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Selective Oxidation of Alcohols over Si_3N_4-Supported Silver Catalysts

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Abstract—Silver-containing catalysts supported on ceramic silicon nitrides and modified with Zr or Al are considered. The catalytic activities of the catalysts in the dehydrogenation and oxidative dehydrogenation of ethanol into acetaldehyde are compared. The introduction of oxygen into the reaction mixture decreases the temperature of 100% ethanol conversion to 270°C and increases the acetaldehyde selectivity to 95% for all of the catalysts. According to temperature-programmed reduction data, the simultaneous presence of Fe and Ag on the catalyst surface enhances the activity of the supported catalysts. It is hypothesized that the Ag/Fe interface plays the key role in the formation of active sites on the catalyst surface.

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INTRODUCTION

The dehydrogenation and oxidative dehydrogenation of alcohols catalyzed by Cu-subgroup metals has been attracting keen interest from researchers for many decades. This area is very promising, as follows from the fact that catalytic systems have been developed for the synthesis of valuable carbonyl compounds, such as formaldehyde [1], glyoxal [2], acetaldehyde [3–5], and acetone. In recent years, there has been increasing interest in the processing of renewable raw materials, including bioethanol. Therefore, designing efficient catalytic systems for alcohol conversion into more valuable (value-added) derivatives is an important stage of the development of “green” chemical technologies.

Usually, the specific surface area, porous structure, and Lewis and/or Brönsted acidity of materials are primarily considered when selecting a support for catalysts to be used in the oxidative or anaerobic dehydrogenation of organic compounds. The thermal conductivity, mechanical strength, and chemical resistance to the reaction medium are not always viewed as the most important properties. Here, we report the synthesis of Ag-containing catalysts supported on ceramic supports with high thermal conductivity (Al- or Zr-modified Si_3N_4) and their catalytic activity in the anaerobic and oxidative dehydrogenation of ethanol.

EXPERIMENTAL

The supports for silver catalysts were silicon nitride–based ceramic materials. They were prepared by self-propagating high-temperature synthesis (SHS) in a nitrogen atmosphere using wasted ferrosilicon ($FeSi_2$, 80 wt % Si) as the starting material [6]. Aluminum and zirconium were introduced into the support by adding 20 wt % $ZrSiO_4$ and Al_2O_3, respectively, to the starting material before the SHS stage [7]. The resulting solids were treated with hydrochloric acid to remove iron. The most important characteristics of the ceramic supports are presented in the table.

In view of the hydrophobic nature of the surface of the ceramic supports [8], silver was deposited from a CF_3COOAg solution in toluene.

Silver on the support surface was quantified by X-ray fluorescent spectroscopy on a Quant’X spectrometer. The relative error in the determination of silver content was 7%. The morphology of the catalysts was studied by scanning electron microscopy (SEM) on a Carl Zeiss EVO50 microscope (Germany) and by transmission electron microscopy (TEM) using a JEOL JEM 2010 microscope (Japan). The phase composition of the supports was studied on an ARL X’TRA diffractometer using CuK_α radiation (λ = 1.5406 Å).

The redox properties of the supports and silver-containing catalysts were investigated by temperature-programmed reduction (TPR) using ChemiSorb-2750 chemisorption analyzer (Micromeritics, United

Chemical and phase composition of the Ag-containing catalysts

Catalyst	Phase composition of the support		Ag, wt %	Iron content of the support, wt %	
	support	modifiers		ICP-AES*	SEM**
$Ag/Fe–Si_3N_4$	α-Si_3N_4 (15%) β-Si_3N_4 (85%)	–	4.9	0.02	0.06
$Ag/Fe–Si_3N_4–Zr$	α-Si_3N_4 (12%) β-Si_3N_4 (60%)	ZrO_2 (monoclinic) (16%) ZrO_2 (orthorhombic) (12%)	4.9	1.15	0.79
$Ag/Fe–Si_3N_4–Al$	α-Si_3N_4 (10%) β-Si_3N_4 (80%)	($Si_3Al_{12}O_9N_{10}$) (10%)	4.9	0.24	0.20

* Determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of the sample.

