Activity of Au, Ni, and Au–Ni Catalysts in the Water-Gas Shift Reaction and Carbon Monoxide Oxidation


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Abstract—Au/Al2O3, NiOx/Al2O3, and (Au + NiOx)/Al2O3 composites have been prepared by ion exchange and impregnation. Their structural and electronic properties, including the size and shape of supported metal particles and the oxidation state and ligand environment of the Au and Ni atoms, have been investigated. The catalytic activity of Au/Al2O3, NiOx/Al2O3, and (Au + NiOx)/Al2O3 in the water-gas shift reaction and carbon monoxide oxidation is reported. At 300–450°C, the CO conversion over (Au + NiOx)/Al2O3 exceeds the sum of the CO conversions over the monometallic catalysts Au/Al2O3 and NiOx/Al2O3 by a factor of 2–3. An explanation is suggested for the nonadditive increase in the CO conversion over the Au–Ni catalysts.

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Deposition of two transition metals onto the surface of a support is a promising way of synthesizing efficient catalysts [1–14]. The catalytic activity of a bimetallic system is often the sum of the catalytic activities of its monometallic analogues. For example, the activity of the (Au + Pd)/SiO2 system in allylene isomerization is the sum of the activities of the Au/SiO2 and Pd/SiO2 catalysts [9]. Likewise, the activity of (Pt + Ni)/MCM-41 in benzene hydrogenation is the sum of the activities of the corresponding Pt- and Ni-based catalysts [10]. However, in some cases the activity of a bimetallic catalyst is not equal to the sum of the activities of its monometallic analogues. This effect is referred to as synergism. For instance, the activity of (Au + NiOx)/SiO2 in alkene isomerization is higher than the activity of Au/SiO2 and NiOx/SiO2 by a factor of 51 and 97, respectively [9]. The rate of 2,4-dichlorophenol hydrodechlorination over (Au + Ni)/Al2O3 is 9 times higher than the rate of the same reaction over a mixture of the Au/Al2O3 and Ni/Al2O3 catalysts [12]. The glycerol-to-syngas conversion over (Au + NiOx)/Al2O3, Au/Al2O3, and NiOx/Al2O3 is 57.6, 5.4, and 16.5%, respectively [13].

The above examples of synergism suggest that Au–Ni catalysts are possibly very efficient in heterogeneous catalytic reactions.

Here, we report the regularities of the catalytic action of M/Al2O3 systems (M = Au, NiOx, or Au + NiOx nanoparticles) in the water-gas shift reaction (CO + H2O → CO2 + H2) and carbon monoxide oxidation (2CO + O2 → 2CO2) and reveal those structural and electronic features of the catalysts which lead to the nonadditive increase in the CO conversion over the Au–Ni systems.

EXPERIMENTAL

Catalyst Preparation

The Au/Al2O3 catalyst was prepared by ion exchange using an alkaline HAuCl4 solution at pH 7.0 [13, 15]. The NiOx/Al2O3 catalysts were obtained by impregnating Al2O3 with an aqueous solution of Ni(NO3)2 [15]. For the synthesis of the bimetallic systems, the freshly prepared Au/Al2O3 catalyst was impregnated with the Ni(NO3)2 solution. The support was γ-alumina with a specific surface area of S_BET = 138 m²/g. Before use, the catalysts were calcined at 350°C in air for 3 h.

Chemical and Structural Analyses of the Catalysts

The weight percentage of Au and/or Ni in the catalysts was determined by atomic absorption spectrometry (AAS) on a Thermo iCE 3000 spectrometer (Thermo Fisher Scientific Inc., United States) via an earlier described procedure [15]. The relative error in the AAS measurements of metal concentrations in solution was ±1%.

Micrographs of the catalysts were obtained by transmission electron microscopy (TEM) on a JEOL JEM 2100F/UHR microscope (JEOL Ltd., Japan) with a resolving power of 0.2 nm. Size distribution curves for supported metal particles were constructed using microscopic data for 250–300 particles.
Energy-dispersive X-ray (EDX) analysis was carried out on a JED-2300 X-ray spectrometer (JEOL Ltd.).

