# SYNTHESIS, ACTIVITY AND THERMAL STABILITY OF GOLD NANOPARTICLE ON MODIFIED NH4-Y TYPE ZEOLITE FOR COOXIDATION

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## ABSTRACT

Gold nanoparticle is the active catalyst for CO oxidation at low temperature. This feature of gold base catalysts is suitable to overcome the problem of cold-start problem of automobile exhaust TWC converters. In this study gold nanoparticle were deposited on modified $NH_4$-Y type zeolite. The activity of synthesized catalyst was measured in a fixed-bed quartz-tubular reactor (7mm i.d.) under atmospheric pressure. In order to investigate the catalytic activities toward CO oxidation reaction, 31mL/min of air and 0.155mL/min of carbon monoxide were mixed and then passed through the reactor. It was found that activity of Au/Y catalyst was 100% at 20°C. The thermal stability of Au/Y catalyst was measured at 400°C for 4h. The activity of the catalyst was decreased to 65% at 20°C after thermal stability test. Results of Energy Dispersive Analysis by X-rays before and after thermal stability have showed that Au content of these samples were 3.89% and 1.76, respectively. It was found that the amount of Au content decreased after thermal stability process. Fourier Transform Infrared (FT-IR) spectra showed no changes in framework structure of zeolite during thermal stabilization process of the catalyst.

**Key words:** Gold nanoparticle; $NH_4$Y-type zeolite; CO oxidation; Catalyst; Thermal stabilization

## INTRODUCTION

Carbon monoxide (CO) is a gaseous pollutant which enters the atmosphere from four major sources: fossil fuel combustion and industrial emissions, biomass burning, oxidation of $CH_4$, and oxidation of hydrocarbons. The presence of CO causes problems to human health, particularly in cases of locally high concentrations, and affects the oxidizing capacity of the troposphere. Automobile emissions are the major urban source of carbon monoxide, and they are also important globally. One estimate by the Japanese Automobile Research Institute (JARI) of the 1990 global CO emissions from automobiles is 231 megatonnes (Mt). The same source gives the USA 1990 emissions as 21Mt, whereas the US Environmental Protection Agency (EPA) estimate 57Mt (Bradley *et al.*, 1999).

The three major pollutants emitted by internal combustion engines are carbon monoxide, unburned hydrocarbons and nitrogen oxides.

Catalysts that are capable of removing these pollutants simultaneously are generally referred to as three-way catalysts (TWCs) and the design of these catalyst systems is continually evolving to meet lower emission requirements (Mellor *et al.*, 2002).

A new catalyst that has been introduced recently for oxidation of CO is gold nanoparticl. The application of gold catalysts to the oxidation of carbon monoxide has been studied extensively, most notably by Haruta *et al.*, 1993.

A significant feature of gold-based catalysts is the low temperature oxidation of carbon monoxide, where the catalysts display activity at temperatures as low as -70°C (Mellor *et al.*, 2002). One application for which low temperature oxidation by gold nanoparticle is automotive pollution abatement. A gold catalyst with low temperature activity towards CO oxidation could be suitable to application as TWCs, especially during the low temperature start-up ("cold start" phase) and idling phases (Ilieva *et al.*, 2006).Carbon monoxide

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emissions from automobiles increase dramatically during cold start-up. This is because cars need more fuel to start at cold temperatures, and because some emission control devices (such as oxygen sensors and catalytic converters) operate less efficiently when they are cold.

There are many factors affecting the catalytic activity of gold nanoparticle; e.g. the size of gold nanoparticles, preparation methods, and pretreatment conditions (Chiang *et al.*, 2006).

The most important factor in catalytic activity is the particle size of gold of which 3 nm is the optimum for CO oxidation (Chiang *et al.*, 2006). Other parameter which determines the catalytic activity is the nature of the support (Pillail and deevis, 2004). Different kinds of materials used for the support, e.g Active supports, such as TiO2 and Fe2O3, which can be easily reduced, or inert supports, like Mg(OH)2, Al2O3, silica, MCM-48 (Bandyopadhyay *et al.*, 2006), Al-SBA-15 (Chiang *et al.*, 2006), activated carbon fibers (Bulushev *et al.*, 2004), Y-type Zeolite (Lin and Wan, 2003), zeolite A (Kuge and Calzaferri, 2003), and H-BEA zeolite (Derouanea *et al.*, 2004).

