Catal Lett (2009) 128:57–63
DOI 10.1007/s10562-008-9724-x

Gold-Nano Particles Supported on Na-Y and H-Y Types Zeolites: Activity and Thermal Stability for CO Oxidation Reaction

S. Jafari · H. Asilian Mahabady · H. Kazemian

Received: 22 June 2008 / Accepted: 7 October 2008 / Published online: 7 November 2008

Abstract Gold nano particles (GNP) were deposited on Na-Y and H-Y zeolite substrates using chloroauric acid ($HAuCl_4$) solution. The synthesized catalysts were then characterized and the catalytic activity toward CO oxidation reaction was investigated using a tubular fix bed micro reactor under atmospheric pressure. It was found that CO conversion of 100% and 5% can be achieved at 20 °C on Au/Na-Y and Au/H-Y fresh catalysts, respectively. Thermal stability of catalysts was also investigated by treating the catalysts at 400 °C for 4 h. After thermal stability test, activity tests of the catalysts at 20 °C were shown that CO conversion of Au/Na-Y catalyst was decreased to 65% whereas the activity of the Au/H-Y at 20 °C was increased up to 15%. Characterization tests were revealed that the structures of the zeolitic supports were remained unchanged after thermal pretreatment.

Keywords Gold nano particle (GNP) · HY · NaY · CO oxidation · Catalyst · Thermal stabilization

1 Introduction

Gold did not attract much attention in heterogeneous catalysis and employed industrially because of its chemical inertness, resulting from an inability to chemisorb molecules like di-oxygen and di-hydrogen at ambient temperature. To the inertness of gold is added the absence of techniques for the dispersion of the metal comparable to those which exist for other metals traditionally used for heterogeneous catalysis and the difficulty for obtaining highly dispersed samples [1].

The application of gold catalysts to the oxidation of carbon monoxide has been studied extensively, most notably by Haruta et al. [2].

One of the significant features of gold-based catalysts is the low temperature oxidation of carbon monoxide, where the catalysts display activity at temperatures as low as −70 °C [3]. There are many factors affecting catalytic activity of gold nano particles (GNP); e.g., the size of gold nanoparticles, preparation methods, and pretreatment conditions [4].

The most important factor in the catalyst reactivity is the GNP size, which is 3 nm as an optimum size for CO oxidation reaction. Various methods have been developed in order to control the GNP size [4].

The nature of catalyst support is one of the critical parameters, which determines the catalytic activity [5]. So far, different kinds of materials have been tested as supports, e.g., active supports, such as TiO_2 and Fe_2O_3, which can be easily reduced and passive(inert) supports such as $Mg(OH)_2$, Al_2O_3, silica, mesoporous materials [4, 6], activated carbon fibers [7], and zeolites [8–10].

The GNP is an active catalyst even without any high temperature pretreatments (activation). For moderately reducible support such as TiO_2 or Al_2O_3, hydrogen reduction at a moderately high temperature is effective. For example, the temperatures of hydrogen reduction are 373 and 473 K for Au/TiO_2 and Au/Al_2O_3, respectively [4], whereas for inert supports such as activated carbon, high-temperature reduction in H_2 (e.g., 673–773 K) is necessary to activate the catalyst [7].

S. Jafari · H. Asilian Mahabady
Department of Occupational and Environmental Health,
Medical Faculty, Tarbiat Modares University, Tehran, Iran

H. Kazemian (✉)
R&D Lab. of SPAG Co., Technology Incubation Center, Sci &
Technol. Park of Tehran University (UTSTP), Tehran, Iran
e-mail: hosseinkazemian@gmail.com

