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ORIGINAL ARTICLES

Silica-Supported Au–Ni Catalysts for the Dehydrogenation of Propane

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Abstract Inspired by previous studies on model systems, a series of silica-supported Au–Ni catalysts were prepared and tested for the conversion of propane in the presence of hydrogen. The Au–Ni/SiO_2 catalysts were prepared by successive impregnation, i.e. Ni was deposited first followed by Au. TEM/EDX results confirmed the presence of bimetallic Au–Ni nanoparticles. The dehydrogenation of propane to propylene was observed on the Au–Ni bimetallic catalysts, whereas only hydrogenolysis products were observed on the monometallic Ni catalyst. The selectivity to propylene was found to increase monotonically with the Au loading. The results are in good agreement with the results on model catalysts.

Keywords Bimetallic catalyst · Nickel · Gold · Dehydrogenation of propane · Propylene

1 Introduction

Gold–nickel bimetallic catalysts have shown enhanced catalytic properties for a number of reactions [1–9], such as steaming reforming of hydrocarbons [1, 2], the water–gas shift reaction [3], and hydrodechlorination [4, 5]. A $MgAl_2O_4$-supported Au–Ni catalyst maintained almost constant activity for the steam reforming of *n*-butane, whereas a monometallic Ni catalyst deactivated rapidly [1]. For the water–gas shift reaction, a Au–Ni/Fe_2O_3 catalyst was found more active than Au/Fe_2O_3 [3]. Furthermore, it was reported that the addition of Au to silica-supported Ni catalysts significantly enhanced the activity of 2,4-dichlorophenol hydrodechlorination [4, 5]. The positive effects of the Au–Ni bimetallic system reported in the literature seem to have been limited to higher catalytic activity or better catalyst stability. The effects of the addition of Au to Ni catalysts on catalytic selectivity have not been explored to a great extent.

Recently we prepared Au–Ni nanoparticles on planar silica thin films and the conversion of propane in the presence of H_2 was used as a probe reaction to study the selectivity effects of these model catalysts [10]. The dehydrogenation of propane to propylene was observed on the Au–Ni bimetallic catalysts, whereas only hydrogenolysis products (methane and ethane) were observed on monometallic Ni catalysts. Infrared reflection absorption spectroscopic (IRAS) data showed that single-atom Ni sites (isolated by Au atoms) appear and become dominant on the surface with the addition of Au to Ni. A correlation was found between the concentration of isolated Ni sites and the catalytic activity for propane dehydrogenation.

Inspired by the model study, we prepared real Au–Ni/SiO_2 catalysts using conventional impregnation methods and a high surface-area silica gel. Similar effects on the catalytic selectivities were observed for the conversion of propane, and the results are presented in this letter.

2 Experimental

The 2 wt% Ni/SiO_2 catalyst was prepared by incipient wetness impregnation of silica with an aqueous solution of nickel(II) nitrate hexahydrate (99.9985 %, Alfa Aesar). The silica support (Davison, Grade 952) was calcined at 873 K

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before impregnation. After impregnation, the sample was dried at 353 K and calcined at 573 K in air for 1 h. The Au–Ni/SiO$_2$ catalysts with nominal Au loadings from 0.2 to 4 wt% were prepared by incipient wetness impregnation of the calcined Ni/SiO$_2$ catalyst with aqueous solutions of hydrogen tetrachloroaurate(III) trihydrate (99.99 %, Alfa Aesar). The impregnated samples were dried at 353 K, and then washed with NH$_4$OH solution and distilled water to remove chloride ions. The resulting samples were dried to 373 K in air. The actual concentrations of Ni and Au were determined by neutron activation analysis.

Catalytic reactions were carried out at 573 K and 1 bar in a glass plug-flow reactor (8 mm i.d.). Two milligrams of the as-prepared catalysts diluted with 100 mg of calcined SiO$_2$ were used for each experiment. The catalyst was activated in a flow of hydrogen (50 mL min^{-1}) from RT to 773 K at 2 K/min and held at this temperature for 2 h. A C$_3$H$_8$/H$_2$/N$_2$ mixture and UHP N$_2$ were used so that the total flow rate was 50 mL min^{-1} and the partial pressure of C$_3$H$_8$ and H$_2$ during reaction was 0.4 and 2 Torr, respectively. The products were analyzed with a HP 5890 gas chromatograph equipped with a flame ionization detector and a HayeSep DB packed column. The selectivity was defined as the moles of carbon in each product normalized by the total moles of carbon of the products, so that the total selectivity of all carbon containing products equals 100 %.