To load the gold nanoparticle, zeolite was used as one of the supports. The advantage of zeolite is due to its high surface area, ion exchange ability, and the stabilization of small gold particles via inserting them into the small cages (Lin and Wan, 2003). Different kinds of Au/Zeolites have been prepared for NO reduction and CO oxidation (Lin *et al.*, 2002). Jiunn-Nan Lin, and co-workers were developed a modified method for the preparation of gold nanoparticles on Y-type zeolite and resulted that catalysts possessed much better activity and stability for CO oxidation than those without any surface pretreatment (Lin and Wan, 2003). Jiunn-Nan Lin and Ben-Zu Wan studied the effects of preparation conditions of gold nanoparticles on the Y-type zeolite (Au/Y) support for CO oxidation. Their results were shown that Au/Y prepared from a gold solution on a surface acidity modified Y-type zeolite, with initial gold concentration of $1.46 \times 10^{-3}$ M, solution pH at 6, would possess an optimum catalytic activity for CO oxidation (Lin and Wan, 2003).

In this study gold nanoparticles supported by the modified $NH_4$-Y type zeolite with deposition-precipitation method was synthesized and characterized using X-rays before and after (XRF), Energy Dispersive Analysis by X-rays (EDAX), and FT-IR. The catalytic activity was studied at different temperature in a fixed-bed reactor and thermal stabilization process was also investigated.

## MATERIALS AND METHHODS

$NH_4$-Y type zeolite (from Sigma-Aldrich Company) was calcined at 550°C in air for 4h. In this process, $NH_3$ gas was evaporated and H-Y zeolite was obtained. In order to modify the catalyst support surface, the obtained H-Y zeolite was contacted with a 1N $NaNO_3$ solution; pH was adjusted to 6 by a 1N sodium hydroxide solution. After the equilibrium (2days), the samples were filtered and dried at 60°C for 4h. With this process Na-Y zeolite was obtained.

In order to deposit the gold nanoparticles on the zeolite substrate, 1g of Na-Y was added to the 125mL chloroauric acid solution (0.032 wt %). The pH of the solution was adjusted to 6 by a 1N NaOH solution. The solution was heated up to 80°C and kept at this temperature for 1h. It should be noticed that, 1–1.5h was needed for the solution temperature to reach to 80°C. Therefore, the time for raising the solution temperature and the mixing time at 80°C for 1h have been enough to form the gold nano species on Na-Y zeolite surface.

The prepared catalyst was filtered and washed with excess amounts of distilled water until the filtrate was free of $Cl^+$ ions ($Ag^+$ test). The resulted samples were dried at 60°C overnight.

*Catalyst characterization*
Chemical analysis of $NH_4$-Y type zeolite was performed by XRF technique. The energy dispersive analysis by X-rays (EDAX) was measured the elemental content of the synthesized Au/Na-Y catalysts. The concentration of Au in chloroauric acid solution after filtration of catalyst was determined by Inductively Coupled Plasma-Atomic Emission spectroscopy (ICP-AE). The framework structure of zeolite was investigated using Fourier Transform Infrared spectroscopy (FTIR).

*Catalytic activities of CO oxidation*
In order to consider the catalytic activities of the prepared catalysts, carbon monoxide oxidation

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reaction was carried out in a quartz tube reactor under atmospheric pressure. To do this, a stream of 31mL/min of dried air and 0.155mL/min of carbon monoxide were mixed and used a reactor feed. A real time gas analyzer device (Babuc), which was equipped with a carbon monoxide detector, was used to measure carbon monoxide concentration at the reactor influent and effluent streams. The reactor was heated by means of tubular heater (Fig. 1). The synthesized catalysts were catalytically evaluated at the range of 20 to 400°C, the reactor setup was maintained at 400°C for 24h.