So far, different types of zeolites were tested as the supports for GNP catalysts. Some of the advantages of zeolite are related to its porous and crystalline structure, which causes its high surface area, high cation exchange capacity as well as the regular nanosized cages and cavities, which can be act as confinement spaces to stabilize the GNP [8]. In this concern so far, several zeolite based GNP catalysts have been reported for NO reduction and CO oxidation reactions [11]. In a research, a modified method for preparation of GNP on Y-type zeolite has been developed. The resulted catalyst possessed higher activity and stability toward CO oxidation reaction in comparison to those catalysts without any surface pretreatment. Effects of the preparation conditions (i.e., chloroauric acid concentration, pH of gold solution, solution temperature, and mixing time) of GNP on the Y-type zeolite (Au/Y) support for CO oxidation have been also investigated. The results revealed that Au/Y catalysts prepared from a gold solution on a surface modified Y-type zeolite with an initial gold concentration of 1.46×10^{-3} M, solution pH of 6, reaction temperature of 80 °C, and mixing time of 1 h, would be the optimized active and effective catalyst for CO oxidation [8]. Researchers were also synthesized GNP catalysts on different zeolite supports (Y, β, and mordenite) using pH-adjusted chloroauric acid solution. The results revealed that the gold loading on the zeolitic substrates was strongly related to the aluminum content; it was also affected by the structure of the used zeolite [12].

The effect of different synthesis parameters on the activity and stability of GNP supported on the zeolitic supports such as preparation conditions (i.e., gold solution concentration, pH of the solution, temperature, mixing time, etc.), structures and nature of cationic sites of the zeolites, and modification of surface acidity have been studied systematically in the literatures [8, 11, 12].

This paper intends to report synthesize and characterization GNP supported on Na-Y and H-Y type zeolites by mean of deposition-precipitation. The catalytic activities of “as synthesized catalysts” were also studied at different temperature in a fixed bed micro reactor. The effect of thermal stabilization process (thermal pretreatment) on the catalyst activity was also investigated.

2 Materials and Methods

2.1 Materials

In this research, NH_4-Y zeolite (Sigma-Aldrich) was used and converted to H-Y and then to Na-Y forms to use as GNP substrates. To obtain H-Y zeolite, the NH_4-Y was calcined at 550 °C for 4 h; by evolving NH_3 molecules; H-Y will be formed.

Ion exchange technique was used to modify the produced H-Y into Na-Y type zeolite. To do this, the obtained H-Y zeolite was contacted with a 1 N solution of $NaNO_3$ for 48 h. Solution pH was adjusted to 6 using 1 N sodium hydroxide solution. After ion exchange, the resulted sample (Na-Y) was filtered, washed with excess amounts of deionized water and dried at 60 °C for 4 h.

Deposition-precipitation technique was used to load GNP on the substrates. Chloroauric acid, which was used as gold precursor in all of the experiments, is produced by dissolving gold metal (plate; 99.98%) into hot aqua regia solution, the solution was heated to evaporate all acids, the remained precipitate is chloroauric acid. Gold solution (0.032 wt%) was prepared by dissolving of chloroauric acid in distilled water.

To prepare the GNP catalysts, GNP promoter was loaded on zeolite supports by adding 1 g of zeolites (Na-Y or H-Y) to a 125 mL portion of chloroauric acid solution (0.032 wt%). The pH of the solution was pre-adjusted to 6 by NaOH solution. The mixture was shaked at 80 °C for 1 h. The resulting catalysts revealed that the reaction time and temperature is suitable to form the GNP on zeolites.

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

2.2 Materials Characterization

Elemental composition of the used NH_4-Y type zeolite was determined by mean of X-ray fluorescence (XRF; Oxford-ED2000). Energy dispersive analysis by X-rays (EDAX) as a result of scanning electron microscopy (SEM, Philips, XL30) tests were used to measure the elemental content of the synthesized Au/Na-Y catalysts. The Au content of chloroauric acid in the solutions before and after Au deposition process was determined using inductively coupled plasma-atomic emission spectrometer (ICP-AES; Varian, Liberty 150 AX Turbo). The structural frameworks of the zeolites were confirmed by mean of Fourier transform infrared spectroscopy (FTIR; ATI Mattson spectrometer).