** Determined by energy-dispersive analysis of the sample surface.

States). Before the TPR experiments, the sample was oxidized in a 10 vol % O_2 + Ar flow in a temperature-programmed mode (flow rate of 20 mL/min, 25–650°C, heating rate of 10 K/min). The sample was held at a constant temperature of 650°C for 10 min and was then cooled to room temperature at a rate of 10 K/min. TPR experiments were performed in the temperature range from 25 to 650°C at a heating rate of 10 K/min using a 10 vol % H_2 + Ar gas mixture (flow rate of 20 mL/min).

Thermogravimetric experiments were carried out on an SDT Q-600 thermal analyzer (TA Instruments, United States) in the DSC–TGA mode in flowing air (20 mL/min). The weight of the sample was 52.5 mg. The composition of the gas phase in thermal analysis was monitored using a ProLab mass spectrometer (Thermo Scientific, United States).

Ethanol was dehydrogenated in a flow reactor while chromatographing the gas phase [3, 4]. Prior to performing dehydrogenation, the catalysts were activated in a 25% O_2 + 75% He flow while raising the temperature from 25 to 500°C. The sample was kept at the final temperature for 1 h, and the reactor was then cooled to 100°C. The dehydrogenation and oxidative dehydrogenation of ethanol were performed in the temperature-programmed mode by raising the temperature from 100 to 500°C at a rate of 2 K/min. The composition of the reaction mixture was EtOH : He = 2 : 98 in dehydrogenation and EtOH : O_2 : He = 2 : 18 : 80 in oxidative dehydrogenation. The volumetric flow rate of the reactants was 60 mL/min. The catalyst weight was 0.5 g.

RESULTS AND DISCUSSION

The main characteristics of the synthesized samples are presented in the table. The Zr-modified sample contains the orthorhombic and monoclinic ZrO_2 phases. These phases are distributed in the silicon nitride matrix in the same way as was observed earlier in the SEM examination of the surface morphology of the modified supports [7]. The support modified with Al_2O_3 contains substitutional phases, specifically, sialons of variable composition ($Si_{6-x}Al_xO_xN_{8-x}$) and is dominated by the high-temperature phase β-Si_3N_4.

The nitriding process yields iron metal particles along with silicon nitride and modifier phases [6, 7]. The impurity iron was removed by dissolving it in hydrochloric acid. However, in spite of this treatment, all of the supports contained residual iron (0.02–1.15 wt %; see the table). This can be due to partial encapsulation of the Fe particles by phases of the support.

The silver catalyst precursors prepared by silver trifluoroacetate deposition followed by solvent (toluene) evaporation and drying at 100°C were studied by SEM (Fig. 1). It can be seen that the salt is uniformly distributed over the surface and forms a film reproducing the support morphology (Figs. 1a, 1b). Similar results were obtained for all of the samples synthesized. The surface morphology of the supported silver catalysts subjected to calcination at 500°C in air is shown in Fig. 1c. The silver particles forming under these conditions, 20–30 nm in size, are mostly located in hollows and in places of contact between coalesced support particles. Evidently, the formation of the Ag particles on the support surface during the oxidation and decomposition of silver trifluoroacetate takes place mainly via a coalescence mechanism. This mechanism includes the diffusion of silver atoms on the support surface and their aggregation in places having excess energy.

