

**CHAPTER IV**  
**SELECTIVE CO OXIDATION IN HYDROGEN RICH STREAM**  
**OVER Au/MnO<sub>x</sub> AND Au/FeO<sub>x</sub> CATALYSTS**

**Abstract**

Gold itself exhibits poor activity but becomes more active for CO oxidation when deposited onto appropriate support. Manganese and ferrous oxides were found to be good supports for gold in selective CO oxidation for fuel cell applications. Catalysts were prepared by co-precipitation method and subjected to several pretreatment conditions before being tested for the activity. The activity was tested by using a gas mixture of 1% CO, 1% O<sub>2</sub>, 2% CO<sub>2</sub>, 2.6% H<sub>2</sub>O, and 40% H<sub>2</sub> balanced in He at the temperature range of 50-190°C. Au/MnO<sub>x</sub> preferred He pretreatment and 300°C calcination temperature while Au/FeO<sub>x</sub> preferred O<sub>2</sub> pretreatment and 400°C calcination temperature. Atomic ratio of 1/30 Au/Fe or Mn was the optimum Au loading for both catalysts. High concentration of CO<sub>2</sub> in the feed gas was also investigated in order to observe the adverse effect due to the equilibrium. Interestingly, both catalysts could resist to H<sub>2</sub>O concentration in the reactant feed up to the level of 10%. Au/MnO<sub>x</sub> gave 93% conversion and 58% selectivity at 130°C and Au/FeO<sub>x</sub> gave 98% conversion and 53% selectivity at 50°C during a 48 h stability test, without any activity drop at all.

*Keywords:* Fuel cells; CO oxidation; Gold; Manganese oxide; Ferrous oxide

**1. Introduction**

Having a lot of advantages over combustion based power sources, fuel cells are receiving increasing attention as potential power sources for stationary and transportation applications. H<sub>2</sub> is the most suitable fuel for the fuel cell technology in comparison with its derivatives such as hydrocarbons, alcohols or coal because of its high electrochemical reactivity. Furthermore, the mechanism of H<sub>2</sub> reaction is

well understood. There are not any side products like the others. However, in order to use  $H_2$  as fuel for fuel cells it is necessary to integrate  $H_2$  production unit with fuel cells because of the  $H_2$  explosion risks and the limitations of  $H_2$  onboard storage.

Steam reforming is an efficient, economical and widely used process for  $H_2$ -production. After doing a two stage water gas shift reaction on the product stream of the reformer the CO amount in the product stream drops to  $\sim 0.5-1\%$ . Even at that such a small amount CO still poisons fuel cell Pt anodes in a matter of seconds thus reducing the overall fuel cell performance. In order to obtain the maximum performance, the CO concentration in the product gas has to be reduced to  $\sim 10$ ppm.

There are four potential ways of reducing the CO: absorption, membrane purification, methanation, and selective oxidation. However, CO removal by adsorption requires large amount of adsorbent. Using Pressure Swing Absorption needs expensive compressors and methanation is very inefficient because of the loss of three moles of hydrogen for each mole of CO. Membrane filtration using Pd based membranes is expensive and does not have high rates of filtration. This leaves selective CO oxidation by  $O_2$  as the most practical choice. Once  $O_2$  is introduced to the  $H_2$  stream containing a small amount of CO of 1%, it can oxidize both CO and  $H_2$  to form  $CO_2$  and  $H_2O$ , respectively. The challenge is to find a catalyst that selectively oxidizes CO and has poor selectivity towards  $H_2$  oxidation while exhibiting high CO oxidation activity at low to mild temperatures. Moreover, high CO conversion ( $\sim 99.9\%$ ) is also in demand in order to satisfy the CO limitation of fuel cells.

Several studies about these processes have been conducted and numerous catalysts have been considered. However, further study is still needed since the catalyst studied in the past could not fully meet high selectivity and conversion requirements simultaneously. Although cobalt oxide catalyst gave high selectivity with high conversion, it was not so stable. Being used as the electrode material, Pt is not only expensive but is also in short supply. Operating temperature is also critical. Most of catalysts required relatively high temperatures in the range of  $200-250^\circ C$ , which is not reasonable for the PEM fuel cells.

Supported Au catalysts have been shown to have very high activity for CO oxidation even at room temperature. This makes them good candidates for selective

CO oxidation. It has been shown that, in contrast to Pt-group metal catalysts, Au is substantially more active for CO oxidation than for H<sub>2</sub> oxidation resulting in higher selectivity [4]. Furthermore, its catalytic activity is enhanced by moisture and almost insensitive to CO<sub>2</sub> [4].

This paper is focused on gold/manganese-oxide catalyst (Au/MnO<sub>x</sub>) and gold/ferrous-oxide catalyst (Au/FeO<sub>x</sub>).

## 2. Experimental

### 2.1. Catalyst preparation

Co-precipitation was used for catalyst preparation. An aqueous solution of 1 M Na<sub>2</sub>CO<sub>3</sub> was added dropwise into an aqueous mixture of 0.1 M Mn(NO<sub>3</sub>)<sub>2</sub> or 0.1 M Fe(NO<sub>3</sub>)<sub>3</sub> and 0.1 M HAuCl<sub>4</sub> under vigorous stirring condition at 80°C. The mixture was kept at a pH of 8 for 1 h. The precipitate was separated out from solution by centrifuge at 2,000 rpm for 5 min. Excess ions were eliminated by washing with warm deionized water. Deionized precipitate was dried at 110°C overnight and calcined for 2 h.

### 2.2. Characterization

The determination of surface area and pore size was done using The Autosorb-1 Gas Sorption System (Quantachrome Corporation). This equipment is based on Brunauer-Emmett-Teller (BET) method. Nitrogen gas with cross-sectional area of  $16.2 \times 10^{-20} \text{ m}^2/\text{molecule}$  was used as the adsorbate at liquid nitrogen temperature of 77 K. Before measurement all samples were outgassed by heating under vacuum at 150°C for 16 h to eliminate absorbed species on the surface. Autosorb Anygas Software Version 2.1 analyzed the result.

The crystalline structure of oxide supports and the mean particle diameter of gold were analyzed by means of a Rigaku X-Ray diffractometer system (RINT-2200) with Cu tube for generating CuK<sub>α</sub> radiation (1.5406 Å) and nickel filter. RINT-2200 was used to obtain XRD pattern at a generator voltage of 40 kV and a generator current

of 30 mA. The goniometer parameters were divergence slit =  $1^\circ$  ( $2\theta$ ); scattering slit =  $1^\circ$  ( $2\theta$ ); and receiving slit = 0.3 mm. The scan speed of  $5^\circ$  ( $2\theta$ )/min with scan step of 0.02 ( $2\theta$ ) was used for the continuous run in 5 to  $90^\circ$  ( $2\theta$ ) range.

The AAS, VARIAN model 300/400 was utilized to determine the actual percent Au loading on supports.

The TEM measurements were carried out using a JEM 2010 operating at 200 kV in bright and dark field modes. Crystallinity and crystal structure of the samples were evaluated from selected area electron diffraction patterns. The way to prepare catalysts in a thin form suitable for TEM is to crush and grind the samples in a mortar. The fine powder thus obtained is dispersed in ethanol by use of an ultrasonic vibrator, and a drop of the suspension is deposited on a thin carbon film supported on a standard electron microscope grid. Image processing for contrast enhancement and image evaluation were done by means of the Digital Micrograph programs.

Thermal Gravity Analysis (TGA) technique was used to determine the phase change of supports using the Du Pont TGA 2950 Thermogravimetric Analyzer. The catalysts were first exposed to a continuous flow of nitrogen (as a protective gas) and air (as a purge gas) at a flow rate of 10 and 20 ml/min, respectively. Then, by applying temperature program from  $30^\circ\text{C}$  to  $700^\circ\text{C}$  with a rate of  $10^\circ\text{C}/\text{min}$ , the mass changes of catalysts were monitored and recorded.

### *2.3. Catalytic activity measurement*

The catalytic activity measurements were carried out in the fixed bed reactor packed with 100 mg catalyst at 80-120 mesh in size. The feed gas contained 1% CO, 2% CO<sub>2</sub>, 1% O<sub>2</sub>, 2.6% H<sub>2</sub>O and 40% H<sub>2</sub> balanced in He passing through the catalyst bed at the total flow rate of 50 ml/min (SV = 30,000 mlg<sup>-1</sup>h<sup>-1</sup>) at atmospheric pressure. Prior to all experiments, catalyst pretreatment at  $200^\circ\text{C}$  for 2 h were needed. The effluent gas was detected by online gas chromatograph. For the water vapor effect, reactant gases were passed through a water bubbler.

### 3. Results and discussion

#### 3.1. BET measurement

Surface area and pore diameter of catalysts are shown in Table 1. For Au/MnO<sub>x</sub>, surface area increased with the increase of calcination temperature from 200°C to 300°C. This increase is most likely due to the conversion of the hydroxides and carbonates to oxides, as a result of which the catalyst developed a porous structure. 300°C-calcined catalyst had a smaller pore size compare to 200°C-calcined catalyst. At the same calcination temperature, surface area showed a weak dependence on Au loading. Higher Au loading resulted in larger pore size and smaller surface area. However, surface area of the sample with the lowest Au/Mn atomic ratio, 1/120, was much lower than the catalyst with a 1/60 ratio.

For the case of Au/FeO<sub>x</sub> catalysts, increase of calcination temperature resulted in lower surface areas. Again there was a weak dependence on Au loading. Atomic ratio of 1/60 had the highest surface area and the smallest pore size.

#### 3.2. XRD study

There was a big difference between two XRD patterns of Au/MnO<sub>x</sub> samples calcined at 200°C and 300°C as illustrated in Figure 1 (patterns a and b). At the lower temperature, there were distinct MnCO<sub>3</sub> peaks and then became lower at 300°C. The peaks of Au were also changed. The Au crystallite sizes calculated from Scherrer Equation are shown in Table 1. At 200°C, a big Au crystallite size of 100 nm was formed which is not the desired size for CO oxidation. The expected size is in the range of 5-10 nm, which is what calcination at 300°C gave for the Au/MnO<sub>x</sub> catalyst. The decrease in the particle size correlates with the increased surface area shown in Table 1. The correlation between pore size and crystallite size of Au can explain for the low surface area of the sample with atomic ratio of 1/120 compared to 1/60 ratio catalyst calcined at the same temperature.

Patterns b, c, and d in Figure 1 represent XRD patterns of Au/MnO<sub>x</sub> with different Au loadings. Along with the increase in atomic ratio was the increase in the

Au peak intensity and the appearance of the larger Au crystallites when the atomic ratio reached 1/30. Figure 2 shows the Au size distributions of three catalysts with varying atomic ratios calcined at the same temperature. It was really homogeneous in case of 1/120 and 1/60-atomic ratio catalysts with Au crystallite size of 10 nm. By reaching atomic ratio of 1/30, some bigger ones appeared but the 10 nm peak intensity was still dominant and higher than that of 1/120 and 1/60-atomic ratio catalysts.

Figure 3 represents XRD patterns of Au/FeO<sub>x</sub>. No peaks of metallic Au were observable implying that Au is well dispersed on the catalyst surfaces. At lower calcination temperature, 300°C, the catalyst was almost amorphous and became crystalline at 400°C. Surprisingly, Au crystallite size of Au/FeO<sub>x</sub> catalyst still remained at the level of < 3 nm while the atomic ratio increased up to 1/30. However, there were some changes in the support morphology. Higher crystallinity tremendously reduced the surface area as illustrated by three samples with different atomic ratios calcined at the same temperature. The sample with 1/120 atomic ratio showing the highest crystallinity had the lowest surface area.