Transmission electron microscopy (TEM) images and energy dispersive X-ray (EDX) spectra were recorded on a field-emission TEM (FEI Tecnai G^2 F20 ST) equipped with an EDAX system. The samples for TEM/EDX analysis were first reduced and then passivated by flowing 1 % O$_2$ in N$_2$ at room temperature.

3 Results and Discussion

A typical TEM image from the passivated 2 % Au–2 % Ni/SiO$_2$ sample is shown in Fig. 1a, indicating that most of the metallic particles are in the range of 1–4 nm in diameter. The EDX spectrum (Fig. 1b) from a single nanoparticle shows that both Au and Ni are present in the particle. EDX analysis also showed that some of the nanoparticles are monometallic Au. Although Au and Ni do not form a bulk alloy at low temperatures due to the large miscibility gap, surface alloys of Au and Ni have been found to be stable in the first atomic layer [11]. The presence of bimetallic Au–Ni nanoparticles was also observed by Molenbroek et al. [12] on MgAl$_2$O$_4$-supported Au–Ni catalysts.

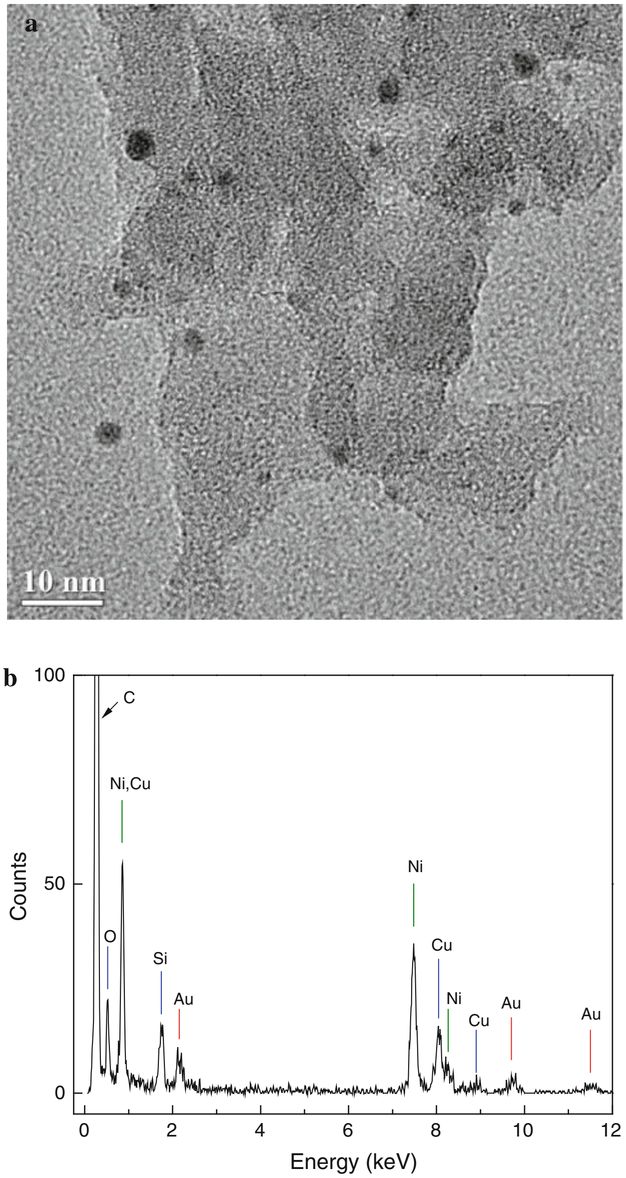

Fig. 1 **a** TEM image from the passivated 2 % Ni–2 % Au/SiO$_2$ sample and **b** EDX spectrum from one of the nanoparticles in (**a**). The Cu peaks are from the TEM grid