2.3 Catalysts Performance Tests

In order to evaluate the catalytic activities of the prepared catalysts in various experimental conditions, carbon monoxide conversion experiments were carried out in a quartz tube micro reactor under atmospheric pressure. To do this, a stream of 0.155 mL/min of carbon monoxide and 31 mL/min of dried air were mixed and used as the reactor feed. A real time gas analyzer device (BABUC/A) equipped to a carbon monoxide detector was used to measure carbon monoxide concentration at the feed and products gas streams. The effect of reactor temperatures on the catalysts performances were examined at various temperature ranging from 20 to 400 °C. Thermal pretreatment tests for evaluation of the catalysts thermal stability was performed at 400 °C for 24 h.

Several parameters were tested to investigate the optimized condition for the catalysts performance. In this concern catalyst activity (conversion as a function of temperature), catalyst durability (conversion as a function of time at constant temperature) as well as catalyst stability (conversion as a function of time and temperature) were investigated.

3 Results

Chemical composition of NH_4-Y zeolite as the parent substrate and “as synthesized” catalysts (Au/Na-Y, and Au/H-Y) are presented in Table 1.

Table 1 Chemical composition (% w/w) of NH_4-Y, Au/Na-Y, and Au/H-Y samples

Component	SiO_2	Al_2O_3	Na_2O	SiO_2/Al_2O_3	Au
NH_4-Y	72.82	24.00	2.44	3.03	–
Au/Na-Y	72.78	19.72	2.39	3.69	3.89
Au/H-Y	73.14	19.28	1.61	3.79	5.77

These results reveal that by modifying the support to H and Na forms and doping the GNP promoters, the SiO_2/Al_2O_3 ratio of the zeolite support (3.03) was increased to 3.69 and 3.79 for Au/Na-Y and Au/H-Y, respectively. Usually, increasing the Si/Al ratio will cause the higher stabilities as well as the stronger acidities of the aluminosilicate materials. GNP loading percentages of the prepared catalysts were 3.69 and 5.77 for Au/Na-Y and Au/H-Y, respectively.

FT-IR spectrum of the sample was used to evaluate structural stability of the catalysts by modification to Na form and converting to GNP loaded catalyst before and after thermal stability test. FT-IR spectra of Au/Na-Y catalyst before and after thermal stabilization test are illustrated in Figs. 1, 2. IR data of a reference Na-Y zeolite is presented in Table 2 [13], in which the absorption band of 563–613 cm^{-1} is the representative band related to double six rings, which is a key structural feature of FAU type (Na-Y zeolite) framework. By comparison of obtained data from the spectra with the reference data, it can be concluded that Na-Y structure remains unchanged during modification and GNP impregnation processes. FT-IR spectra of the Au/H-Y catalyst before and after thermal stabilization treatment were shown the same results.

Results of the CO catalytic conversion tests over Au/Na-Y and Au/H-Y catalysts, which were carried out at temperature of 20 °C for a time period of 4 h are illustrated in Fig. 3.