### 3.3 TEM results

The Au crystallite size of Au/MnO<sub>x</sub> and Au/FeO<sub>x</sub> catalysts could be clearly observed in TEM photo as shown in Figures 4 and 5, respectively. Figure 4 shows the image of Au/MnO<sub>x</sub> calcined at 300°C with atomic ratio of 1/30 while Figure 5 shows that of Au/FeO<sub>x</sub> calcined at 400°C with the same atomic ratio. There was a good agreement with XRD result about the Au crystallite size. Crystallite sizes of Au/MnO<sub>x</sub> were about 10 nm with some even larger. For Au/FeO<sub>x</sub>, the Au crystallites were almost uniform in size 3 nm and quite homogenous in size. Interestingly, Au crystallite was found to be hemispherical in shape and that attached to the support by their flat plane [13].

### 3.4. TGA measurement

Dried samples were tested in this characterization in order to understand about phase change during the calcination step.

As shown in Figure 6, there was a big change in the Au/MnO<sub>x</sub> catalyst weight at temperature of 400°C because of the support decomposition. Between 200°C and 300°C, there were also two small weight drops. It was proposed that at 200°C, water from Mn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O was separated out and MnCO<sub>3</sub> which is the precipitate was decomposed to form MnO<sub>x</sub> at 300°C.

From Figure 7, we see that the behavior of ferrous support is different from the manganese support. There were two small weight drops at 300°C and 400°C, respectively. We speculate that water in Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O came out at almost 300°C and then at 400°C, the precipitated Fe<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>, Fe(OH)<sub>3</sub>, and Fe(OH)<sub>2</sub> were decomposed to the form Fe<sub>2</sub>O<sub>3</sub> which is well crystallized.

### 3.5. AAS measurement

Table 2 shows the actual percent Au loading of prepared catalysts obtained by AAS. Three atomic ratios of 1/120, 1/60 and 1/30 resulted in three percentages of Au loading of 1.67, 2.86, and 5.70 % for Au/MnO<sub>x</sub> and 1.21, 2.08, and 5.38 % for Au/FeO<sub>x</sub>, respectively. These values were about the same as calculated.

### 3.6. Activity test

The reaction was carried out in the fixed bed reactor packed with 100 mg catalyst at 80-120 mesh in size. The feed gas contained 1% CO, 2% CO<sub>2</sub>, 1% O<sub>2</sub>, 2.6% H<sub>2</sub>O and 40% H<sub>2</sub> balanced in He passing through the catalyst bed at the total flow rate of 50 ml/min (SV = 30,000 mlg<sup>-1</sup>h<sup>-1</sup>) at atmospheric pressure.

### 3.6.1. *Effect of pretreatment condition*

Three pretreatment conditions, which are He, O<sub>2</sub>, and H<sub>2</sub>, were performed for both catalysts. The conversion and selectivity of Au/MnO<sub>x</sub> and Au/FeO<sub>x</sub> catalysts pretreated differently versus temperature are shown in Figures 8 and 9, respectively.

Figure 8 shows the comparison between activities of Au/MnO<sub>x</sub> calcined at 200°C with atomic ratio of 1/120 pretreated differently. Au/MnO<sub>x</sub> was well conditioned by He pretreatment [2,28] with the flow rate of 50 ml/min. It seems that the as prepared catalyst was already an active catalyst without further treatment. It was necessary to remove adsorbed species on the catalyst surface by He flow. This was an advantage of Au/MnO<sub>x</sub> catalyst over the others particularly in applications where catalyst pretreatment is not possible.

However, Figure 9 shows that Au/FeO<sub>x</sub> which were calcined at 400°C with atomic ratio of 1/60 required oxidative pretreatment [6,21] with 10% O<sub>2</sub> in He and flow rate of 50 ml/min. O<sub>2</sub> may cause the formation of Fe<sub>2</sub>O<sub>3</sub> – hematite, which is the desired support form because of the O<sub>2</sub> storage capacity. Reductive pretreatment with 10% H<sub>2</sub> in He and flow rate of 50 ml/min reduced catalyst activity because of the FeO<sub>x</sub> reduction by H<sub>2</sub> to form metallic Fe.

From this point forward, He pretreatment and O<sub>2</sub> pretreatment were chosen for Au/MnO<sub>x</sub> and Au/FeO<sub>x</sub>, respectively.

### 3.6.2. *Effect of calcination temperature*

From the result of TGA, it was found that 400°C is not good for manganese support in term of thermal stability. Low calcination temperatures of 200°C and 300°C were used with this support. Figure 10 represents activities of Au/MnO<sub>x</sub> pretreated by He with atomic ratio of 1/120 calcined differently at 200°C and 300°C. The sample calcined at 300°C had higher activity [4]. This result can be explained by the results of the characterizations. The Au crystallite size, which is very important in Au supported catalyst, has to be in the 5-10 nm range to have optimum activity in CO oxidation according to Bethke and Kung [10]. Calcination at 300°C produced 10 nm Au crystallites. In comparison, calcination at 200°C resulted in crystallite sizes of up to 100 nm. Surface area is also important contributing to the higher activity. There was a big difference in the surface area between two samples



calcined at 200°C and 300°C. The oxidation state of the support also plays an important role in oxidation reactions.  $\text{MnO}_x$ , was found to be the dominant phase in the sample calcined at 300°C as determined from XRD and TGA results.

Figure 11 shows that for the  $\text{Au/FeO}_x$  catalyst, calcination at 400 °C gives a more active catalyst [6] although it resulted in a lower surface area catalyst. The reason for the higher activity of the catalyst calcined at 400 °C is the crystallinity of the support. There is a big difference in the support morphology in XRD patterns of  $\text{Au/FeO}_x$  catalyst. Calcination at 300°C resulted in an amorphous support while 400°C calcination produced hematite- $\text{Fe}_2\text{O}_3$ , which is believed to be the preferred support for catalysis [14].

As a result, He pretreatment and 300°C calcination temperature was chosen for  $\text{Au/MnO}_x$  while  $\text{O}_2$  pretreatment and 400°C calcination temperature were selected for  $\text{Au/FeO}_x$  catalysts.

### 3.6.3. *Effect of Au loading*

To determine the effect of Au loading, Au/Mn atomic ratio was varied from 1/120 to 1/30. Figure 12 shows the activities of  $\text{Au/MnO}_x$  pretreated by He calcined at 300°C with different atomic ratios. It was found that, the increased Au loading resulted in increased activity. Atomic ratio of 1/30, which corresponds to 5.7%, Au loading gave the highest conversion and selectivity of 93% and 58%, respectively at the relatively low temperature of 130°C. It was proposed that the CO oxidation reaction solely takes place at the perimeter between Au crystallites and the support [11,13,14]. If the Au crystallite size stays constant then the activity should increase with Au loading. According to the XRD results the crystallite size of the 1/30 and 1/60 atomic ratio catalysts was the same 10nm except the signal for the 1/30 was stronger indicating the presence of more crystallites which would lead to the observed higher activity.

In the same manner as  $\text{Au/MnO}_x$ ,  $\text{Au/FeO}_x$  activity also increased with Au loading according to Figure 13, which shows the activities of  $\text{Au/FeO}_x$  pretreated by  $\text{O}_2$ , calcined at 400°C with different atomic ratios. Based on XRD results Au was well dispersed onto the support even at high loading. All three catalysts had no XRD detectable Au crystallites since the loading is not high enough to detect Au

crystallites; the absence of Au peaks from the XRD is due to the small crystallite size (3nm).

Au/MnO<sub>x</sub> preferred He pretreatment, 300°C calcination temperature, and atomic ratio of 1/30 with the maximum conversion and selectivity of 93% and 58% at 130°C, respectively. Au/FeO<sub>x</sub> preferred O<sub>2</sub> pretreatment, 400°C calcination temperature, and atomic ratio of 1/30 with the maximum conversion and selectivity of 98% and 53% at 50°C, respectively.

### 3.7. *Effect of CO<sub>2</sub>*

The effect of the presence of CO<sub>2</sub> in the feed stream on the catalytic behavior of both catalysts is shown in Figures 14 and 15, respectively. First, activities of the Au/MnO<sub>x</sub> and Au/FeO<sub>x</sub> were tested with a reactant gas composition of 10% CO<sub>2</sub>, 1% CO, 1% O<sub>2</sub>, and 40% H<sub>2</sub> balanced in He at 130°C and 50°C, respectively. Then, CO<sub>2</sub> was cut off while everything was kept the same in order to determine the difference in activity with and without CO<sub>2</sub>. It can be seen that for both catalysts, the conversion increased and the selectivity remained unchanged when CO<sub>2</sub> was eliminated from the reactant gas stream implying that CO<sub>2</sub> is detrimental [2]. The negative effect CO<sub>2</sub> was more with the Au/MnO<sub>x</sub> but became negligible with Au/FeO<sub>x</sub>. The detrimental effect of CO<sub>2</sub> on catalyst activity can be due to two reasons: 1) formation of carbonates which will prevent oxygen adsorption and splitting on the support and/or 2) the reverse water gas shift reaction.

### 3.8. *Effect of water vapor*

Generally, the catalytic activity of a catalyst is depressed in the presence of water. Figures 16 and 17 show the effect of water vapor in the reaction gas mixture on the conversion and selectivity of Au/MnO<sub>x</sub> and Au/FeO<sub>x</sub> catalysts, respectively. The same procedure as CO<sub>2</sub> effect was carried out but the composition of the reactant gas at the beginning was 10% H<sub>2</sub>O, 1% CO, 1% O<sub>2</sub>, 40% H<sub>2</sub> balanced in He. The conversion and selectivity were about the same between with and without water indicating that both catalysts could resist to that much water [16]. Water seemed to

be innocuous to the catalytic activity because it can provide hydroxyl group, which is necessary for the reaction to take place.

### 3.9. Deactivation test

Catalyst activity was tested at constant temperature for 48 h in order to observe the stability with time. The reactant gas was 1% CO, 2% CO<sub>2</sub>, 1% O<sub>2</sub>, 2.6% H<sub>2</sub>O and 40% H<sub>2</sub> balanced in He. The operating temperature was 130°C and 50°C for Au/MnO<sub>x</sub> and Au/FeO<sub>x</sub>, respectively. Figures 18 and 19 show that both catalysts exhibited a stable catalytic performance during the tested time [15].

Table 3 summarizes the results of catalytic activity tests.

### 3.10. Comparison of activity with others work

The catalytic activity of Au/MnO<sub>x</sub> catalyst in this study is compared to the results reported by Sanchez *et al* [4] as shown in Figure 20. In this work, Au/MnO<sub>x</sub> catalyst performed 93% conversion at 130°C, which is relatively close to 95% conversion of the catalyst prepared by Sanchez *et al.* at 80°C. Most likely the differences in activity are due to the difference in the operating conditions. The reactant gas in the work of Sanchez *et al.* did not contain CO<sub>2</sub> and H<sub>2</sub>O as in this work. As mentioned above, the presence of CO<sub>2</sub> caused the detrimental effect to the catalytic activity. Thus, CO<sub>2</sub>-free reactant gas allowed Au/MnO<sub>x</sub> reach the higher conversion. In addition, the absence of CO<sub>2</sub> shifts the maximum conversion to the lower temperature of 80°C instead of 130°C as in this work.

Figure 21 represents the comparative study of Au/FeO<sub>x</sub> in this work and in the work done by Kahlich *et al.* [6]. Both catalysts were in a good agreement by nearly reaching 100% conversion at the relatively low operating temperature. Au/FeO<sub>x</sub> in this work showed 98% conversion at 50°C and Kahlich *et al.* found that Au/FeO<sub>x</sub> could reach 99% conversion at 80°C.