The decomposition of the silver trifluoroacetate film yielding silver metal particles on the support surface was investigated by thermogravimetric analysis in flowing air (Fig. 2a). The greatest weight loss of the sample occurred at 150–350°C (Fig. 2a, curve *1*). As the temperature was further increased, a weight gain was observed at 600–1000°C. The DTA curve indicated two endotherms at 252 and 945°C and three exotherms at 341, 673, and 770–900°C (Fig. 2a, curve *2*). The endotherms are due to the melting of silver trifluoroacetate at 257–260°C [9] and silver metal, respectively. The sharp exothermic peak at 341°C was assigned to the decomposition of silver trifluoroace-

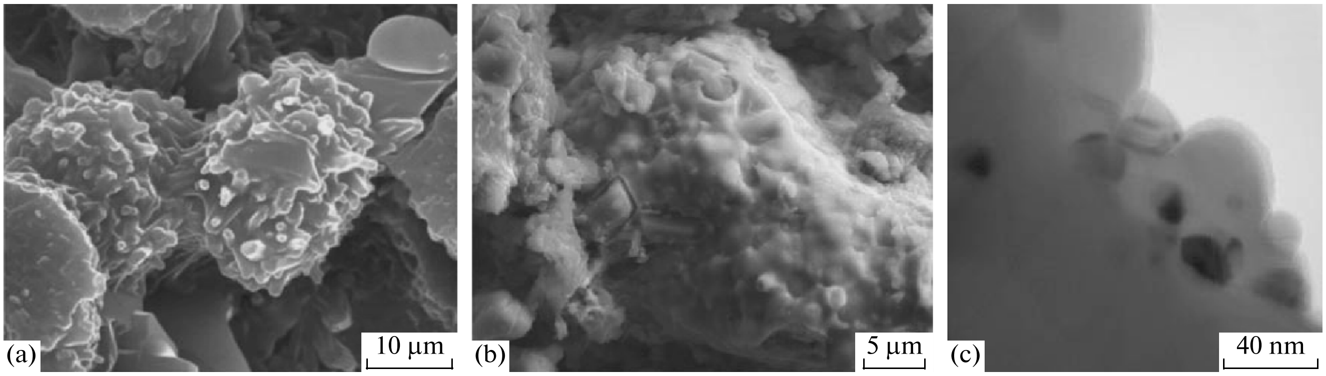

Fig. 1. Surface morphology of the (a) Fe–Si_3N_4–Zr support and (b, c) Ag/Fe–Si_3N_4–Zr catalyst, both heat-treated at 500°C in air.