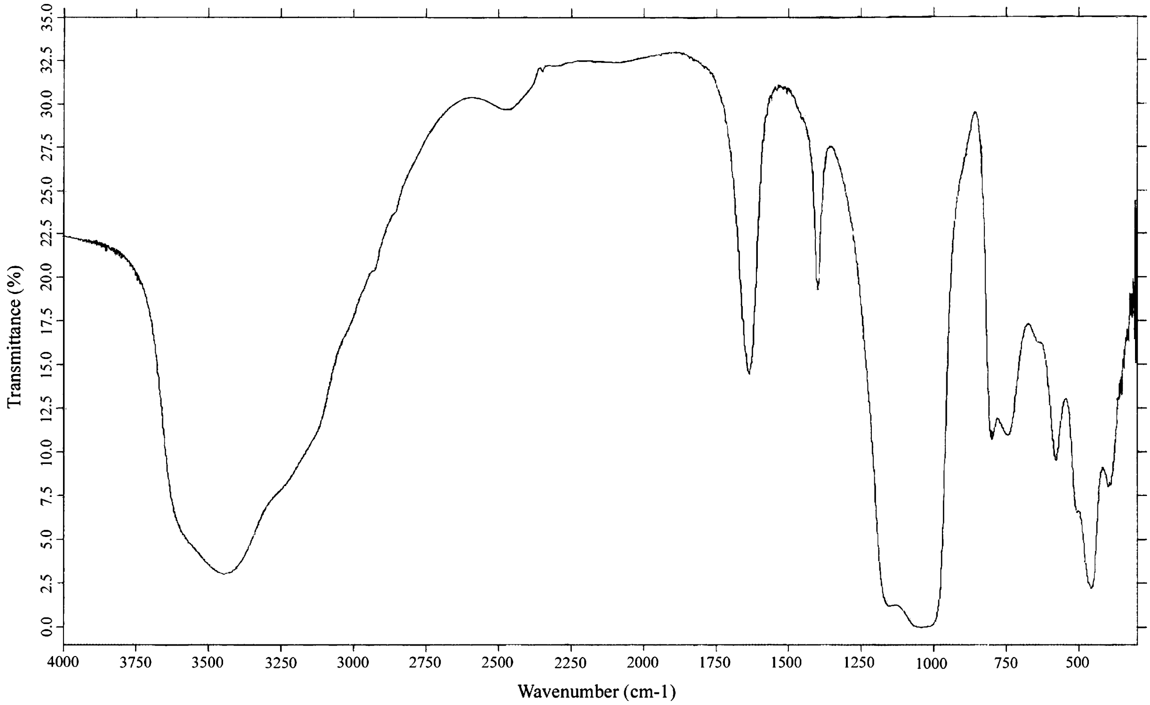


Fig. 1 FT-IR spectrum of Au/Na-Y catalyst before thermal pretreatment

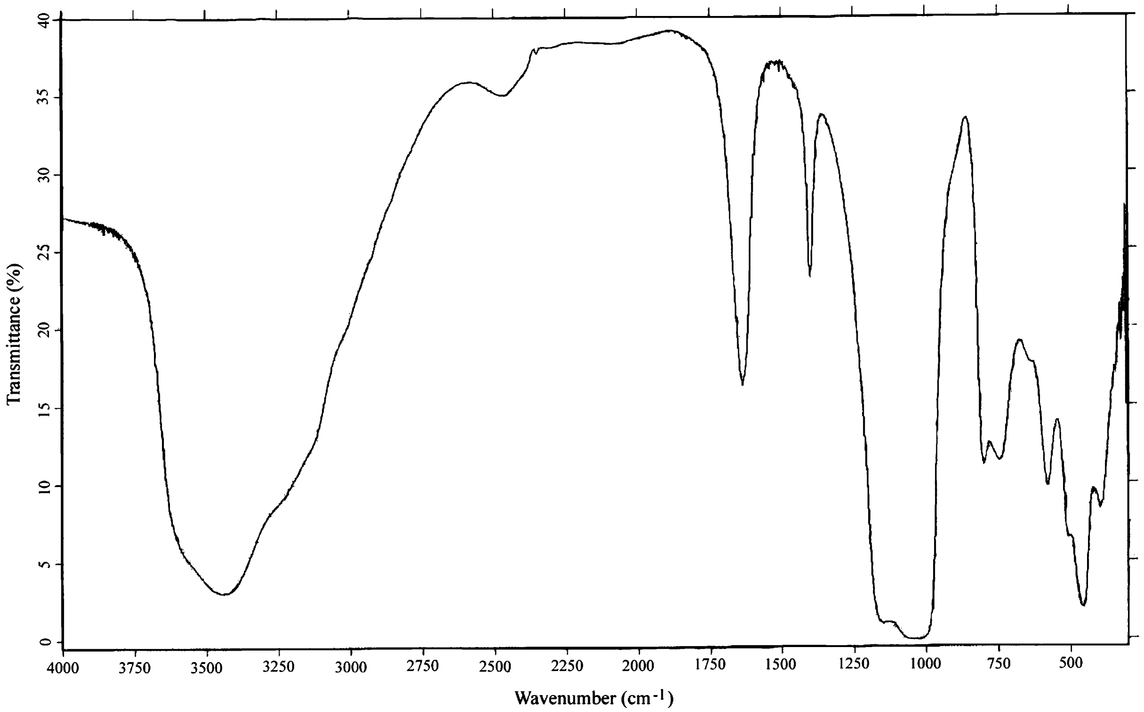


Fig. 2 FT-IR spectrum of Au/Na-Y catalyst after thermal pretreatment (400 °C, 24 h)

It was found that for Au/Na-Y catalyst, the conversion was reached up to 100% after 170 min of reaction and remained in this steady condition at least for more 70 min (total test time was 4 h), whereas, the CO conversion on the Au/H-Y catalyst was not more than 5% at the same conditions and during the entire test time. Since the Au loading percentage of the Au/H-Y catalysts (5.77%) was higher than of Au/Na-Y (3.89%), it can be concluded that the Au loading percentage is not the key parameter, which affects the catalytic performance of Au based catalysts, but GNP size is more important.

Effect of thermal pretreatment (thermal stability test) at higher temperatures were not investigated in previous works [e.g., 6, 11]. In this study, this effect was examined for the catalysts by heating at 400 °C for 24 h.