#### 4. Conclusions

Two catalysts (Au/MnO<sub>x</sub> and Au/FeO<sub>x</sub>) were prepared and tested for their catalytic activity for the selective oxidation of CO in the presence of H<sub>2</sub>. Variety of parameters was examined in order to determine the optimal operating conditions. The effects of the presence of CO<sub>2</sub> and H<sub>2</sub>O in the reactant feed over the catalytic activity as well as their stability were also investigated. Several conclusions can be drawn from this work:

Au/MnO<sub>x</sub> preferred He pretreatment condition while Au/FeO<sub>x</sub> preferred O<sub>2</sub> pretreatment condition.

Calcination temperature of 300°C was the best for Au/MnO<sub>x</sub> but it was 400°C for Au/FeO<sub>x</sub>.

Atomic ratio of 1/30 was the optimal for both catalysts.

Au crystallite size as well as support morphology played an important role in the catalytic activity.

Au/MnO<sub>x</sub> could give 93% conversion and 58% selectivity at 130°C.

Au/FeO<sub>x</sub> could give 98% conversion and 53% selectivity at 50°C.

Au/MnO<sub>x</sub> and Au/FeO<sub>x</sub> had not only superior activity but also excelled in operating temperature.

CO<sub>2</sub> caused the detrimental effect over both catalysts. The effect over Au/MnO<sub>x</sub> was stronger in the comparison with Au/FeO<sub>x</sub>.

Both catalysts could resist to H<sub>2</sub>O concentration up to the level of 10%.

Catalytic lifetime of both catalysts was 48 h without any activity drop at all.

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## References

- [1] S.H. Oh, R.M. Sinkevitch, *J. Catal.*, 142 (1993) 254.
- [2] G.B. Hoflund, S. D. Gardner, *Langmuir*, 11 (1995) 3431.
- [3] H. Igarashi, H. Uchida, M. Suzuki, Y. Sasaki, M. Watanabe, *Applied Catal. A: General*, 159 (1997) 159.
- [4] R.M. Terres Sanchez, A. Ueda, K. Tanaka, M. Haruta, *J. Catal.*, 168 (1997) 125.
- [5] Y. Teng, H. Sakurai, A. Ueda, T. Kobayashi, *Inter. J. Hydrogen Energy*, 24 (1999) 355.
- [6] M.J. Kahlich, H. A. Gasteiger, R.J. Behm, *J. Catal.*, 182 (1999) 430.
- [7] S.I. Ito, T. Fujimori, K. Nagashima, K. Yuzaki, K. Kunimori, *Catal. Today*, 57 (2000) 247.
- [8] O. Korotkikh, R. Farrauto, *Catal. Today*, 62 (2000) 249.
- [9] T. Utaka, K. Sekizawa, K. Eguchi, *Applied Catal. A: General*, 194/195 (2000) 21.
- [10] G.K. Bethke, H.H. Kung, *Applied Catal. A: General*, 194/195 (2000) 43.
- [11] L. Guzzi, D. Horvath, Z. Paszti, G. Peto, *Catal. Today*, 72 (2002) 101.
- [12] R.J.H. Grisel, C.J. Weststrate, A. Goossens, M.W.J. Craje, A.M. Kraan, B.E. Nieuwenhuys, *Catal. Today*, 72 (2002) 123.
- [13] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, *J. Catal.*, 144 (1993) 175.
- [14] N.A. Hodge, C.J. Kiely, R. Whyman, M.R. H. Siddiqui, G.J. Hutchings, Q.A. Pankhurst, F.E. Wagner, R.R. Rajaram, S.E. Golunski, *Catal. Today*, 72 (2002) 133.
- [15] M. Haruta, A. Ueda, S. Tsubota, R.M.T. Sanchez, *Catal. Today*, 29 (1996) 443.
- [16] G.Y. Wang, H.L. Lian, W.X. Zhang, D.Z. Jiang, T.H. Wu, *Kinetics Catal.*, 43 (2002) 433.
- [17] M. Haruta, *Catal. Today*, 36 (1997) 153.
- [18] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, *J. Catal.*, 171 (1997) 93.
- [19] H.S. Oh, J.H. Yang, C.K. Costello, Y.M. Wang, S.R. Bare, H.H. Kung, M.C. Kung, *J. Catal.*, 210 (2002) 375.
- [20] M.M. Schubert, H.A. Gasteiger, R.J. Behm, *J. Catal.*, 172 (1997) 256.
- [21] S.K. Tanielyan, R.L. Augustine, *Applied Catal. A: General*, 85 (1992) 73.
- [22] S. Schimpf, M. Lucas, C. Mohr, U. Rodemerck, A. Bruckner, J. Radnik, H. Hofmeister, P. Claus, *Catal. Today*, 72 (2002) 63.
- [23] Y.M. Kang, B.Z. Wan, *Catal. Today*, 26 (1995) 59.
- [24] W.S. Epling, G.B. Hoflund, J.F. Weaver, *J. Phys. Chem.*, 100 (1996) 9929.
- [25] C.H. Lin, S.H. Hsu, M.Y. Lee, S.D. Lin, *J. Catal.*, 209 (2002) 62.
- [26] M.A. Debeila, N.J. Coville, M.S. Scurrall, G.R. Hearne, *Catal. Today*, 72 (2002) 79.
- [27] I.H. Son, M. Shamsuzzoha, A.M. Lane, *J. Catal.*, 210 (2002) 460.
- [28] G.B. Hoflund, S.D. Gardner, D.R. Schryer, B.T. Upchurch, E.J. Kielin, *Applied Catal. B: Envir.*, 6 (1995) 117.

## FIGURES CAPTIONS

### FIGURE

- [1] XRD patterns of Au/MnO<sub>x</sub> catalyst calcined at different temperatures:  
 (a) 200°C; (b) 300°C with Au/Mn atomic ratio of 1/120;  
 and different Au/Mn atomic ratios: (b) 1/120; (c) 1/60; (d) 1/30  
 calcined at 300°C: (♣) Au; (♥) MnCO<sub>3</sub>; (♦) Mn<sub>3</sub>O<sub>4</sub>.
- [2] Au crystallite size distribution of Au/MnO<sub>x</sub> catalyst with different  
 Au/Mn atomic ratios: (▣) Au/Mn = 1/120; (□) Au/Mn = 1/60;  
 (⊠), Au/Mn = 1/30 calcined at 300°C.
- [3] XRD patterns of Au/FeO<sub>x</sub> catalyst calcined at different temperatures:  
 (a) 300°C; (b) 400°C with Au/Fe atomic ratio of 1/30;  
 and different Au/Fe atomic ratios: (b) 1/30; (c) 1/60; (d) 1/120  
 calcined at 400°C: (♣) Fe<sub>2</sub>O<sub>3</sub>.
- [4] TEM image of Au/MnO<sub>x</sub> catalyst calcined at 300°C, atomic ratio of 1/30.
- [5] TEM image of Au/FeO<sub>x</sub> catalyst calcined at 400°C, atomic ratio of 1/30.
- [6] TGA result of Au/MnO<sub>x</sub> catalyst: (—) wt.%; (—) derivative (°C/%).
- [7] TGA result of Au/FeO<sub>x</sub> catalyst: (—) wt.%; (—) derivative (°C/%).
- [8] Effect of pretreatment condition on Au/MnO<sub>x</sub> catalyst calcined  
 at 200°C, atomic ratio of 1/120: (●) He pretreatment;  
 (■) H<sub>2</sub> pretreatment; (▲) O<sub>2</sub> pretreatment; (—), conversion; (-----), selectivity.
- [9] Effect of pretreatment condition on Au/FeO<sub>x</sub> catalyst calcined  
 at 400°C, atomic ratio of 1/60: (●) O<sub>2</sub> pretreatment;  
 (■) He pretreatment; (▲) H<sub>2</sub> pretreatment; (—) conversion; (-----) selectivity.
- [10] Effect of calcination temperature on Au/MnO<sub>x</sub> catalyst,  
 He pretreatment, atomic ratio of 1/120: (●) 300°C; (▲) 200°C;  
 (—) conversion; (-----) selectivity.
- [11] Effect of calcination temperature on Au/FeO<sub>x</sub> catalyst,  
 O<sub>2</sub> pretreatment, atomic ratio of 1/30: (●) 400°C; (▲) 300°C;  
 (—) conversion; (-----) selectivity.
- [12] Effect of Au loading on Au/MnO<sub>x</sub> catalyst calcined at 300°C,

- He pretreatment: (●) Au/Mn=1/30; (■) Au/Mn=1/60; (▲) Au/Mn=1/120;  
(—) conversion; (.....) selectivity.
- [13] Effect of Au loading on Au/FeO<sub>x</sub> catalyst calcined at 400°C,  
O<sub>2</sub> pretreatment: (●) Au/Mn=1/30; (■) Au/Mn=1/60;  
(▲) Au/Mn=1/120; (—) conversion; (.....) selectivity.
- [14] Effect of CO<sub>2</sub> on Au/MnO<sub>x</sub> catalyst, calcined at 300°C,  
He pretreatment, atomic ratio of 1/30: (●) conversion ; (▲) selectivity;  
(from the beginning up to the time marked by the small vertical line)  
in the presence of 10 % CO<sub>2</sub>; (for the remaining time period) without CO<sub>2</sub>.
- [15] Effect of CO<sub>2</sub> on Au/FeO<sub>x</sub> catalyst, calcined at 400°C,  
O<sub>2</sub> pretreatment, atomic ratio of 1/30: (●) conversion; (▲) selectivity;  
(from the beginning up to the time marked by the small vertical line)  
in the presence of 10 % CO<sub>2</sub>; (for the remaining time period) without CO<sub>2</sub>.
- [16] Effect of H<sub>2</sub>O on Au/MnO<sub>x</sub> catalysts, calcined at 300°C,  
He pretreatment, atomic ratio of 1/30: (●) conversion; (▲) selectivity;  
(from the beginning up to the time marked by the small vertical line)  
in the presence of 10 % H<sub>2</sub>O ; (for the remaining time period) without H<sub>2</sub>O.
- [17] Effect of H<sub>2</sub>O on Au/FeO<sub>x</sub> catalysts, calcined at 400°C,  
O<sub>2</sub> pretreatment, atomic ratio of 1/30: (●) conversion; (▲) selectivity;  
(from the beginning up to the time marked by the small vertical line)  
in the presence of 10 % H<sub>2</sub>O; (for the remaining time period) without H<sub>2</sub>O.
- [18] Deactivation test of Au/MnO<sub>x</sub> catalyst, calcined at 300°C,  
He pretreatment, atomic ratio of 1/30: (●) conversion; (▲) selectivity.
- [19] Deactivation test of Au/FeO<sub>x</sub> catalyst, calcined at 400°C,  
O<sub>2</sub> pretreatment, atomic ratio of 1/30: (●) conversion; (▲) selectivity.
- [20] A comparative study of Au/MnO<sub>x</sub> catalyst: (●) conversion in this work;  
(○) conversion in the previous work.
- [21] A comparative study of Au/FeO<sub>x</sub> catalyst: (●) conversion in this work;  
(○) conversion in the previous work.