Different tests were carried out in order to investigate the catalyst activity (conversion as a function of temperature), catalyst durability (conversion as a function of time at constant temperature) and catalyst stability (conversion as a function of time and temperature).
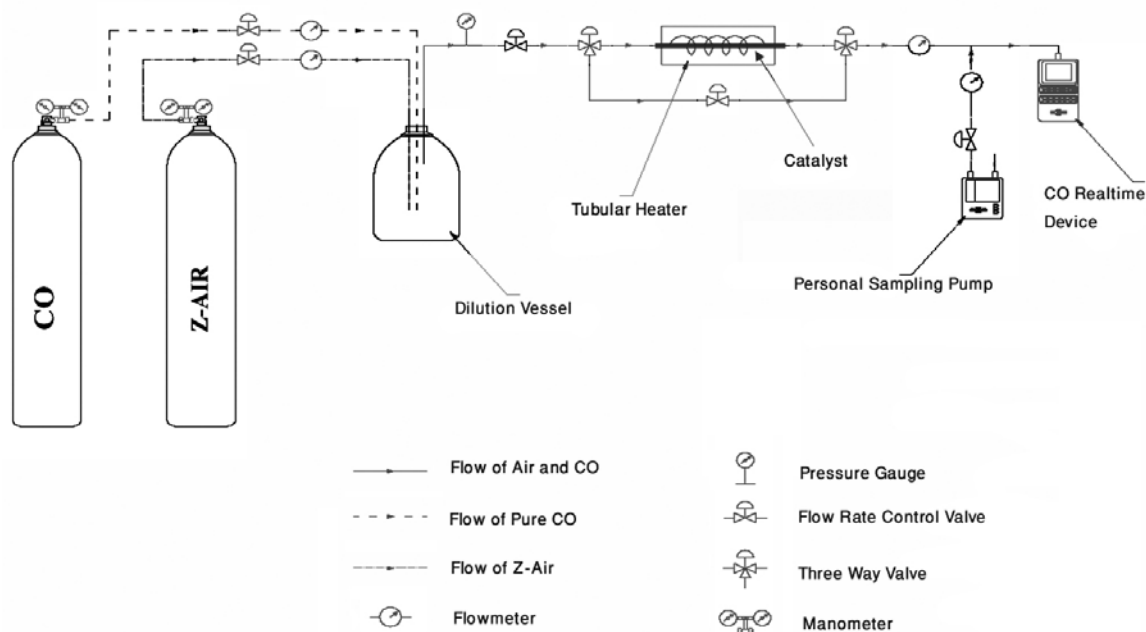


Fig. 1: Schematic diagram of flow reaction system

## RESULTS

Elemental analysis of $NH_4$-Y zeolite substrate, which was obtained by mean of XRF technique, is presented in Table 1. From these data, it can be concluded that the Si/Al ratio of the utilized zeolite support was about 3.

Table 1: The elemental analysis of $NH_4$-Y type zeolite by means of XRF

| Component | $SiO_2$ | $Al_2O_3$ | $Na_2O$ | MgO | Ti | $SO_3$ | LOI |
|---|---|---|---|---|---|---|---|
| Content (%) | 50.984 | 16.812 | 1.714 | 0.08 | 0.021 | 0.019 | 30.37 |

Results of CO catalytic conversion tests (CO to $CO_2$) over 0.5g of Au/Na-Y catalyst at 20°C and atmospheric pressure for 4h are presented in Fig.

2. It was found that after 170min of reaction the conversion was reached to 100% and maintained at 100% conversion for at least 4h.

Under the condition of 400°C and 24h, which is the thermal stabilization process, the CO conversion reaction was complete.

Fig. 3 shows the experimental results of CO conversion over Au/Na-Y catalyst in different temperatures after thermal stabilization of the catalyst at 400°C and 24h. It was found that in comparison to the fresh used catalyst at 20°C, conversion reached upto 65% and hen decreased to 35%. Based on the results in this test, the complete conversion was achieved at 65°C, while

in the case of fresh catalysts; the complete conversion was achieved at 20°C.