The effects of reaction temperatures on the CO conversion on the Au/H-Y catalyst before and after thermal pretreatment are illustrated in Fig. 4.

Table 2 IR data of a reference Na-Y type zeolite [13]

Wave numbers (cm^{-1})	Assignment
507–530	T-O bend
563–613	Double 6 ring
670–792	O-T-Osym stretching
748–837	O-T-Osym stretching
975–1,084	O-T-Oas stretching
1,057–1,210	O-T-Oas stretching

The temperatures in which 50% and 100% of CO conversions were happened over the catalyst before thermal stabilization process were 90 and 150 °C respectively, whereas these temperatures for the catalyst after thermal pretreatment were 80 and 140 °C respectively. These results reveal that the performance of Au/H-Y catalyst was increased remarkably.

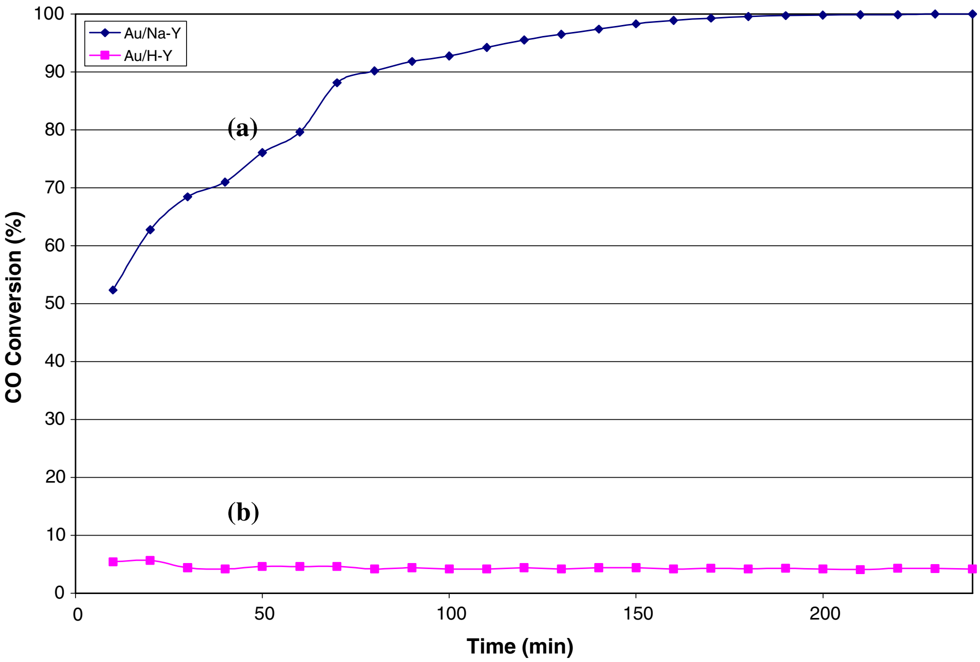
The effect of reactor temperature on the CO conversion for the thermal stabilized Au/Na-Y catalyst is illustrated in Fig. 5.