**Table 1** Surface area, pore and crystallite sizes of prepared catalysts

Type of catalyst	Calcination temperature (°C)	Atomic ratio	Surface area (m <sup>2</sup> /g)	Pore size (nm)	Average Au crystallite size *
Au/MnO <sub>x</sub>	200	1/120	67.00	13.22	100.0
	300	1/120	87.75	9.20	10.0
	300	1/60	100.30	11.27	10.0
	300	1/30	68.00	14.35	14.6
Au/FeO <sub>x</sub>	300	1/30	210.10	6.62	<3.0
	400	1/30	115.00	8.74	<3.0
	400	1/60	163.80	6.84	<3.0
	400	1/120	53.11	14.86	<3.0

\*From XRD result



**Table 2** Actual Au loading on prepared catalysts

Type of catalyst	Atomic ratio	Au loading * (%)
Au/MnO <sub>x</sub>	1/120	1.67
	1/60	2.86
	1/30	5.70
Au/FeO <sub>x</sub>	1/120	1.21
	1/60	2.08
	1/30	5.38

\*From AAS result

**Table 3** Result summarization

	Catalyst type	Pretreatment condition	Calcination temperature (°C)	Atomic ratio	Run no.	Maximum conversion (%)	Maximum selectivity (%)
Effect of pretreatment condition	Au/MnO <sub>x</sub>	He	200	1/120	1	78	45
		O <sub>2</sub>	200	1/120	2	70	45
		H <sub>2</sub>	200	1/120	3	75	45
	Au/FeO <sub>x</sub>	He	400	1/60	4	65	35
		O <sub>2</sub>	400	1/60	5	80	50
		H <sub>2</sub>	400	1/60	6	54	33
Effect of calcination temperature	Au/MnO <sub>x</sub>	He	200	1/120	-	78	45
		He	300	1/120	7	86	50
	Au/FeO <sub>x</sub>	O <sub>2</sub>	300	1/30	8	95	52
		O <sub>2</sub>	400	1/30	9	100	55
Effect of atomic ratio	Au/MnO <sub>x</sub>	He	300	1/120	-	86	50
		He	300	1/60	10	86	47
		He	300	1/30	11	93	60
	Au/FeO <sub>x</sub>	O <sub>2</sub>	400	1/120	12	70	35
		O <sub>2</sub>	400	1/60	-	65	35
		O <sub>2</sub>	400	1/30	-	100	55
Effect of CO <sub>2</sub> with CO <sub>2</sub> with out CO <sub>2</sub>	Au/MnO <sub>x</sub>	He	300	1/30	13	90	52
						95	52
	Au/FeO <sub>x</sub>	O <sub>2</sub>	400	1/30	14	98	52
						100	52
Effect of H <sub>2</sub> O with H <sub>2</sub> O with out H <sub>2</sub> O	Au/MnO <sub>x</sub>	He	300	1/30	15	97	52
						97	52
	Au/FeO <sub>x</sub>	O <sub>2</sub>	400	1/30	16	98	50
						98	50
Deactivation test	Au/MnO <sub>x</sub>	He	300	1/30	17	93	58
	Au/FeO <sub>x</sub>	O <sub>2</sub>	400	1/30	18	98	53

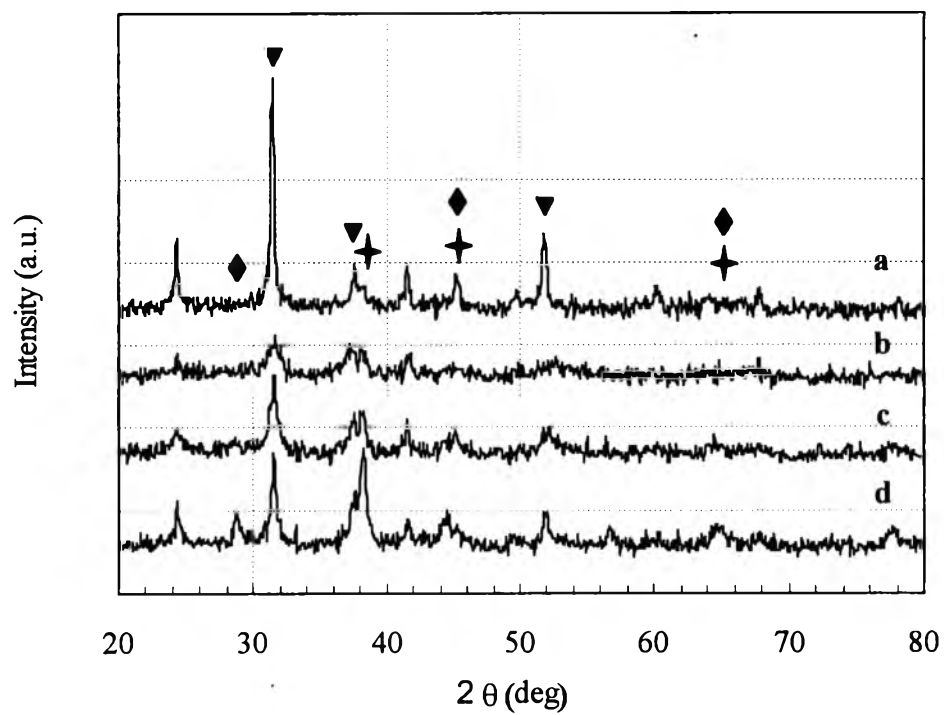


Fig. 1. XRD patterns of Au/MnO<sub>x</sub> catalyst calcined at different temperatures: (a) 200°C; (b) 300°C with Au/Mn atomic ratio of 1/120; and different Au/Mn atomic ratios: (b) 1/120; (c) 1/60; (d) 1/30 calcined at 300°C: (+) Au; (▼) MnCO<sub>3</sub>; (◆) Mn<sub>3</sub>O<sub>4</sub>.

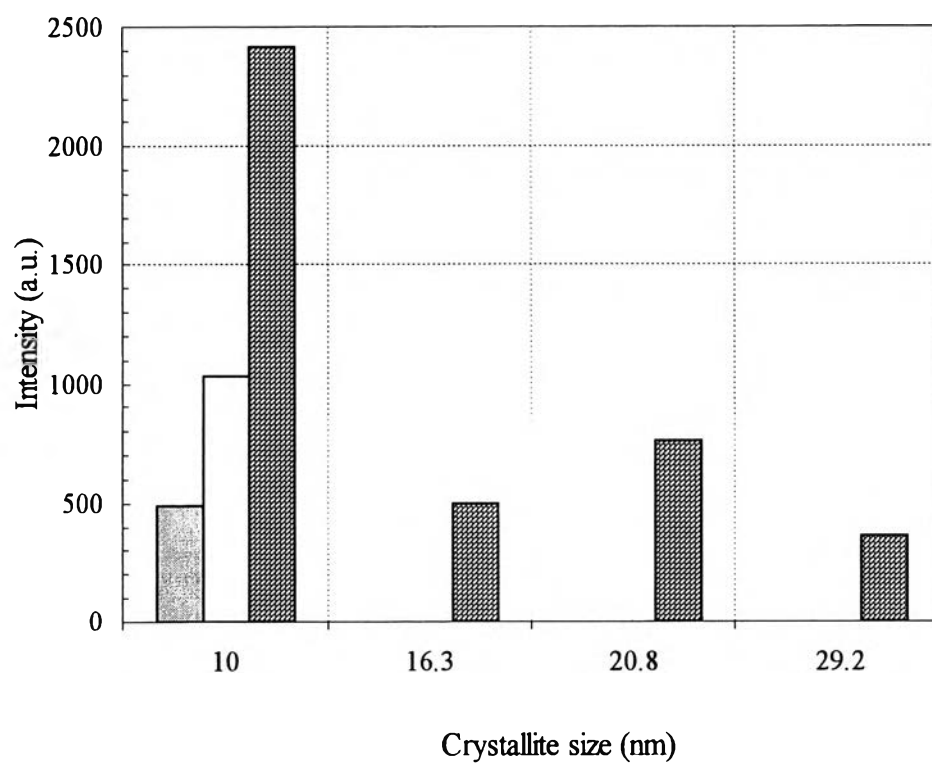


Fig. 2. Au crystallite size distribution of Au/MnO<sub>x</sub> catalyst with different Au/Mn atomic ratios: (▨) Au/Mn = 1/120; (□) Au/Mn = 1/60; (⊗), Au/Mn = 1/30 calcined at 300°C.

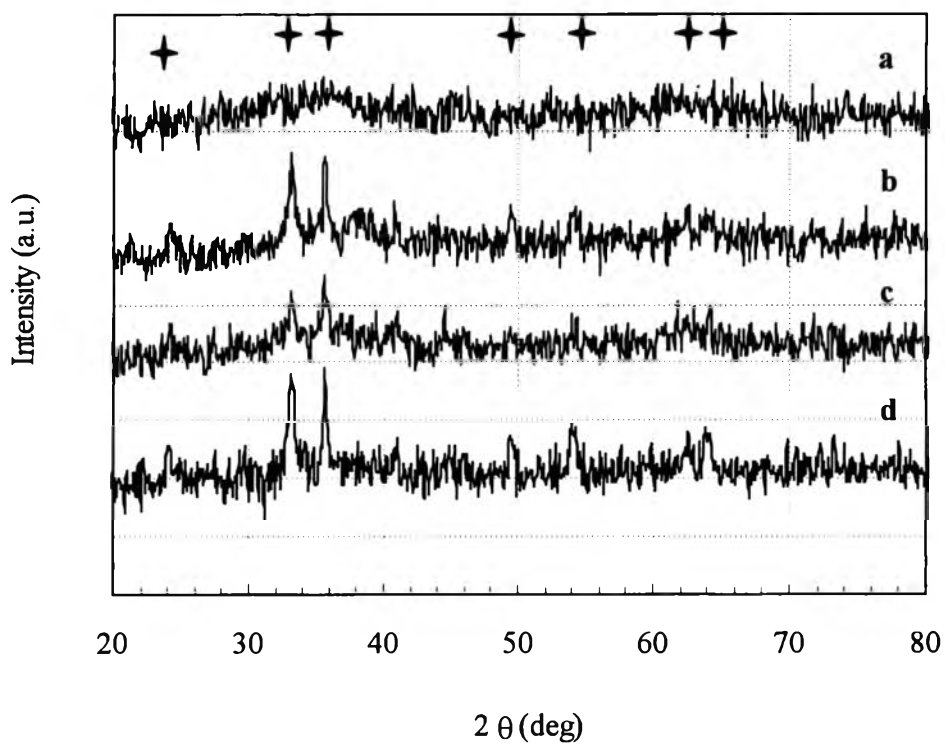


Fig.3. XRD patterns of Au/FeO<sub>x</sub> catalyst calcined at different temperatures: (a) 300°C; (b) 400°C with Au/Fe atomic ratio of 1/30; and different Au/Fe atomic ratio: (b) 1/30; (c) 1/60; (d) 1/120 calcined at 400°C: ( $\blackcross$ ) Fe<sub>2</sub>O<sub>3</sub>.

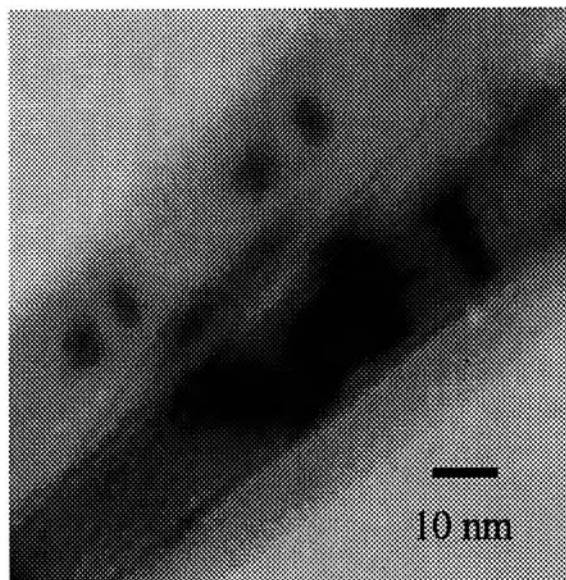


Fig. 4. TEM image of Au/MnO<sub>x</sub> catalyst calcined at 300°C, atomic ratio of 1/30.