Results of elemental analysis of gold loaded catalysts by means of EDAX technique, which are determined before and after thermal stabilization tests (Fig. 4 and Fig. 5, respectively)

resulted 3.89wt% and 1.76wt% of Au, respectively. It was found that the catalyst contain spectra of AuM and AuL in structures. The Au content of the catalyst decreased after thermal stabilization test. Although the results determined that catalyst contain of Na was 2.39wt%.
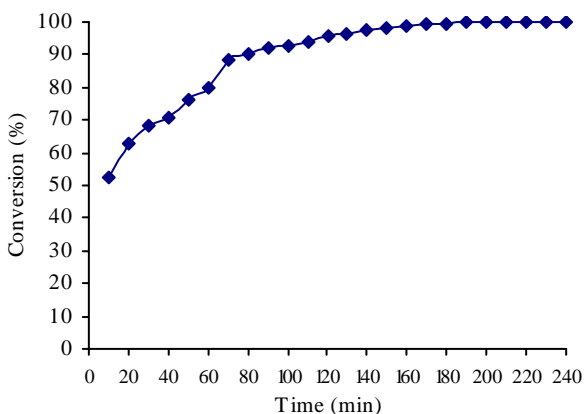
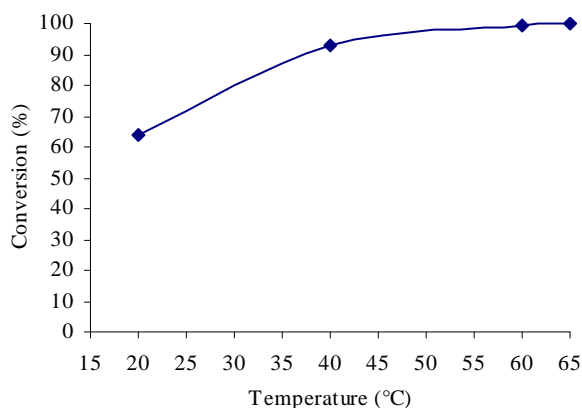Fig. 2: CO conversion vs reaction time over AU/Na-Y at 20°C

Fig. 3: CO conversion vs temperature over AU/Na-Y after stability test at 400°C and 24h
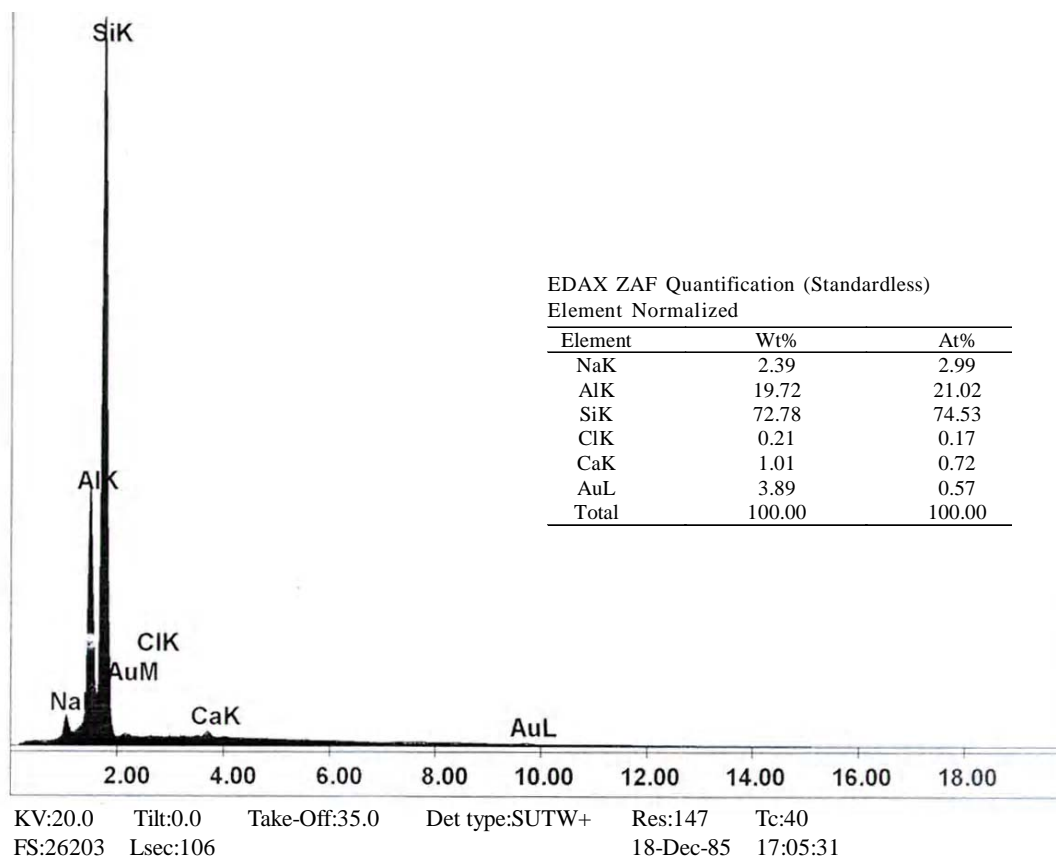
EDAX ZAF Quantification (Standardless)
Element Normalized