The results show that the CO conversion at 20 °C on the thermal stabilized Au/Na-Y was reached up to 65%, whereas in the case of untreated Au/Na-Y catalyst, at this temperature and after 170 min of reaction, the complete CO conversion was achieved (Fig. 3). Based on the results, the complete CO conversion on the thermal pretreated Au/Na-Y was achieved at 65 °C.

4 Discussions

The framework of Y-type zeolite (FAU zeolite group) consist of three different kinds of pores within the crystal structure: (a) the supercages with a pore opening of 7.4 Å (0.74 nm) and an inner space-diameter of 12 Å, (b) the sodalite cage (or β-cage) with a pore opening of 2.6 Å and an inner diameter of 6.6 Å, and (c) the hexagonal prism with a smaller opening than that of sodalite cage [12].

Fig. 3 The effect of reaction time on the CO conversion at 20 °C

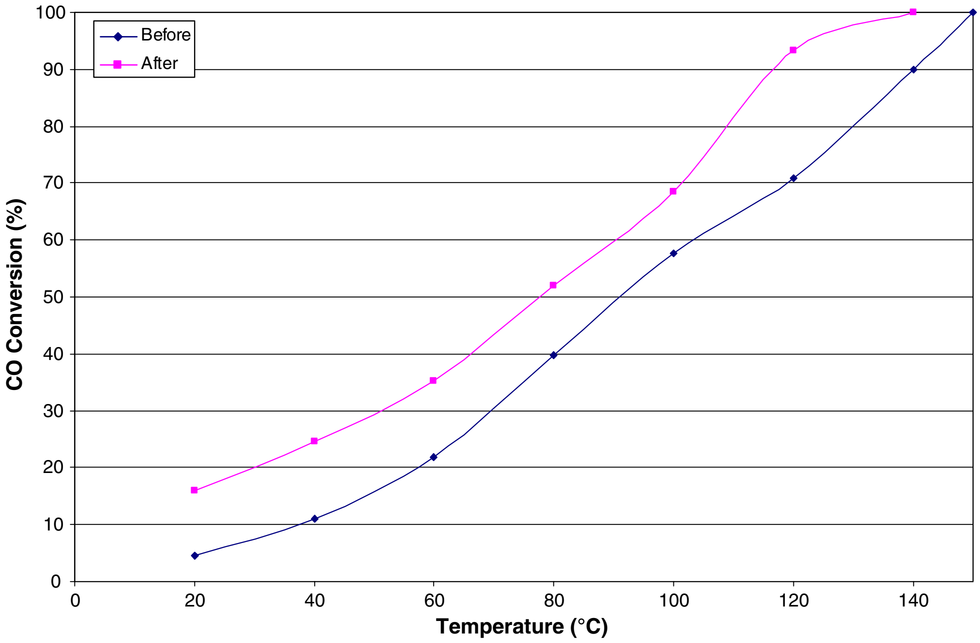


The surface charge of Y type zeolite is negative. This negative charge can prevent vigorous deposition of gold species with negative charges, such as $Au(OH)_{4-x}Cl_x^-$, on the surface of zeolites. Usually, there are more negative charges on the surface of Na-Y in comparison to the H-Y surface that is why the deposition of negative gold species on Na-Y should be less than those on H-Y [11]. The reason of different loading amount on the two substrates may be related to surface property of Na-Y and H-Y zeolite.