The electronic state of Au in the catalysts was studied by X-ray absorption spectroscopy (XANES). The X-ray absorption spectra of Au (L$_3$ edge at 11991.9 eV) were recorded in the transmission mode at a synchrotron radiation center (HASYLAB, DESY, Hamburg) using a Si(111) dual-crystal monochromator at 77 K in order to reduce the effect of the Debye–Waller disorder factor. Prior to recording their spectra, the samples were pressed into pellets 13 mm in diameter. The sample weight was set so as to optimize the signal-to-noise ratio. The XANES spectra of standard compounds were recorded under the same conditions. Spectroscopic data were processed using the VIPER program [16].

**Water-Gas Shift Reaction**

A tubular quartz reactor containing 1 g of a catalyst was placed in a furnace and was heated there to the preset temperature. Thereafter, the reactor was fed with a 33% CO + 66% H$_2$O mixture at 1 atm and a gas hourly space velocity of 2170 h$^{-1}$. The mixture leaving the reactor was analyzed by GLC on a Kristallyuks 4000M chromatograph (Metakhrom, Russia) fitted with a flame-ionization detector and columns packed with the HaySep-Q phase (for CO$_2$ and H$_2$O quantification) and molecular sieve 5A (for H$_2$ and CO quantification). Catalytic activity was estimated in terms of CO conversion at a given temperature.

**Carbon Monoxide Oxidation**

A catalyst (0.1 g) was loaded into a tubular quartz reactor, and helium was passed through the reactor at a flow rate of 30 mL/min [17]. The reactor, placed in a furnace, was heated to the preset temperature. Thereafter, 1-mL pulses of a 2% CO + 1% O$_2$ + 97% He mixture were introduced into the reactor. The mixture leaving the reactor was analyzed on a Kristallyuks 4000M chromatograph fitted with a thermal-conductivity detector and a column packed with Porapak Q. Catalytic activity was estimated in terms of CO conversion at a given temperature.

**RESULTS AND DISCUSSION**

Some characteristics of the Au- and/or Ni-based catalysts with a metal content of 0.09 to 0.19 wt % are listed in the table. The nickel-based catalyst (sample 1) was grayish. The gold-based catalyst (sample 2) consisted of uniformly colored lilac granules. Its color was within the color spectrum of the gold-containing catalyst prepared by ion exchange [4, 6]. The catalysts containing both gold and nickel (samples 3–5) were violet.

**Electronic State of Supported Metal Particles**

The electronic state of the metals in the M/Al$_2$O$_3$ (M = Au, NiO$_x$, or Au + NiO$_x$) catalysts

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>[Au] wt %</th>
<th>[Ni] wt %</th>
<th>D$_{max}$ nm</th>
<th>D$_{max}^{*}$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.09</td>
<td>1.5–9</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0</td>
<td>1–9</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.01</td>
<td>3.0</td>
<td>6.5</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>0.03</td>
<td>1–15</td>
<td>3.5</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>0.09</td>
<td>4.0</td>
<td>4.3</td>
</tr>
</tbody>
</table>

$D$ is the linear particle size, $D_{max}$ is the position of the maximum in the particle size distribution histogram for the fresh catalyst, and $D_{max}^{*}$ is the position of the maximum in the particle size distribution histogram for the catalyst calcined at 500°C in air for 6 h.

**Fig. 1.** Au L$_3$-edge XANES spectra of catalysts 2 and 4 and reference gold compounds: (1) gold foil, (2) AuPC$_{18}$H$_{15}$Cl, (3) HAuCl$_4$, (4) 0.1%Au/Al$_2$O$_3$, and (5) (0.1%Au + 0.03%Ni)/Al$_2$O$_3$.
The activity of Au, Ni, and Au–Ni states. The spectrum of sample 2, which contains 0.1 wt % Au, is identical to the spectrum of gold foil. Therefore, the oxidation state of gold atoms in sample 2 is zero. The spectrum of bimetallic sample 4 (0.1 wt % Au, 0.03 wt % Ni) is similar to the spectrum of HAuCl₄. At the same time, the lower intensity of the “white” line in the spectrum of the bimetallic catalyst, the absence of a peak at 119936 eV in this spectrum, and the presence of a peak at 119949 eV, which is characteristic of gold foil, indicate that sample 4 contains both Au³⁺ and Q Au⁰.