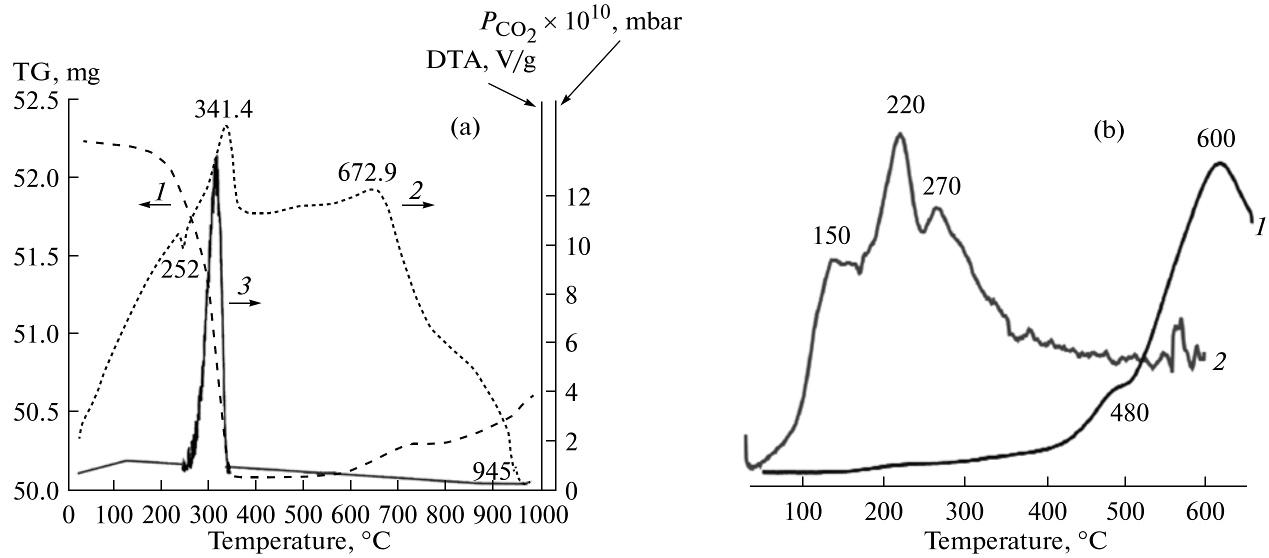

Fig. 2. (a) Results of thermal analysis of CF_3COOAg/Fe–Si_3N_4 with mass spectrometric monitoring of the gas phase: (*1*) TG curve, (*2*) DTA curve, and (*3*) CO_2 evolution curve. (b) TPR profiles of (*1*) Fe–Si_3N_4 and (*2*) Ag/Fe–Si_3N_4 preoxidized in the temperature-programmed mode.

tate for the reason that the CO_2 evolution curve recorded by mass spectrometry showed a peak in the 150–360°C range (Fig. 2a, curve *3*). The two diffuse exotherms at 550–900°C in the DTA curve may be due to the oxidation of iron. This assignment is confirmed by the increase in the sample weight (Fig. 2a, curve *1*) and by the absence of a signal from CO_2 in the mass spectrum (Fig. 2a, curve *3*) in this temperature range.

Thus, as the silver trifluoroacetate film is heat-treated in the oxidizing atmosphere, it decomposes in the temperature range from 150 to 350°C to form silver particles on the support surface, and this is accompanied by the oxidation of iron to iron oxides.

The reactivity of active sites on the sample surfaces was studied by TPR with hydrogen (Fig. 2b) before and after the deposition of silver onto the Fe–Si_3N_4 support. The samples were preoxidized with a flowing oxygen-containing reaction mixture (see Experimental). The TPR profile of the support indicates H_2 uptake in the 430– 650°C range, which is due to the reduction of iron oxides (Fig. 2b, curve *1*). For α-Si_3N_4 from Sigma Aldrich (99.9%), which contained no iron, no hydrogen uptake was observed in this temperature range. The deposition of silver onto the Fe–Si_3N_4 surface shifts the hydrogen uptake signal to lower temperatures of 50–350°C (Fig. 2b, curve *2*). This is due to the existence of Ag/Fe-containing site contacts, which alter the mechanism of the interaction of H_2 molecules with the active surface of the catalyst.

The catalytic properties of the synthesized materials were studied in the dehydrogenation and oxidative dehydrogenation of ethanol. The results obtained for the Ag/Fe–Si_3N_4 sample are presented in Fig. 3. Under the anaerobic dehydrogenation conditions, complete ethanol conversion is achieved only above 400°C (Fig. 3a). The maximum acetaldehyde selectivity (~67%) is observed in the temperature range from

