic NO<sub>x</sub> reduction at 1 atm and 300°C using 1000 ppm C<sub>3</sub>H<sub>6</sub>, 1000 ppm NO and 3% O<sub>2</sub> with balance of He.

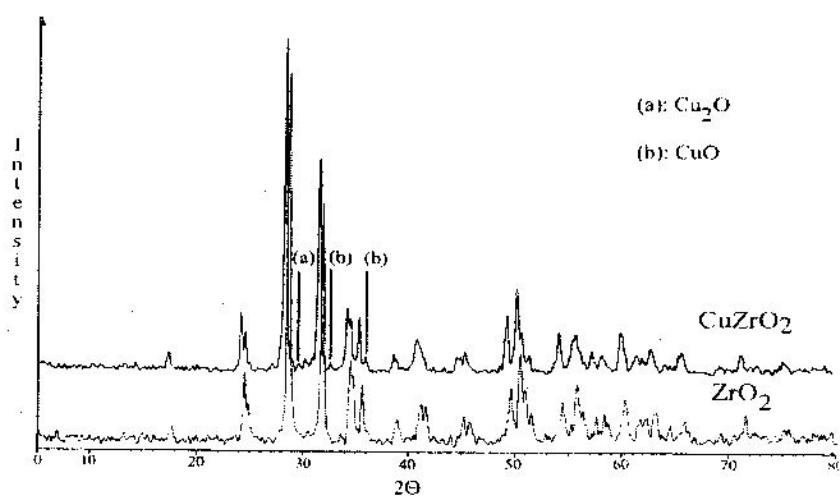
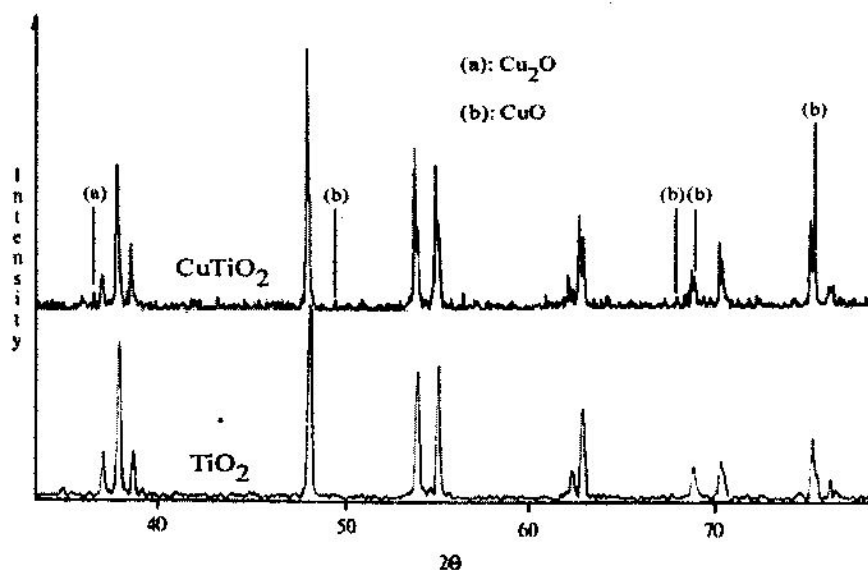
## RESULTS AND DISCUSSION

#### Catalyst Characterization

The XRD results of CuZrO<sub>2</sub> and CuTiO<sub>2</sub> catalysts are shown in Figures 2 and 3. All diffraction angles corresponding to CuO and Cu<sub>2</sub>O are listed in Table 1. The crystalline structure of CuZrO<sub>2</sub> and CuTiO<sub>2</sub> did not differ greatly from the pure ZrO<sub>2</sub> and TiO<sub>2</sub>. The XRD diffraction patterns indicate that the coppers were highly dispersed on the surface of ZrO<sub>2</sub> and TiO<sub>2</sub> to form surface-dispersed copper oxide species. The XRD patterns also revealed that CuO was the major crystalline phase formed in both catalysts. The CuO crystallites seen by XRD must be at least 4 nm [9]. In addition, the detected crystalline CuO peaks for CuTiO<sub>2</sub> were relatively more than CuZrO<sub>2</sub>. The results suggested that the TiO<sub>2</sub> has a higher tendency than ZrO<sub>2</sub> to form crystalline CuO under the same preparation mode. The peaks corresponding to Cu<sub>2</sub>O were also detected for CuZrO<sub>2</sub> (2 $\theta$  = 29.5°) and CuTiO<sub>2</sub> (2 $\theta$  = 36.5°). There were no obvious effects observed from crystallite Cu<sub>2</sub>O due to the amount of the peak for both catalysts are equivalent.

Table 1: The diffraction angle ( $2\theta$ ) for crystalline CuO and Cu<sub>2</sub>O phases in CuZrO<sub>2</sub> and CuTiO<sub>2</sub> traced by XRD.