The XANES data obtained in this study are in agreement with the data reported earlier [18]. It follows from our results that the introduction of NiOₓ into Au/Al₂O₃ generates gold atoms in the oxidation state +3. This is likely due to the formation of new structures, specifically, gold nanoparticles that are in contact with nonstoichiometric nickel oxide NiOₓ. When nanosized metal and oxide particles are close together, new positively charged centers can indeed form via electron density transfer from metal clusters to oxide clusters [5–8, 19].

**Morphology and Size of Supported Metal Particles**

A typical TEM image of NiOₓ/Al₂O₃ containing 0.09 wt % nickel (sample 1) is presented in Fig. 2. Nickel can be seen to be deposited as spherical particles on the supported surface. The NiOₓ particle size distribution is comparatively narrow and unimodal. The surface has 1.5- to 9-nm particles, and their average size is 3 nm. The shape and size of the NiOₓ particles observed in sample 1 are in agreement with morphologic data for nickel particles in a (Ni + NiO)/Al₂O₃ catalyst (3 wt % Ni) obtained by impregnation [12]. In this catalyst, nickel on the Al₂O₃ surface was observed as 3.7-nm spherical particles. The aggregation resistance of the NiOₓ particles was estimated in the following way. The fresh catalyst (sample 1) was calcined at 500°C in air for 6 h, its TEM image was then obtained, a particle size distribution histogram was constructed, and the average particle size was calculated. It turned out that prolonged heating exerts no effect on the shape of the NiOₓ particles and only increases their average size to the small extent of 0.5 nm (table). The high aggregation resistance of the NiOₓ particles is in agreement with earlier data for NiOₓ/Al₂O₃ catalysts [7, 15].

A typical TEM image of Au/Al₂O₃ containing 0.1 wt % gold (sample 2) is shown in Fig. 3. The Au particles on the support surface are spherical, and their size distribution is narrow and unimodal. The size of the particles ranges between 1 to 9 nm, and the average size is 3 nm. The morphological properties of the particles in this catalyst are consistent with TEM data for gold particles deposited onto alumina by ion exchange [14]. The calcination of Au/Al₂O₃ (sample 2) at 500°C in air for 6 h causes an approximately threefold increase in the average size of the gold particles, with the shape of the particles remaining roundish. The low aggregation resistance of the gold particles in sample 2 is in agreement with data of other authors [8] and is explained by the weakness of the metal—support interaction in the Au/Al₂O₃, Au/SiO₂, and Au/C type systems [2, 7, 15].

A typical TEM image of the Au–Ni catalyst containing 0.1 wt % nickel and 0.09 wt % gold (sample 5) is presented in Fig. 4. The introduction of NiOₓ into the Au/Al₂O₃ catalyst causes a broadening of the particle size distribution and a slight increase in the average particle size. The same tendency is observed for the other bimetallic catalysts (compare samples 3–5 to samples 1 and 2 in the table). Note that, along with spherical particles, particles having a more complex shape are present in the bimetallic samples. Figure 5 shows the TEM images of some of these particles and the corresponding EDX data. These data indicate that
the complex-shaped particles contain both nickel and gold. The complex-shaped particles in catalyst 3 (0.1 wt % Au, 0.01 wt % Ni) account for 27% of the total number of particles. As the Ni content of the Au–Ni catalyst is increased, the number of complex-shaped particles increases and their highest concentration, observed in sample 5 (0.1 wt % Au, 0.09 wt % Ni), is 44% of the total number of particles.

In some cases, the intimate contact between gold and nickel results in the formation of alloys and intermetallides. For example, Au–Ni alloys were identified in Au–Ni/MgAl₂O₄ [20] and Au–Ni/Al₂O₃ [21] catalysts heat-treated at 550 and 1000°C, respectively. The formation of the Au₃Ni₅ intermetallide was detected by X-ray diffraction in a gold–nickel mixture heated to 1060°C [22].