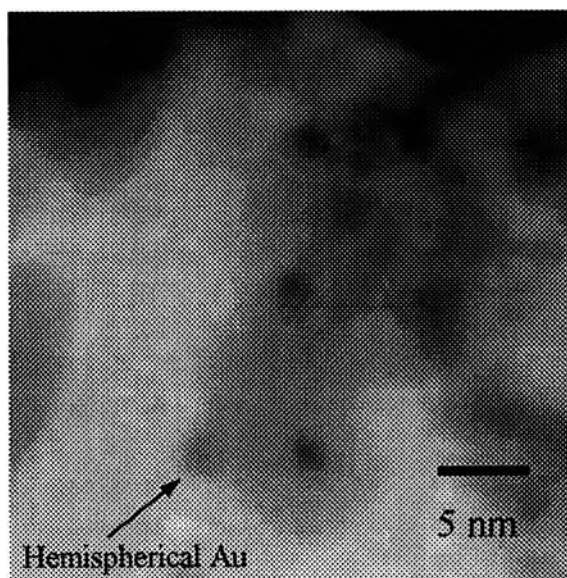


Fig. 5. TEM image of Au/FeO<sub>x</sub> catalyst calcined at 400°C, atomic ratio of 1/30.

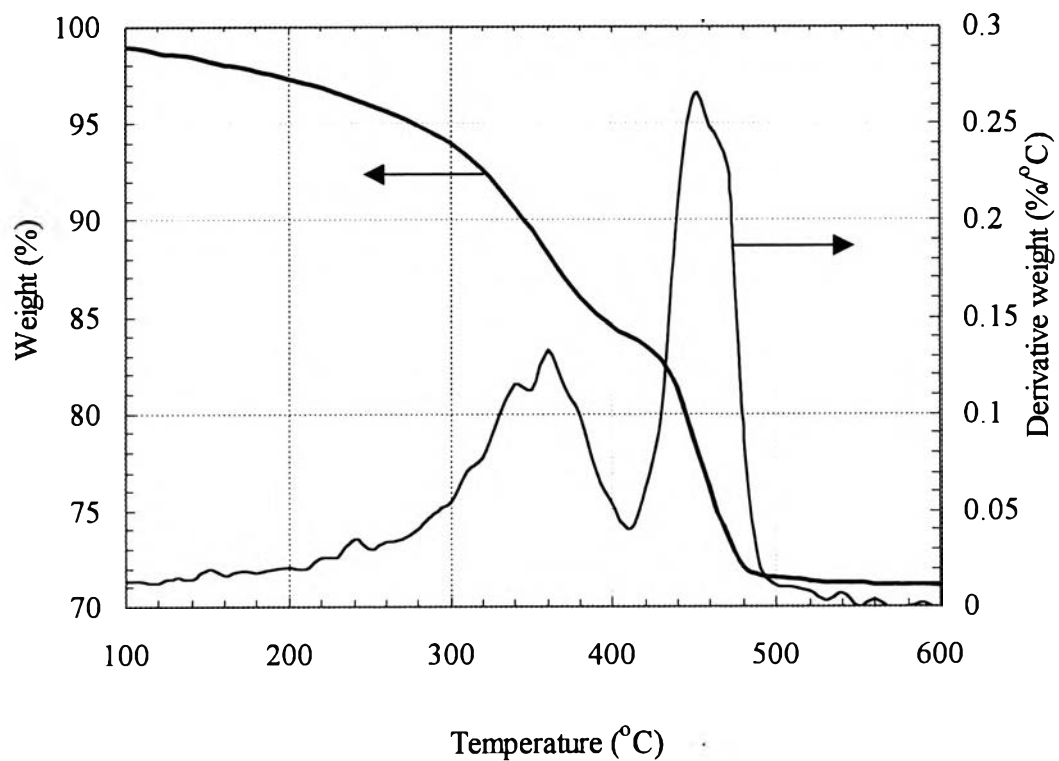


Fig. 6. TGA result of Au/MnO<sub>x</sub> catalyst: (—) wt.%; (---) derivative (°C/%).



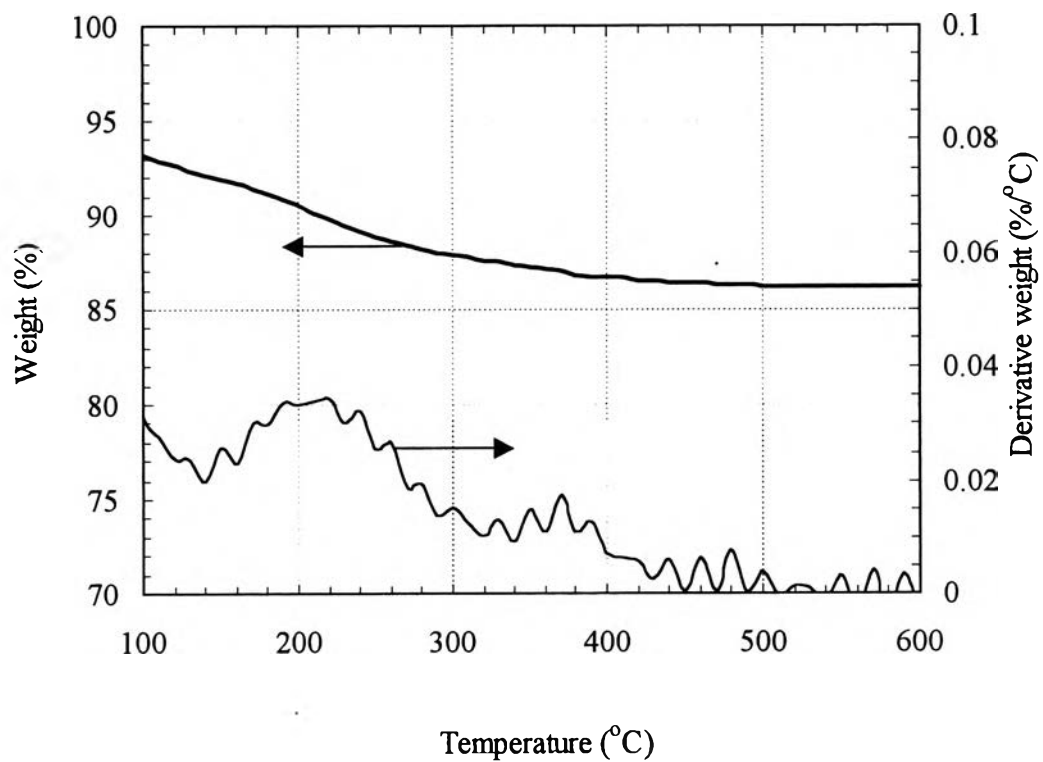


Fig. 7. TGA result of Au/FeO<sub>x</sub> catalyst: (—) wt.%; (---) derivative (°C/%).

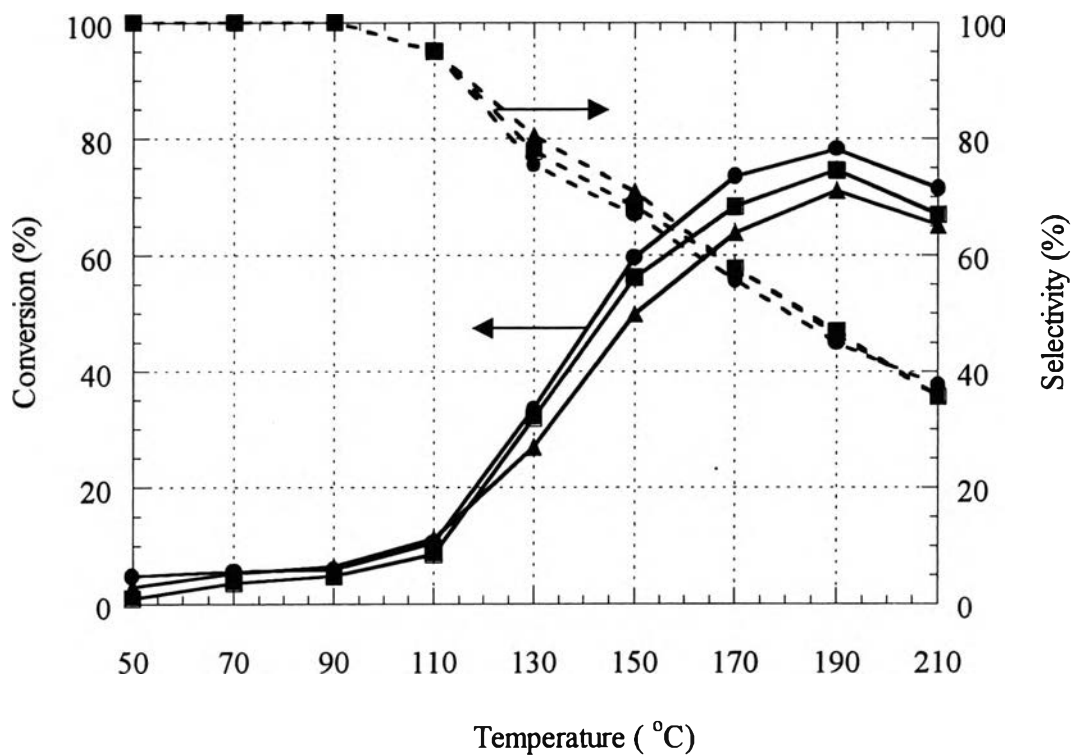


Fig. 8. Effect of pretreatment condition on Au/MnO<sub>x</sub> catalyst calcined at 200°C, atomic ratio of 1/120: ( ● ) He pretreatment; ( ■ ) H<sub>2</sub> pretreatment; ( ▲ ) O<sub>2</sub> pretreatment; (—), conversion; (-----), selectivity.

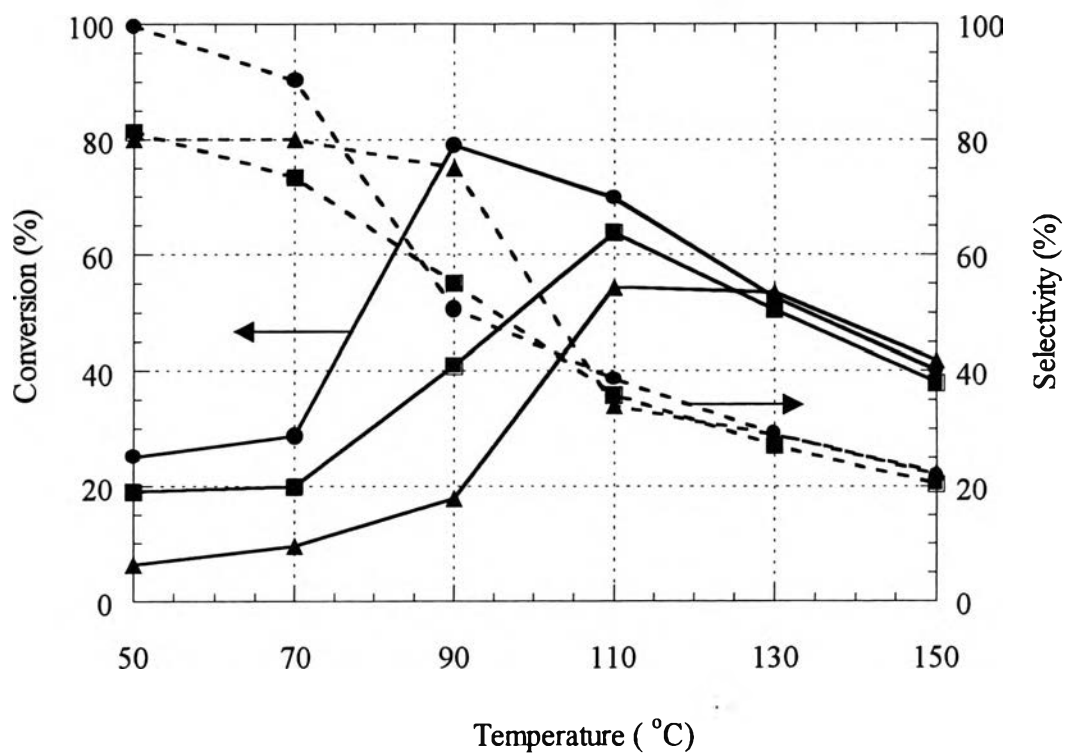


Fig. 9. Effect of pretreatment condition on Au/FeO<sub>x</sub> catalyst calcined at 400°C, atomic ratio of 1/60: (●) O<sub>2</sub> pretreatment; (■) He pretreatment; (▲) H<sub>2</sub> pretreatment; (—) conversion; (.....) selectivity.