Diffraction angle $2\theta$	CuZrO <sub>2</sub>		CuTiO <sub>2</sub>	
	CuO	Cu <sub>2</sub> O	CuO	Cu <sub>2</sub> O
	32.5	29.5	49.5	36.5
	35.5		67.8	
			68.9	
			75.2	

Figure 2: X-ray diffraction patterns for ZrO<sub>2</sub> and CuZrO<sub>2</sub> obtained using Cu-K $\alpha$  radiation with scanning speed, 3°/min.Figure 3: X-ray diffraction patterns for TiO<sub>2</sub> and CuTiO<sub>2</sub> obtained using Cu-K $\alpha$  radiation with scanning speed, 3°/min.**NO<sub>x</sub> and C<sub>3</sub>H<sub>6</sub> Conversion**

The catalytic activities of CuZrO<sub>2</sub> and CuTiO<sub>2</sub> for NO<sub>x</sub> + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> reaction conducted at 1 atm and 300°C are presented in Figures 4 and 5. In Figure 4, the conversion of NO<sub>x</sub> is higher using CuZrO<sub>2</sub> than

CuTiO<sub>2</sub>. The activity of CuZrO<sub>2</sub> catalyst remained consistent in reducing the NO<sub>x</sub> and did not show any deactivation signs after five hours on stream. This is probably due to more copper species appeared as crystalline CuO in CuTiO<sub>2</sub> compared to CuZrO<sub>2</sub> as was concluded from the XRD spectra. As suggested by Hu et al. [7], the formation of crystalline CuO will reduce the NO<sub>x</sub> conversion and the active component for the copper supported catalysts at low temperature is surface-dispersed CuO species. The maximum NO<sub>x</sub> conversion achieved by CuZrO<sub>2</sub> was approximately 54%. For CuTiO<sub>2</sub> catalyst, NO<sub>x</sub> conversion reached its maximum after 30 minutes of experiment running period. The CuTiO<sub>2</sub> catalyst also showed rapid deactivation sign and the NO<sub>x</sub> conversion reduced to about 14%. Thus, these results indicate that copper based catalyst supported on zirconia can perform better under lean conditions compared to titania as support.

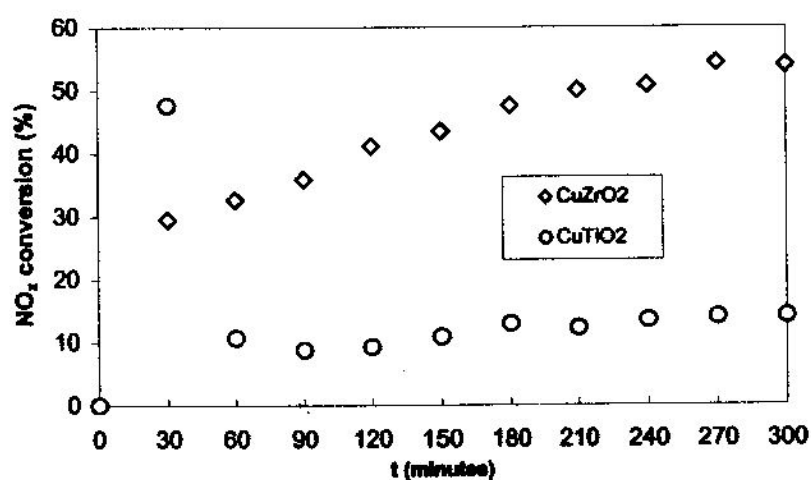


Figure 4: The catalytic conversion of NO<sub>x</sub> by propene at 300°C and 1 atm using CuZrO<sub>2</sub> and CuTiO<sub>2</sub>.

As shown in Figure 5, the presence of C<sub>3</sub>H<sub>6</sub> in the reactor effluent was totally eliminated using CuZrO<sub>2</sub> and CuTiO<sub>2</sub> at 300°C and 1 atm in the early part of the experiment. After four hours on stream, the catalytic conversion of C<sub>3</sub>H<sub>6</sub> using CuZrO<sub>2</sub> was remarkably reduced from 100% to 30%. In contrast, the CuTiO<sub>2</sub> catalyst still exhibited sustainable performance in catalytic oxidation of C<sub>3</sub>H<sub>6</sub>. This can be explained that the crystalline CuO phase is more likely to form in CuTiO<sub>2</sub> than CuZrO<sub>2</sub> as was observed from the XRD diffractograms. The crystalline CuO phase plays a significant role in hydrocarbon oxidation, but suppresses the NO<sub>x</sub> conversion [4, 9].