Generally, GNP will be deposited in different sites of Y-type zeolite, namely inside the supercages, inside the sodalite cages and on the exterior surface of the zeolite structure. If the GNP locates inside the sodalite cages, they are not accessible to CO molecules due to the smaller size of sodalite cages opening windows (2.6 Å) in comparison to the kinetic diameter of CO molecule(3.7 Å) [12].

The average diameter of GNP in the super cages is about 2 nm [8], which are in the range of GNP optimum size for CO oxidation reaction at low temperatures [4]. Higher CO conversion catalytic activity of untreated Au/Na-Y can be interpreted as a result of formation of accessible GNP in

Fig. 4 The effect of reactor temperatures on the CO conversion over the Au/H-Y catalyst before and after thermal pretreatment at 400 °C



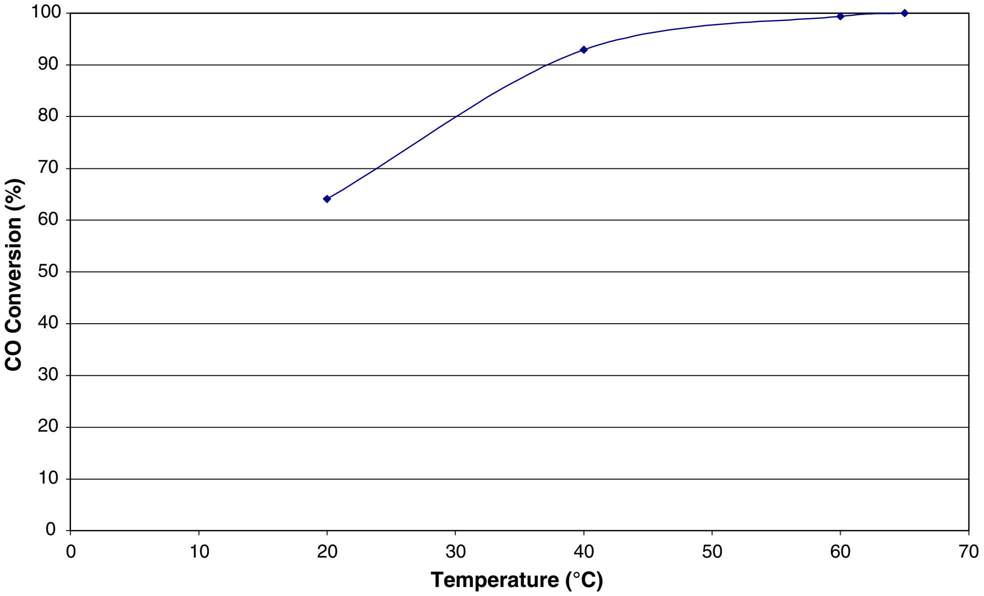


Fig. 5 The effect of reactor temperatures on the CO conversion over the Au/Na-Y catalyst after thermal pretreatment

the range of 2–3 nm, inside the supercages as well as on the external surface of zeolite particles.

Based on the gold solution chemistry, $\mathrm{AuCl_2(OH)_2^-}$ and $\mathrm{AuCl(OH)_3^-}$ species are the predominant gold complexes in the pH range of 6–7 at a transient state [11]. Therefore, it is possible to have some chloride ions along with GNP. Lower CO conversion at the initial stages of reaction on the Au/Na-Y catalyst at 20 °C can be related to existence of chloride ions. The initiation of 170 min is necessary to remove the surface chlorides.

Due to the higher degree of freedom on the external surface of the catalyst support, in comparison to the supercages, the size of GNP deposited on the exterior should be larger than that in the supercages. This implies that such particles are much less active in the CO oxidation reaction. Furthermore, GNPs on the external surface are less stable, because of a very weak bonding energy between Au and Si atoms. That is why, Au atoms on the surface tend to aggregate and grow to larger GNP [4]. The problem of aggregation of GNP can be overcome by confinement in nanopores spaces (e.g., zeolite supercages).