In an earlier work [15], X-ray diffraction patterns were obtained for M/Al₂O₃ catalysts that contained 0.2–0.4 wt % metals and had been prepared via the same procedure as in the present study. It was demonstrated that gold and nickel in the Au–Ni catalysts exist as two individual phases—Au and NiOₓ. No Au–Ni alloy was identified. The results of that work suggest that the Au–Ni particles observed in samples 3–5 (Fig. 5) very likely consist of separate gold and nickel oxide phases. Samples 3–5 and the catalysts reported in Ref. [15] differ from the catalysts described by other authors [20–22], and the difference can apparently be explained in terms of preparation conditions. The heat-treatment temperature for the first group of catalysts was no higher than 500°C, while the samples of the second group were calcined at higher temperatures.

Calcination of the Au–Ni catalysts at 500°C in air for 6 h causes an increase in the particle size: the average particle size in samples 3, 4, and 5 is 6.5, 5.2, and
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4.4 nm, respectively. An analysis of TEM data for the initial catalysts and for those calcined at 500°C (table) suggests that, in the presence of NiOx, the gold particles are less prone to aggregation. Calcination of the Au–Ni catalysts increases the proportion of complex-shaped particles. As the nickel content of the bimetallic catalysts is increased from 0.01 to 0.09 wt % (samples 3–5), the concentration of complex-shaped particles increases from 36 to 62%.

**Water-Gas Shift Reaction**

Figure 6 plots the temperature dependences of CO conversion for the water-gas shift reaction over catalysts 1–5. The NiOx/Al2O3 sample (curve 1) is inactive at 200–400°C; at 500°C, the CO conversion does not exceed 5%. The slight activity of sample 1 at 500°C may be due to NiO reduction to Ni0 via the reaction NiO + CO → Ni0 + CO2.

The water-gas shift reaction over Au/Al2O3 (Fig. 6, curve 2) proceeds at a noticeable rate starting at 200°C; as the temperature is raised to 500°C, the CO conversion increases from 2 to 19%. The water-gas shift reaction over catalysts based on 3–6 nm Au particles was investigated in earlier works [23–28], in which it was demonstrated that the 50% CO conversion temperature for the Au/TiO2, Au/Fe2O3, and Au/Co3O4 catalysts is 300, 280, and 230°C, respectively. The higher efficiency of these catalysts compared to Au/Al2O3 (sample 2) is due to the difference between the concentrations of supported gold. The samples reported in Ref. [23–27] contained 3 wt %

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**Fig. 5.** (a) TEM images of complex-shaped particles (1 and 2) in catalyst 5. (b) EDX spectra of the indicated areas on the surface of particles 1 and 3.
the introduction of orders of magnitude \[3\]. Our TEM studies showed that the CO oxidation rate increases by more than two orders of magnitude as the size decreases from 20 to 9 nm, the amount of adsorbed carbon monoxide increases by a factor of 5. As their aggregation upon heating (table). Therefore, the second cause of the synergism in the activity of the Au–Ni catalysts in the water-gas shift reaction is that small, highly reactive gold particles persist in samples 3–5.

The synergism in the activity of the Au–Ni catalysts can be influenced by the complex shape of Au–Ni particles. At a given temperature, the CO conversion over the Au–Ni catalysts increases in the following order: sample 3 < sample 4 < sample 5 (Fig. 6). The proportion of complex-shaped particle increases just in the same order. It can be assumed that the complex-shaped gold particles contain more atoms with a small coordination number than the spherical particles do. As was mentioned above, gold atoms with a small coordination number are more reactive in heterogeneous catalytic processes \[2, 8, 11, 30\].

Lowering the reaction temperature from 300 to 200°C decreases the activity of samples 3–5 and eliminates the synergistic effect (Fig. 6). The decrease in the activity of the gold-containing catalysts at relatively low temperatures is apparently due to the weak activation of water on Au \[31, 32\]. The absence of synergism at low temperatures may be a consequence of the reduction of Au\+\+ cations by carbon monoxide, since this process occurs even at room temperatures \[31\]. At relatively high temperatures (above 450°C), the synergistic effect disappears as well (Fig. 6). This can be due to the encapsulation of supported particles in support pores and/or particle aggregation \[4, 7\], both processes reducing the total number of active sites on the catalyst surface.