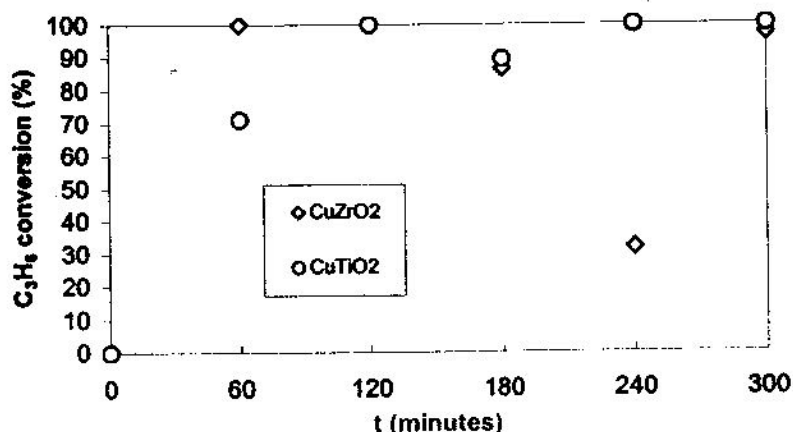


Figure 5: The catalytic conversion of C<sub>3</sub>H<sub>6</sub> at 300°C and 1 atm using CuZrO<sub>2</sub> and CuTiO<sub>2</sub>.

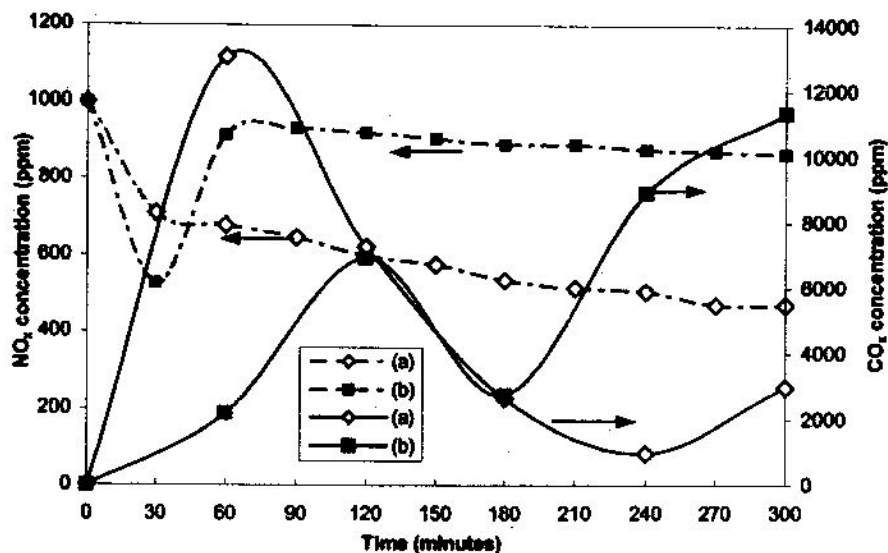


Figure 6: The concentration of  $\text{NO}_x$  (---) and  $\text{CO}_x$  (—) resulted from the catalytic reduction of  $\text{NO}_x$  by propene at  $300^\circ\text{C}$  and 1 atm using (a)  $\text{CuZrO}_2$  and (b)  $\text{CuTiO}_2$ .

The concentration of  $\text{CO}_x$  and  $\text{NO}_x$  measured from the  $\text{NO}_x + \text{C}_3\text{H}_6 + \text{O}_2$  reaction using  $\text{CuZrO}_2$  and  $\text{CuTiO}_2$  are shown in Figure 6. Maximum  $\text{CO}_x$  peaks were observed using both catalysts ( $\text{CuZrO}_2$  @  $t = 60$  minutes;  $\text{CuTiO}_2$  @  $t = 120$  minutes). The peaks occurred probably due to the simultaneous oxidation of  $\text{C}_3\text{H}_6$  by  $\text{NO}_x$  and  $\text{O}_2$  to produce  $\text{CO}_x$ . For  $\text{CuZrO}_2$ , the concentration of  $\text{CO}_x$  was reduced as the  $\text{NO}_x$  concentration nearly achieved the constant level. However, the  $\text{CO}_x$  level resulted from the catalytic reduction of  $\text{NO}_x$  using  $\text{CuTiO}_2$  increased gradually although the  $\text{NO}_x$  consumption rate was slowed down. Thus, it is presumed that the propene is continuously oxidized to  $\text{CO}_x$  by oxygen due to the superior  $\text{C}_3\text{H}_6$  oxidation activity enhanced by the formation of crystalline  $\text{CuO}$  phases [4, 9] in  $\text{CuTiO}_2$ .

## CONCLUSION

The catalytic reduction of  $\text{NO}_x$  via copper modified zirconia or titania catalysts were affected by the type of copper oxide species formed. The formation of surface-dispersed copper oxide species will ensure sustainable reduction of  $\text{NO}_x$  as shown by  $\text{CuZrO}_2$ . The appearance of crystalline  $\text{CuO}$  phase as in  $\text{CuTiO}_2$  totally suppressed the  $\text{NO}_x$  conversion. In contradictory, the  $\text{C}_3\text{H}_6 + \text{O}_2$  reaction using  $\text{CuTiO}_2$  was promoted by the crystalline  $\text{CuO}$  species.

## NOTATION

$\theta$	Diffraction angle
$t$	Experiment running duration
XRD	X-ray diffraction

## ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support received in the form of a research grant (Vot 72172) from the Ministry of Science, Technology and Environment, Malaysia.

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