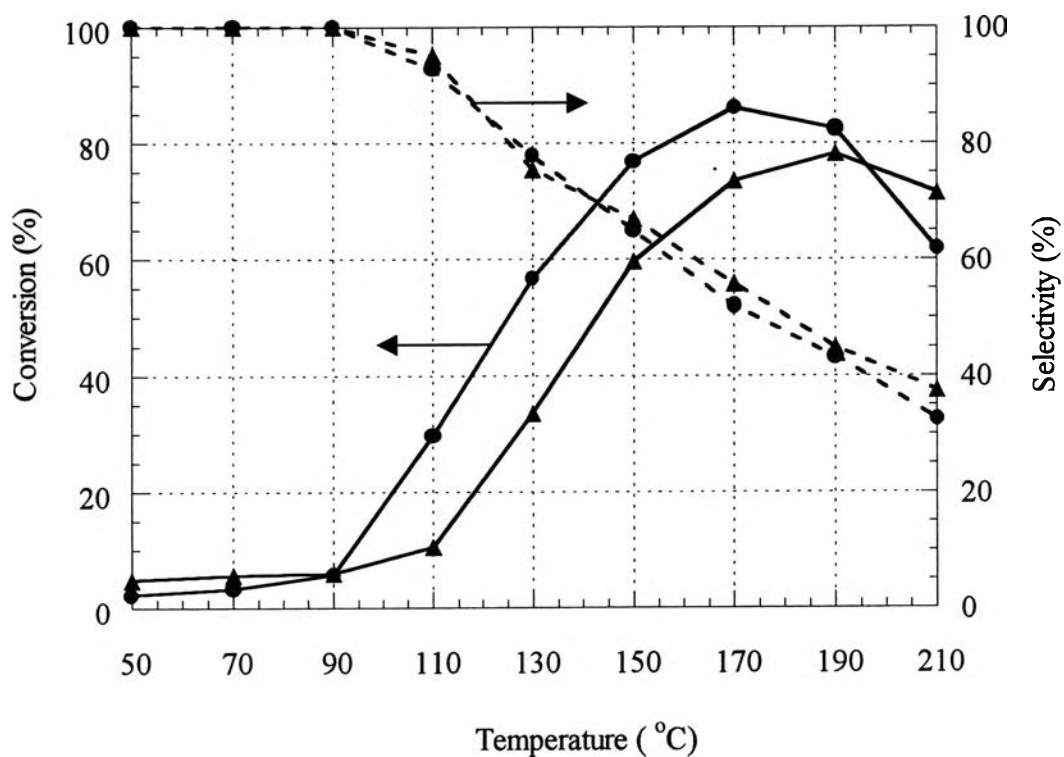


Fig. 10. Effect of calcination temperature on Au/MnO<sub>x</sub> catalyst, He pretreatment, atomic ratio of 1/120: (●) 300°C; (▲) 200°C; (—) conversion; (-----) selectivity.

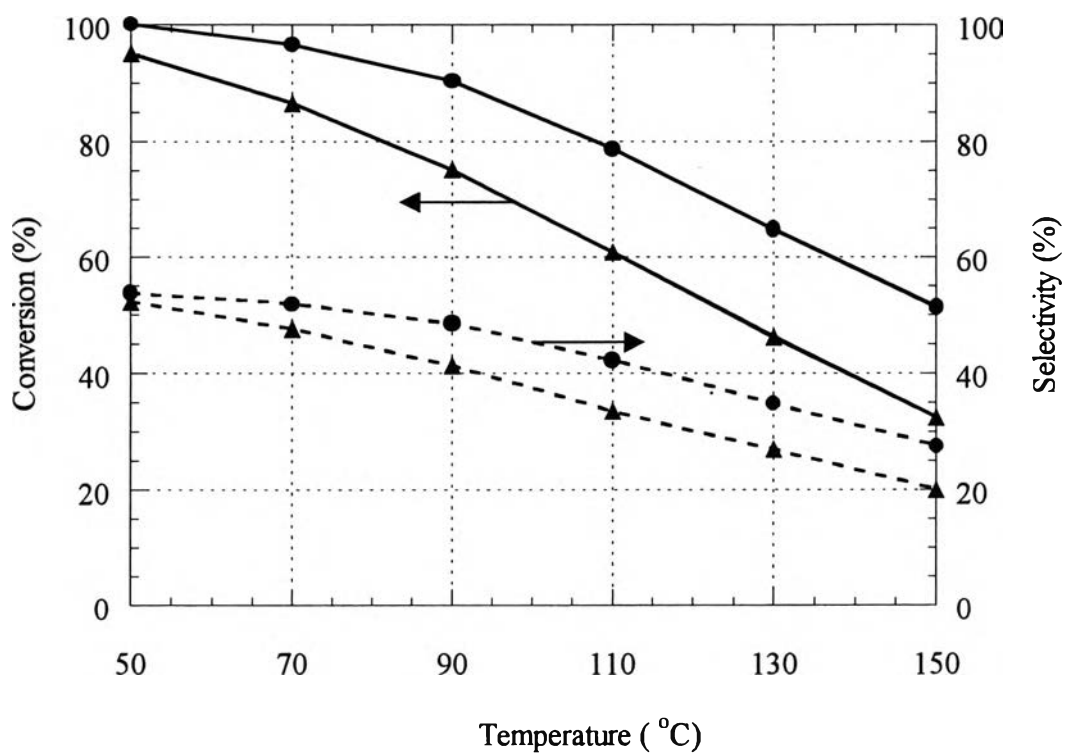


Fig. 11. Effect of calcination temperature on Au/FeO<sub>x</sub> catalyst, O<sub>2</sub> pretreatment, atomic ratio of 1/30: (●) 400°C; (▲) 300°C; (—) conversion; (-----) selectivity.

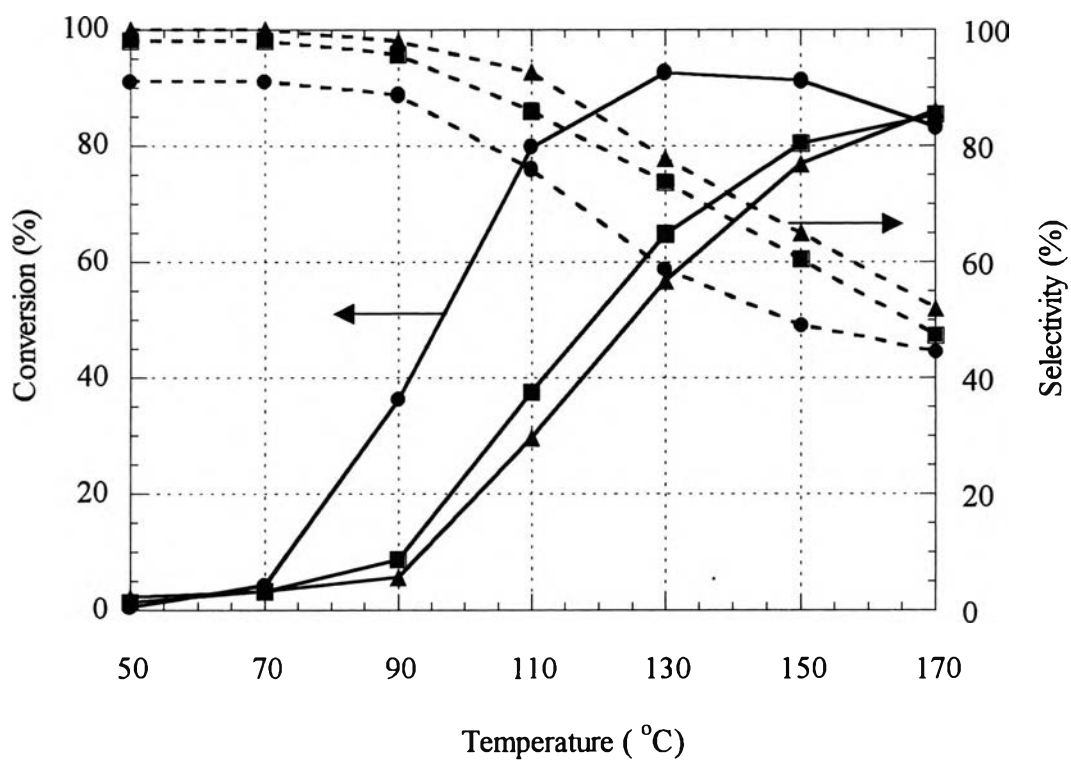


Fig. 12. Effect of Au loading on Au/MnO<sub>x</sub> catalyst calcined at 300°C, He pretreatment: (●) Au/Mn=1/30; (■) Au/Mn=1/60; (▲) Au/Mn=1/120; (—) conversion; (-----) selectivity.

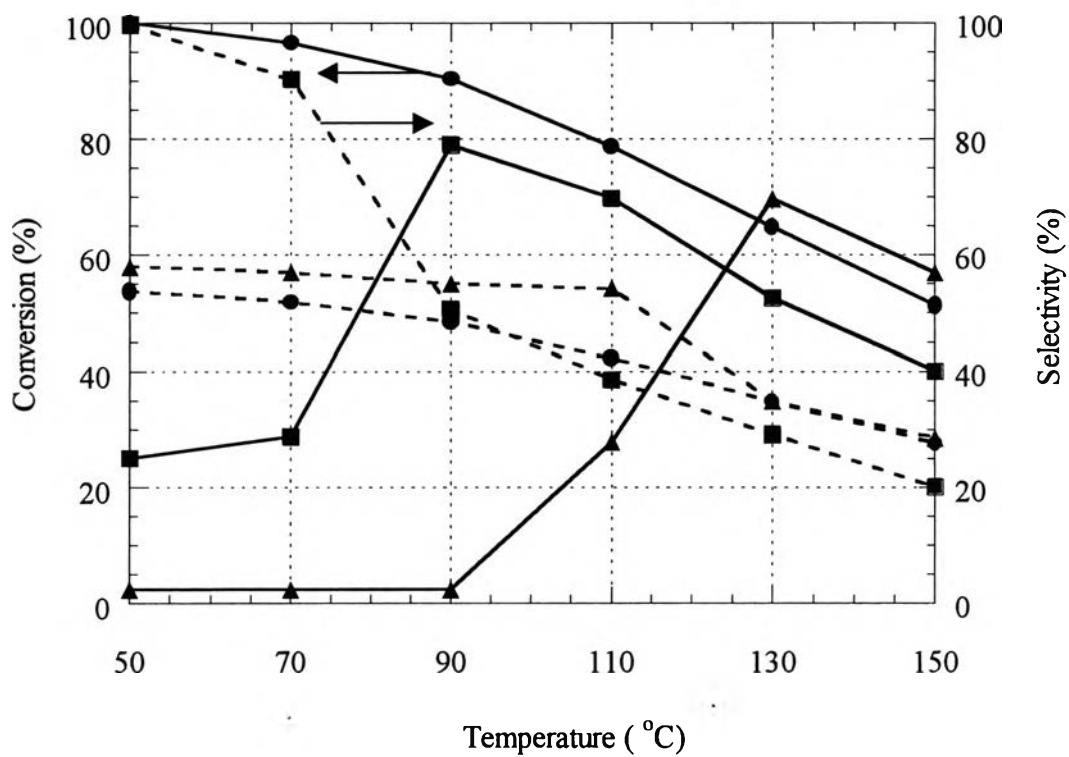


Fig. 13. Effect of Au loading on Au/FeO<sub>x</sub> catalyst calcined at 400°C, O<sub>2</sub> pretreatment: (●) Au/Mn=1/30; (■) Au/Mn=1/60; (▲) Au/Mn=1/120; (—) conversion; (-----) selectivity.