| Element | Wt% | At% |
|---------|--------|--------|
| NaK | 2.39 | 2.99 |
| AlK | 19.72 | 21.02 |
| SiK | 72.78 | 74.53 |
| ClK | 0.21 | 0.17 |
| CaK | 1.01 | 0.72 |
| AuL | 3.89 | 0.57 |
| Total | 100.00 | 100.00 |

KV:20.0    Tilt:0.0    Take-Off:35.0    Det type:SUTW+    Res:147    Tc:40
FS:26203    Lsec:106                                      18-Dec-85    17:05:31

Fig. 4: Elemental analysis of Au/Na-Y catalyst by means of EDAX before thermal stabilization

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| Element | Wt% | At% |
|---|---|---|
| NaK | 2.52 | 3.09 |
| AlK | 19.45 | 20.28 |
| SiK | 76.05 | 76.20 |
| AuM | 1.76 | 0.25 |
| ClK | 0.22 | 0.17 |
| Total | 100.00 | 100.00 |

EDAX ZAF Quantification (Standardless)
Element Normalized

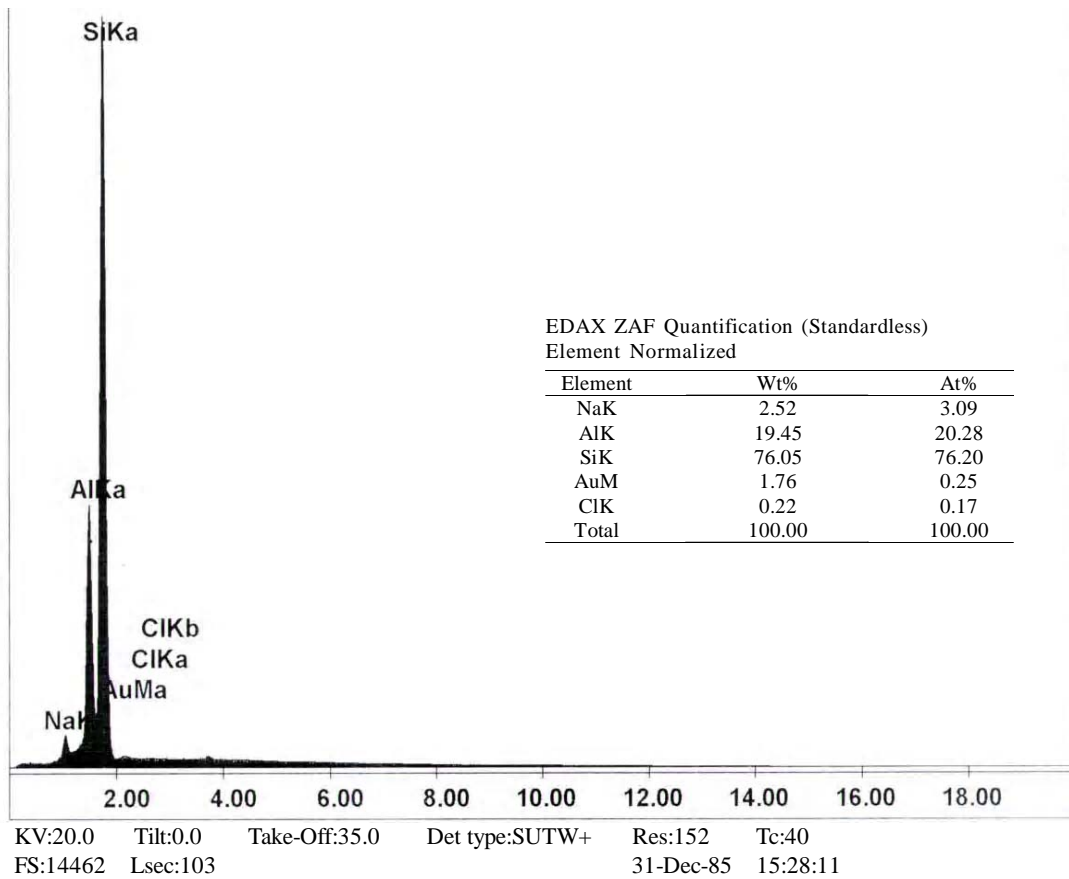KV:20.0  Tilt:0.0  Take-Off:35.0  Det type:SUTW+  Res:152  Tc:40
FS:14462  Lsec:103  31-Dec-85  15:28:11