One of the reasons, which can be suggested for the observed partial deactivation of thermally treated Au/Na-Y can be related to migration, aggregation, and growing of none confined GNP in the exterior surface of zeolite substrate.

The lower conversion performance of thermally untreated Au/H-Y catalyst at 20 °C, which was about 5%, in comparison to complete conversion performance of Au/Na-Y, while the GNP loading of Au/H-Y was higher (5.77% vs. 3.89%), can be interpreted as a result of deposition of larger GNPs. Due to the stronger negative charge of the H-Y in comparison to Na-Y, the deposited GNPs sizes on the external surface of Au/H-Y is larger. Slightly higher Co conversion performance of Au/H-Y after thermal pretreatment can be attributed to formation of more GNPs confined inside the zeolite supercages by migration at higher temperature. Removal of chlorides of deposited GNPs on exterior surface of the substrate can be suggested as another reason for further activation of the catalyst after thermal stabilization process.

5 Conclusions

Two GNP based catalysts were successfully synthesized on the H and Na forms of NH_4-Y type zeolite as the substrates; Au/H-Y and Au/Na-Y, by using chloroauric acid ($HAuCl_4$) solution as Au precursor, and then characterized.

The synthesized Au/Na-Y catalyst was shown higher activity for CO oxidation at lower temperatures (e.g., 20 °C) in comparison to the Au/H-Y catalyst. An induction period of about 170 min was needed for the Au/Na-Y catalyst to become fully activated for CO oxidation at 20 °C, probably due to the chloride ion removal from the catalyst active sites.

Thermal pretreatment (thermal stability process) of the catalysts at 400 °C for 24 h will enhance the catalytic performance of the Au/H-Y catalyst whereas its diverse effect on the Au/Na-Y is obvious. Structural investigations of the thermally pretreated catalysts were implied that the crystalline structures of zeolitic substrates remained unchanged.

Acknowledgments The authors would like to acknowledge H. Ghasemi Mobtaker, A. Malekinejad and S.M. R. Pakzad for their fruitful helps. Iranian Department of Environment supports is also acknowledged.

References

1. Riahi G, Guillemot D, Polisset-Thfoin M, Khodadadi AA, Fraissard J (2002) Catal Today 72:115
2. Haruta M, Tsubota S, Kobayashi T, Kageyama H, Genet MJ, Delmon B (1993) J Catal 144:175
3. Mellor JR, Palazov AN, Grigorova BS, Greyling JF, Reddy K, Letsoalo MP, Marsh JH (2002) Catal Today 72:145
4. Chiang CW, Wang A, Mou CY (2006) Catal Today 117:220
5. Pillai UR, Deevi S (2004) New Technol Res 23:8
6. Bandyopadhyay M, Korsak O, Van den Berg MWE, Grünert W, Birkner A, Li W, Schüth F, Gies H (2006) Microporous Mesoporous Mater 89:158
7. Bulushev DA, Yuranov I, Suvorova EI, Buffat PA, Kiwi-Minsker L (2004) J Catal 224:8
8. Lin JN, Wan BZ (2003) Appl Catal B 41:83
9. Kuge K, Calzaferri G (2003) Gold-loaded zeolite A. Microporous Mesoporous Mater 66:15–20
10. Derouanea EG, Schmidtb I, Lachasa H, Christensen CJH (2004) Catal Lett 95:13
11. Lin JN, Chen JH, Hsiao CY, Kang YM, Wan BZ (2002) Appl Catal B 36:19
12. Chen JH, Lin JN, Kang YM, Yu WY, Kuo CN, Wan BZ (2005) Appl Catal A Gen 291:162
13. Lohse U, Pitsch I, Shreier E, Parlitz B, Schnabel KH (1995) Appl Catal A Gen 129:189