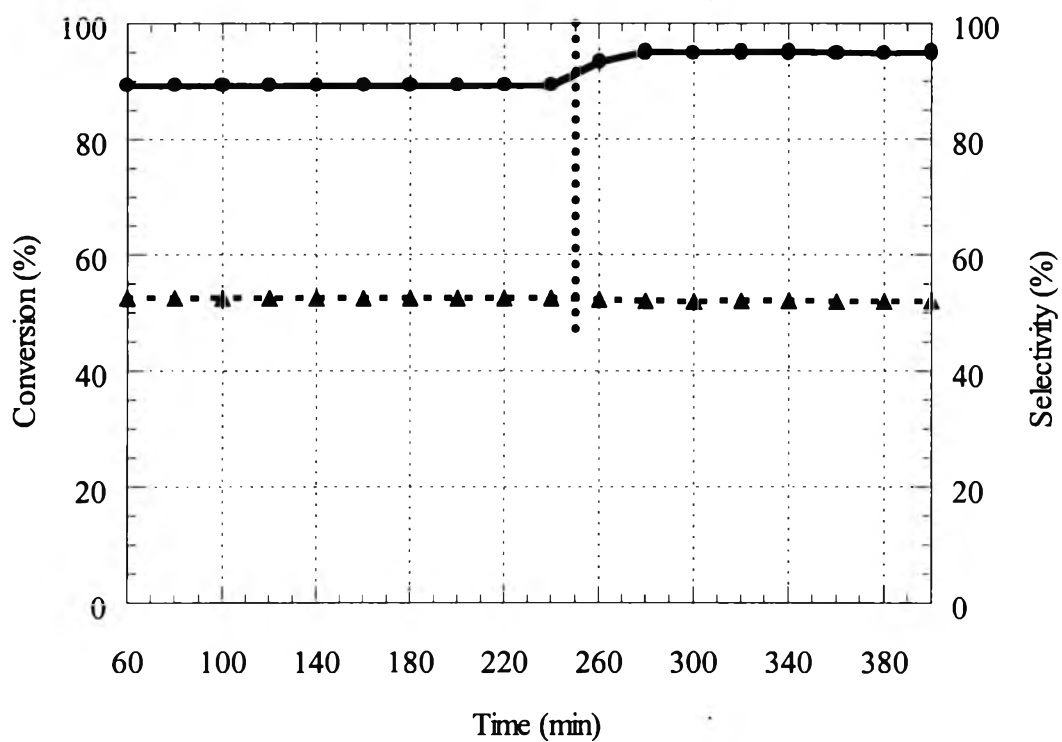


Fig. 14. Effect of CO<sub>2</sub> on Au/MnO<sub>x</sub> catalyst, calcined at 300°C, He pretreatment, atomic ratio of 1/30: (●) conversion; (▲) selectivity; (from the beginning up to the time marked by the small vertical line) in the presence of 10% CO<sub>2</sub>; (for the remaining time period) without CO<sub>2</sub>.



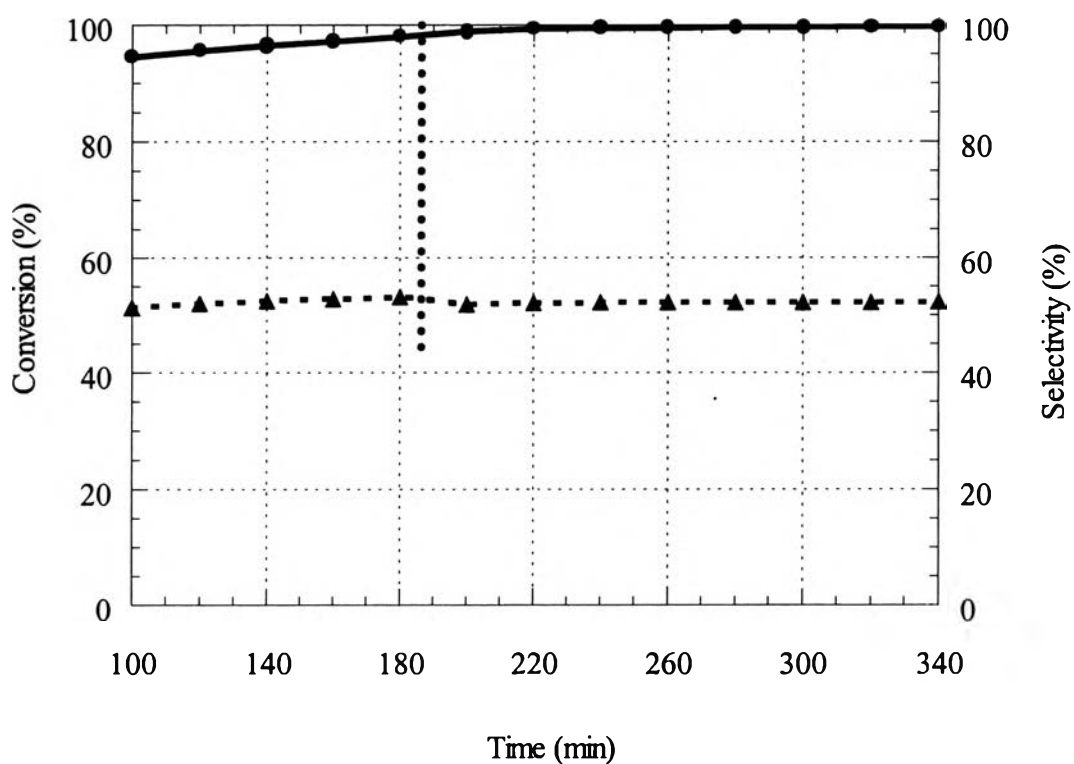


Fig. 15. Effect of CO<sub>2</sub> on Au/FeO<sub>x</sub> catalyst, calcined at 400°C, O<sub>2</sub> pretreatment, atomic ratio of 1/30: (●) conversion; (▲) selectivity; (from the beginning up to the time marked by the small vertical line) in the presence of 10% CO<sub>2</sub>; (for the remaining time period) without CO<sub>2</sub>.

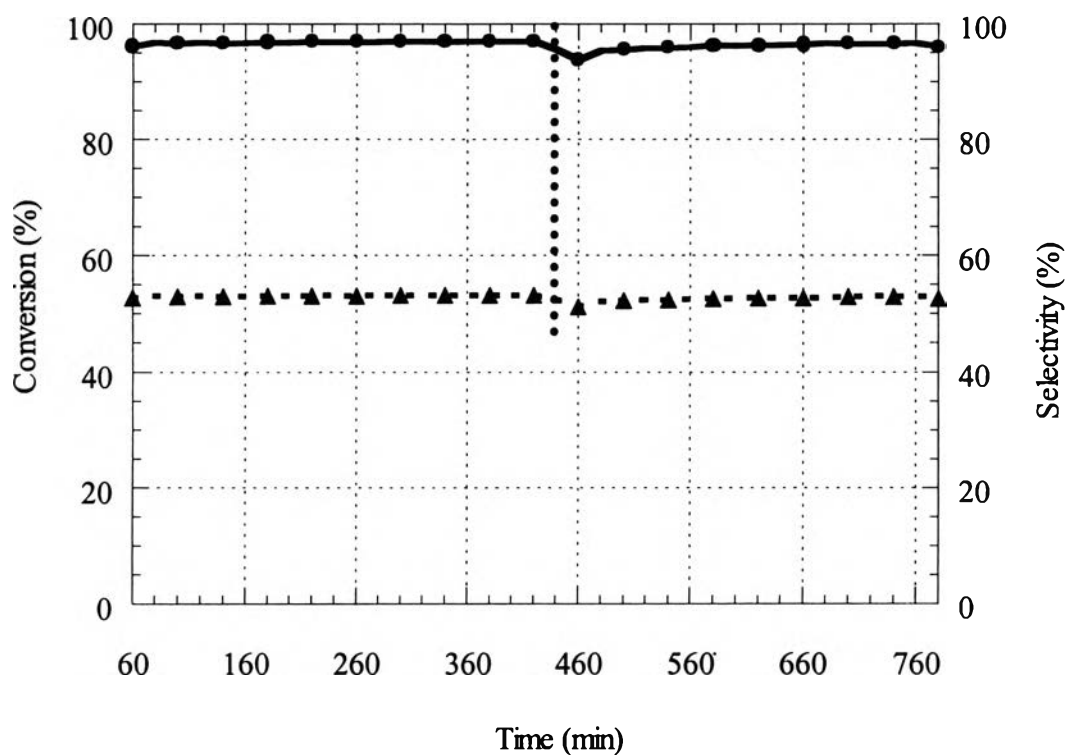


Fig. 16. Effect of H<sub>2</sub>O on Au/MnO<sub>x</sub> catalysts, calcined at 300°C, He pretreatment, atomic ratio of 1/30: (●) conversion; (▲) selectivity; (from the beginning up to the time marked by the small vertical line) in the presence of 10% H<sub>2</sub>O; (for the remaining time period) without H<sub>2</sub>O.

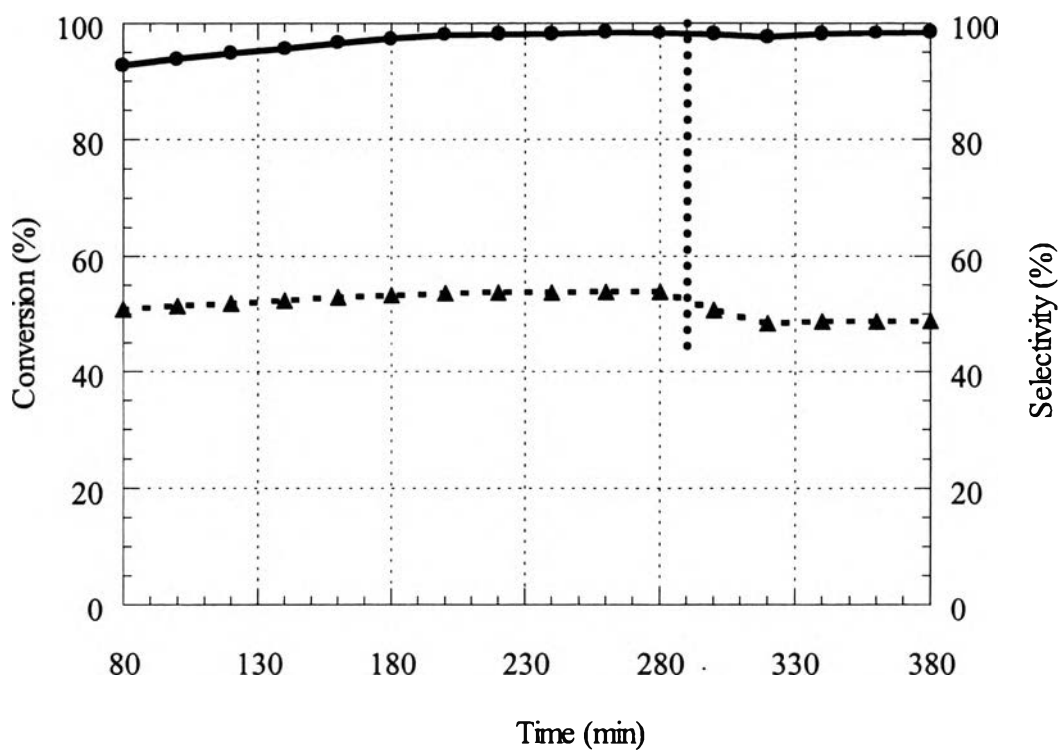


Fig. 17. Effect of H<sub>2</sub>O on Au/FeO<sub>x</sub> catalysts, calcined at 400°C, O<sub>2</sub> pretreatment, atomic ratio of 1/30: (●) conversion; (▲) selectivity; (from the beginning up to the time marked by the small vertical line) in the presence of 10% H<sub>2</sub>O; (for the remaining time period) without H<sub>2</sub>O.