Fig. 5: Elemental analysis of Au/Na-Y catalyst by mean of EDAX after thermal stabilization

Figs. 6 and 7 show the results of FT-IR from Au/Na-Y catalyst before and after thermal stabilization test (400°C, 24h) respectively. The spectra showed no difference between structures.

The concentration of gold in the solution after filtering was 196 ppm that by ICP-AE. This result suggested that 61.25% of gold as gold nanoparticles were loaded on the Na-Y zeolite.
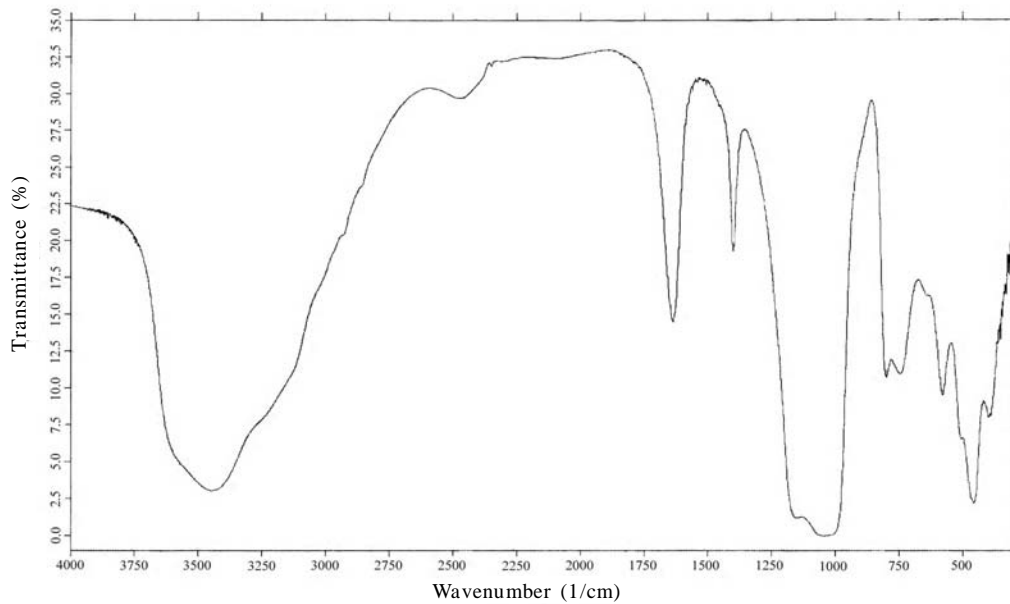
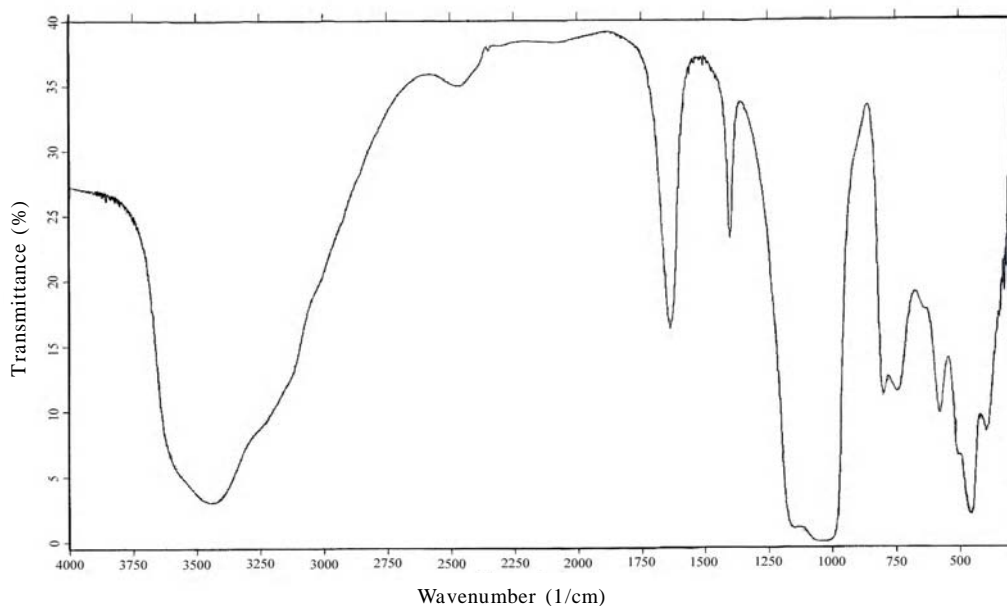Fig. 6: FT-IR spectrum of Au/Na-Y catalyst before thermal stabilization process