Catalytic reactions were carried out at 573 K with a 1:5 propane/hydrogen mixture diluted in nitrogen. On the monometallic 2 wt% Ni/SiO$_2$ catalyst, methane was formed predominantly with a selectivity of 99.9 %, and the only other product was ethane. On the bimetallic Au–Ni/SiO$_2$ catalysts, propylene formation was observed. Figure 2 shows the propane conversion and the selectivity to propylene as a function of time on the 0.5 % Au– 2 % Ni catalyst. The conversion dropped significantly in the first 30 min of reaction and then became relatively stable. The propylene selectivity was 0.7 % after 5 min and increased considerably with time. After 2 h of reaction, the selectivity to propylene was almost 50 %. It is noteworthy that no propylene was observed on the Ni/SiO$_2$ catalyst even after 3 h of reaction under the same reaction conditions.

Other Au–Ni/SiO$_2$ catalysts followed similar trends in activity and selectivity, i.e., initial rapid deactivation and increasing propylene selectivity with time on stream.

However, the propylene selectivity was generally higher on those samples with higher Au loadings. For example, the initial selectivity to propylene was 0.3 % on the 0.2 wt% Au–Ni/SiO_2 and 19 % on the 4 wt% Au–Ni/SiO_2. After 30 min of reaction, the selectivities increased to 7.5 and 46 %, respectively. Figure 3 shows the selectivity to propylene as a function of Au loading from 0 to 4 wt%. The selectivities were measured after 5 and 30 min of reaction. Both curves show that the propylene selectivity increases monotonically with the Au loading.

The addition of Au to Ni catalysts also changed the distribution of hydrogenolysis products (methane and C_2 products) dramatically. Figure 4 shows the selectivities to methane and C_2 products measured after 30 min of reaction as a function of Au loading. The selectivity to methane dropped from 99.9 % on Ni/SiO_2 to 27 % on 4 % Au–Ni/SiO_2. Meanwhile, the selectivity to C_2 products (ethane and ethylene) increased from 0.1 to 27 %.

The propylene selectivity as a function of Au loading shown in Fig. 3 is in good agreement with our studies on model Au–Ni catalysts deposited on planar SiO_2 films [10]. IRAS data showed that, with the addition of Au to Ni, the number of contiguous Ni sites declines rapidly while isolated Ni sites (single Ni atoms isolated by Au atoms) form and become dominant on the surface. It has been generally accepted that the hydrogenolysis of light alkanes is a structure sensitive reaction and requires multiple adjacent surface atoms or ensembles to proceed [13–16]. It was derived from kinetic studies that the hydrogenolysis of C_2–C_4 alkanes requires ensembles of between 12 and 20 adjacent nickel atoms [17]. With Au replacing some Ni atoms on the surface, the number of ensembles with enough adjacent Ni atoms declines, so does the hydrogenolysis activity. The addition of more gold results in the appearance of isolated Ni atoms, which are active for dehydrogenation reactions but not for hydrogenolysis. As a result, propylene starts to form and its selectivity increases with Au loading, as shown in Fig. 3.

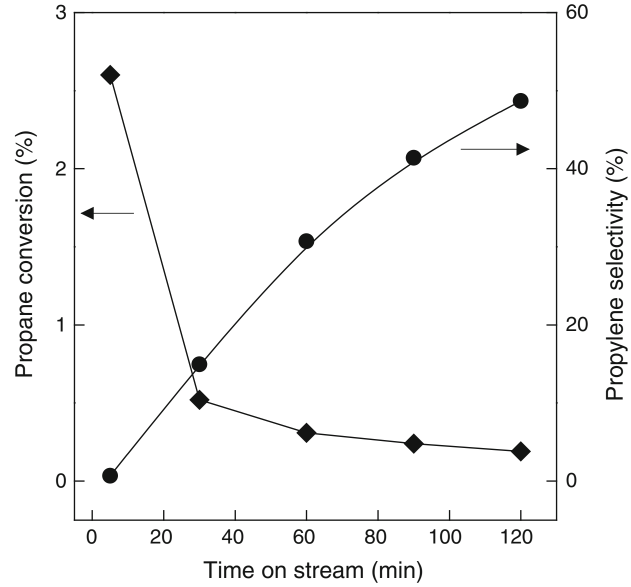

Fig. 2 Propane conversion and propylene selectivity as a function of time on 2 % Ni–0.5 % Au/SiO_2