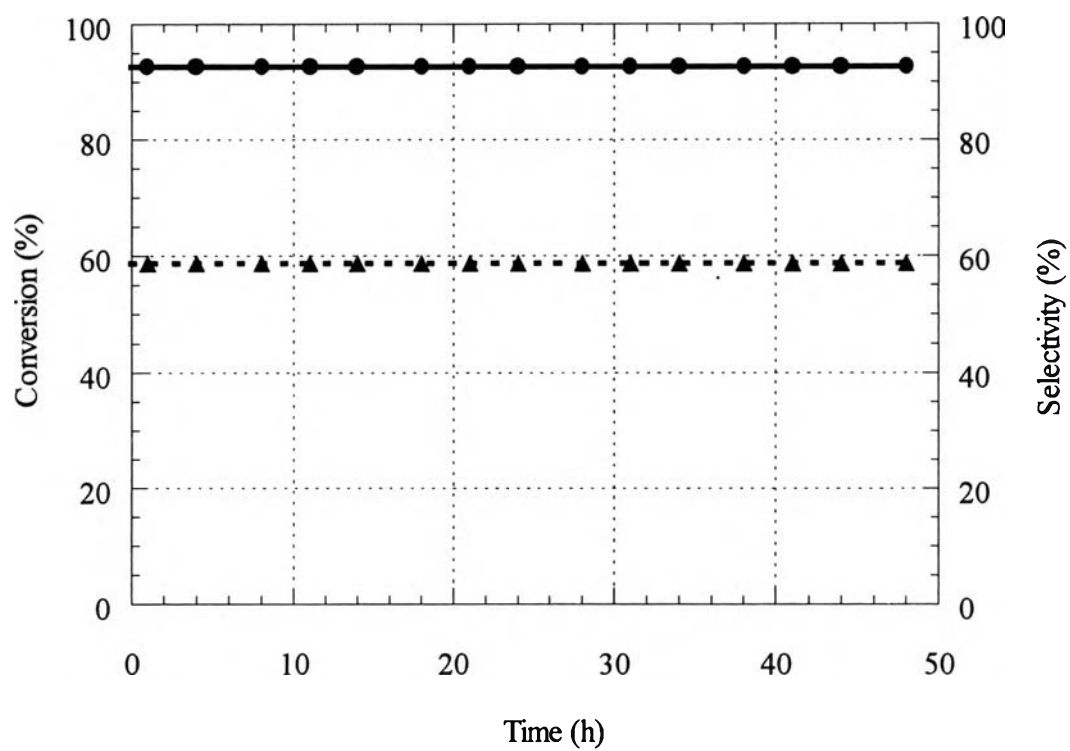


Fig. 18. Deactivation test of Au/MnO<sub>x</sub> catalyst, calcined at 300°C, He pretreatment, atomic ratio of 1/30: (● ) conversion; (▲ ) selectivity.

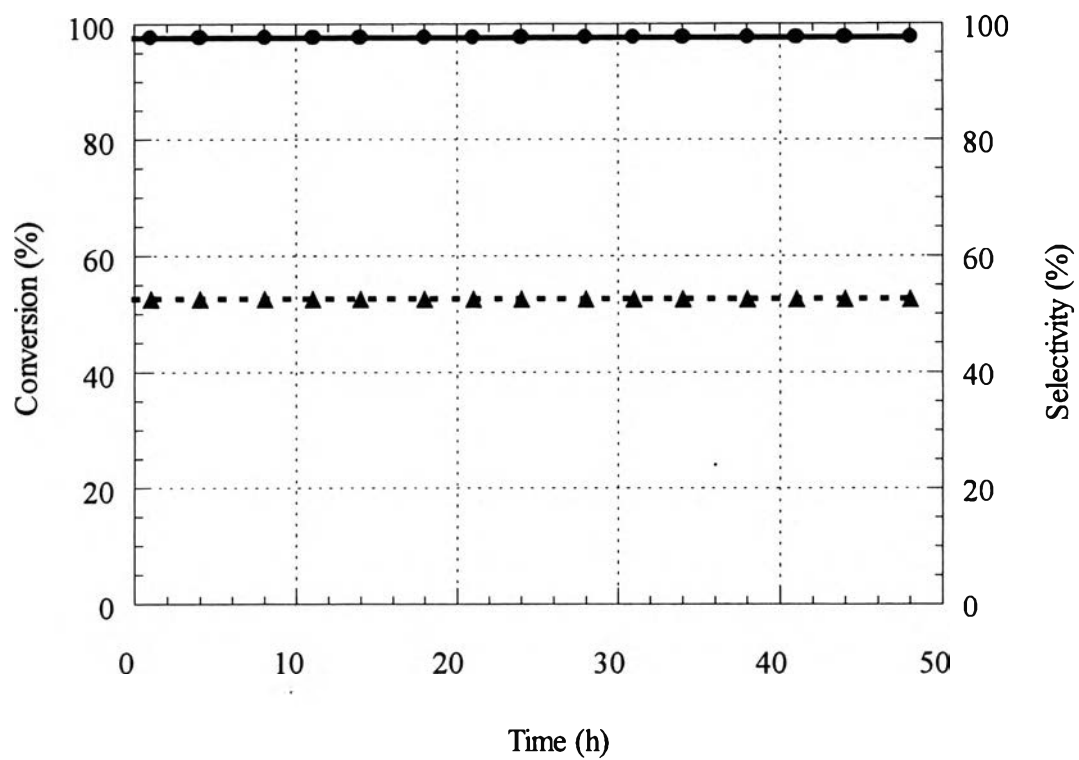


Fig. 19. Deactivation test of Au/FeO<sub>x</sub> catalyst, calcined at 400°C, O<sub>2</sub> pretreatment, atomic ratio of 1/30: (●) conversion; (▲) selectivity.

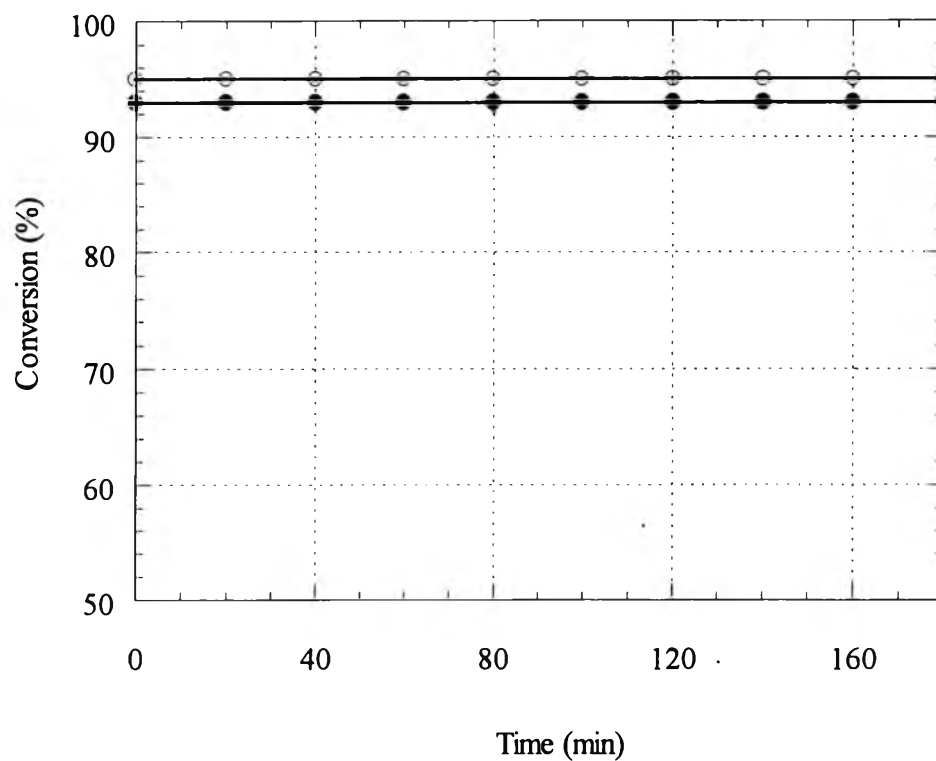


Fig. 20. A comparative study of Au/MnO<sub>x</sub> catalyst: (●) conversion in this work; (○) conversion in the previous work.

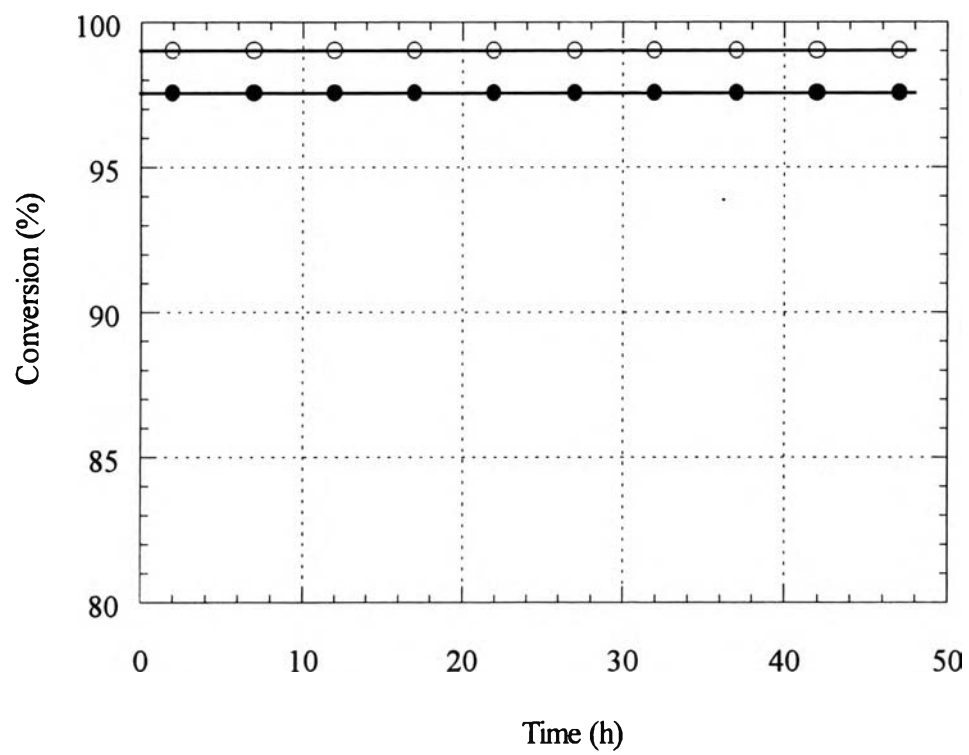


Fig. 21. A comparative study of Au/FeO<sub>x</sub> catalyst: (●) conversion in this work; (○) conversion in the previous work.