Carbon Monoxide Oxidation with Dioxygen

Figure 7 plots the temperature dependences of the CO conversion for CO oxidation over catalyst samples 1, 2, and 4. The main regularities in the catalytic action of these catalysts in CO oxidation are the same as in the water-gas shift reaction (compare Figs. 6 and 7). In particular, NiO\_2-based sample 1 is the least active. Au-based sample 2 is more active. The activity of sample 4, which contains both Au and NiO\_2, exceeds the sum of the activities of samples 1 and 2. The existence of this synergistic effect is consistent with the data according to which the 95% CO oxidation temperature for CoO\_x/Al\_2O\_3, Au/Al\_2O\_3, and (Au + CoO\_x)/Al\_2O\_3 catalysts is 340, 140, and 110°C, respectively \[14\].

There have been detailed studies on the nature of active sites in the hydrocarbon and carbon monoxide oxidation reactions over gold-containing catalysts \[33–35\]. It was demonstrated that the most active methanol oxidation sites are Au\+\+ atoms \[33, 34\]. It was found \[35\] that the highest CO oxidation rate is attained at practically equal proportions of Au\+\+ and Au\+ species in the Au/MgO catalyst. These data \[33–35\] suggest that the high rate of CO oxidation over catalyst 4 (Fig. 7) is due to the presence of Au\+\+ atoms in the Au–Ni particles.

The high activity of sample 4 in CO oxidation (Fig. 7) and in the water-gas shift reaction may be due
to the size effect and the morphology of the Au–Ni particles. In addition, the synergistic effect observed in CO oxidation over sample 4 can be caused by the appearance of new reaction pathways. Carbon monoxide oxidation over transition metals [2, 14, 36, 37] is described by the Langmuir–Hinshelwood scheme. The mechanism of CO oxidation on Au particles includes equations (I)–(III) [14, 37]. Since gold gas a reduced O–O bond breaking capacity [2], the rate-limiting step is the dioxygen adsorption of O₂ (reaction (I)):

\[
\begin{align*}
O_2(\text{gas}) + 2Au & \rightarrow 2O(\text{ads})Au, \quad (I) \\
CO(\text{gas}) + Au & \rightarrow CO(\text{ads})Au, \quad (II) \\
CO(\text{ads})Au + O(\text{ads})Au & \rightarrow CO_2(\text{gas}) + 2Au. \quad (III)
\end{align*}
\]

There has been a report on the mechanism of CO oxidation over Au/MOx/Al2O3 catalysts [14]. The authors of that report believe that the contact between the Au nanoparticles and MOx particles brings about a catalytic cycle in which oxygen atoms, forming on the MOx surface, pass onto the Au surface, where they react with activated CO molecules. By analogy, the higher in the activity of the Au–Ni catalysts in CO oxidation can be explained by the spillover of O atoms from the surface of NiOx clusters to Au clusters.

Thus, we discovered that, in the water–gas shift and carbon monoxide oxidation reactions at 300–450°C, the CO conversion over (Au + NiOx)/Al2O3 is 2–3 times higher than the sum of the CO conversions over Au/Al2O3 and NiOx/Al2O3. The increased activity of the bimetallic catalysts is due to the specific features of their electronic structure and the structural organization of Au and NiOx particles on the support surface. In particular, new Auatoms sites form on the Au–Ni catalysts. As is known from the literature, these sites are highly active in steam reforming and oxidation processes. The introduction of NiOx into the Au/Al2O3 catalyst enhances the aggregation resistance of the Au particles, making it possible to retain small, active Au particles under catalytic testing conditions. A certain contribution to the activity of the Au–Ni catalysts can be made by the complicated morphology of the surface of the Au–Ni particles and, in the case of CO oxidation, by the spillover of oxygen atoms from NiOx clusters to Au clusters.

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