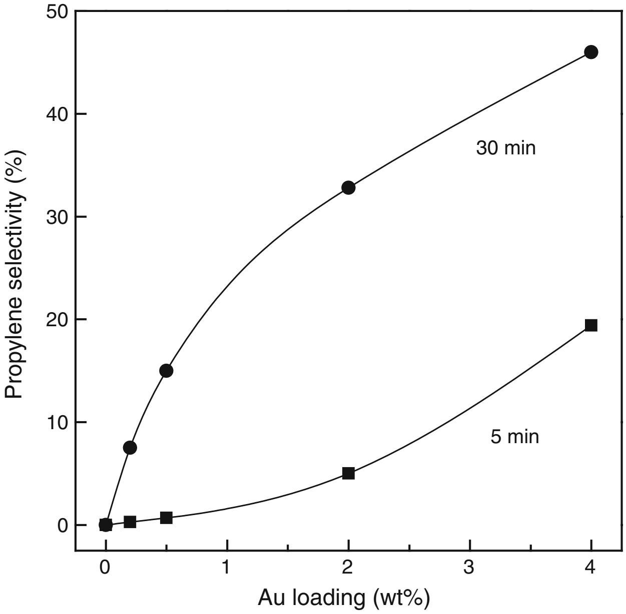

Fig. 3 Propylene selectivities measured after 5 and 30 min of reaction as a function of Au loading

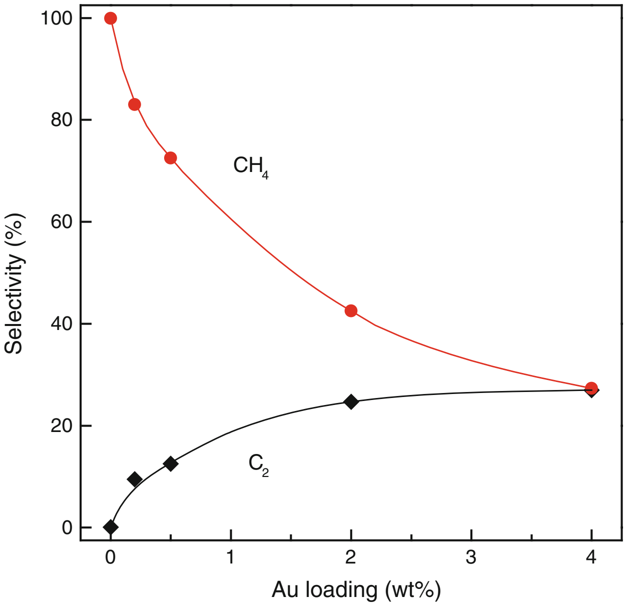

Fig. 4 Selectivity to CH_4 and C_2 products as a function of Au loading. The selectivities were measured after 30 min of reaction

As discussed earlier, Ni/$MgAl_2O_4$ was found to deactivate much faster than Au–Ni/$MgAl_2O_4$ for the steam reforming of *n*-butane [1]. Both DFT calculations and surface science studies predicted that the deactivation of monometallic Ni catalysts is caused by carbon deposition. This has been confirmed by the weight increase of the catalysts in thermogravimetric analysis [12]. The rapid deactivation in the first 30 min of reaction shown in Fig. 2 is probably due to carbon deposition on contiguous Ni sites. Isolated Ni sites are less prone to carbon deposition and contribute to the relative stable activity after the initial period. The rapid poisoning of contiguous Ni sites, which are active for hydrogenolysis, also explains the increase in propylene selectivity with time.

4 Conclusions

In the present work, we show that, by modifying the surface composition and structure of Ni catalysts with Au, the conversion of propane in the presence of hydrogen can be shifted from hydrogenolysis to dehydrogenation. The presence of bimetallic Au–Ni nanoparticles was confirmed by TEM-EDX analysis. The study was inspired by work on model systems and the results are in excellent agreement.

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