Fig. 7: FT-IR spectrum of Au/Na-Y catalyst after thermal stabilization process (400C, 24h)

## DISCUSSION

Zeolites are crystalline aluminosilicates that have relatively rigid threedimensional structures formed by TO4 tetrahedra (T=Si and Al). Each T-atom is connected by oxygen to four other T-atoms to create well-defined pores and channels (Krista *et al.*, 2005). Zeolites provide an appropriate housing media for stabilizing high dispersion metallic phase in nanometer size regime. Y-type zeolite from FAU group has three kinds of spaces within the crystal structure; a) the supercage with a pore opening of 7.4A° (0.74nm) and an inner space-diameter of 12A°; b) the sodalite cage (or b-cage) with a pore opening of 2.6A° and an inner diameter of 6.6A°; and c) the hexagonal prism with a smaller opening than that of sodalite cage (Chen *et al.*, 2005).

Generally, gold nanoparticles locate in the supercages and sodalite cages and on the exterior surface of Y-type zeolite. If the gold nanoparticles are located in the sodalite cage, due to the kinetic diameter of CO molecule, which is 0.37nm (larger than the window size of sodalite cage), are not available for as catalyst site to promote CO oxidation reaction.

Due to the degree of freedom on the external surface of the catalyst support, which is much larger than that in the supercage, the particle size of gold nano clusters deposited on the exterior should be much bigger than that in the supercage.

This implies that such particles have much less effective surface to facilitate catalyitcal reactions. Furthermore, gold nanoparticles on the external surface have poor stability due to probable migration, tending to grow to larger gold particles and finally the most important reason is the very weak bonding energy of gold and Si atoms (Chiang *et al.*, 2006), this confirms by results of EDAX, where the Au content(wt%) of catalyst decreases from 3.89% in fresh catalyst to 1.76 after thermal stabilization process (400°C and 24h).Therefore this causes decrease the activity (at 20°C) over fresh catalyst and thermally stabilized catalyst from 100% to 65% respectively.

Gold nanoparticles in the super cage have the mean diameters of <2nm (Lin and Wan, 2003) and may be one of the possible reasons that its catalytic activity was better that of gold nanoparticle on the exterior surface. As well as the gold nanoparticles confined in supercages are of the optimum size for catalysis of CO oxidation after high-temperature thermal stability process. The problem of excessive sintering and migration and growing of gold nanoparticles is overcome by confining them in nanopores. Therefore this causes thermal stability of gold nanoparticle and increasing of catalyst activity after thermal stabilization.

From the gold solution chemistry, it was found that

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$AuCl_2(OH)_2^-$ and $AuCl(OH)_3^-$ were the predominant gold complexes in the pH range of 6–7 at a transient state (Lin *et al.*, 2002). Therefore, it was inevitable to possess some chloride ions over these gold catalysts. The decrease of initial activity of Au/Y at 20°C may be from that its surface was covered with some chloride ions. Therefore, it took about 170min of initiation time to remove these surface chlorides. FTIR spectra before and after a 24h and 400°C thermal stabilization process, which are shown no changes during thermal stability process are presented in Fig. 5 and Fig. 6. Thus, it is suggested that during the thermal stability process of catalyst, the zeolite structure remains unchanged.

## AKNOWLEDGEMENTS

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