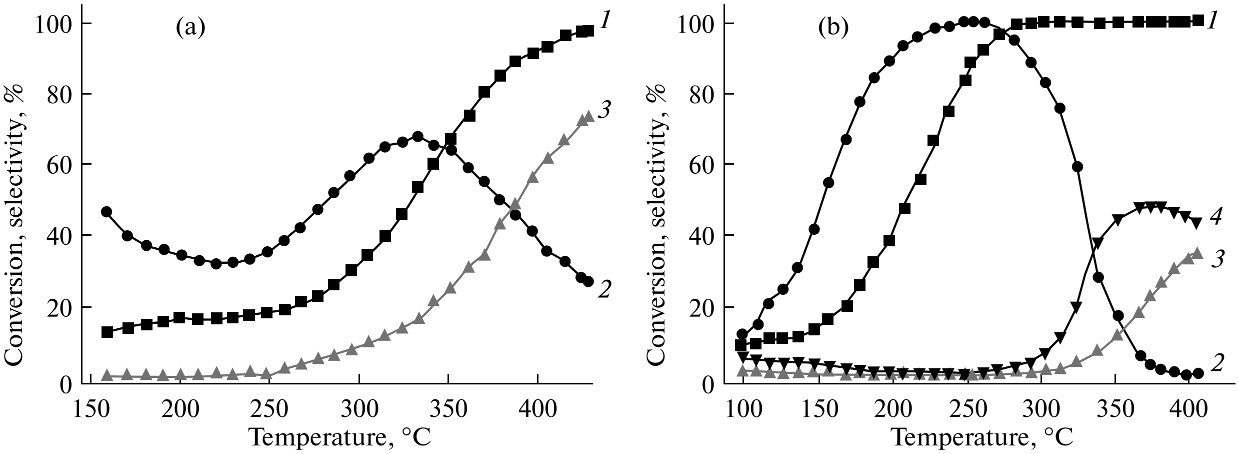

Fig. 3. Catalytic properties of Ag/Fe–Si_3N_4 in the (a) dehydrogenation and (b) oxidative dehydrogenation of ethanol: (*1*) ethanol conversion, (*2*) acetaldehyde selectivity, (*3*) ethylene selectivity, and (*4*) CO_x selectivity.

320 to 350°C. Above 350°C, ethanol dehydration into ethylene on acid sites of the catalyst surface competes strongly with the dehydrogenation process.

In the case of oxidative dehydrogenation, complete ethanol conversion is attained at 270°C (Fig. 3b). The highest acetaldehyde selectivity (98%) is observed near 250°C. As the temperature is increased, the acetaldehyde selectivity decreases. Above 300°C, the dominant reactions are the oxidation of organics to CO and CO_2 and ethanol dehydration.

The Ag/Fe–Si_3N_4, Ag/Fe–Si_3N_4–Al, and Ag/Fe–Si_3N_4–Zr catalysts show similar catalytic activities in the anaerobic dehydrogenation reaction (Fig. 4). However, on passing from the unmodified sample to the aluminum- and zirconium-modified samples, the maximum acetaldehyde yield decreases progressively and the highest yield temperature increases (Fig. 4b). This is likely due to the fact that the samples differ in their iron content (table). The effect of iron on the activity of supported metal catalysts in the dehydrogenation of organic compounds is known from the literature. For instance, the specific activity of Pt–Fe/SiO_2 catalysts in cyclohexane dehydrogenation as a function of Fe content (0.03–0.57 wt %) was observed to pass through an extremum [10]. The authors of that work hypothesized that the Fe^0 sites participate in cyclohexane dehydrogenation along with the Pt and Pt–Fe bimetallic species of the surface of the supported catalysts.

The dehydrogenation of alcohols into carbonyl compounds on the surface of metal particles is believed to proceed via two basic stages. The first stage is the breaking of the O–H bond in the alcohol molecule and the formation of an adsorbed alkoxide-type intermediate. The second stage is the cleavage of the β-C–H bond in the alkoxide intermediate and the formation of the corresponding carbonyl compound in enol form [5, 11]. Both stages may involve oxygen adsorbed on the catalyst surface or not. However, the presence of oxygen-containing species on the catalyst surface ensures the oxidation of adsorbed hydrogen atoms and shifts the equilibrium toward the reaction products.

A comparison of the experimental data obtained under dehydrogenation and oxidative dehydrogenation conditions (Figs. 3a, 3b) demonstrated that the presence of oxygen in the reaction mixture not only increases the acetaldehyde formation rate, but also enhances the acetaldehyde selectivity by suppressing the dehydration reaction. Moreover, a comparison between the TPR profiles for Fe–Si_3N_4 and Ag/Fe–Si_3N_4 (Fig. 2b) suggests that the simultaneous presence of silver and iron enhances the activity of the catalysts in hydrogen oxidation. It is likely that the high activity of the silver catalysts in the oxidative dehydrogenation of ethanol to acetaldehyde is mainly due to the existence of Ag/Fe interfaces.

There have been studies on individual Fe- and Ag-containing catalysts supported on manganese oxide in the form of hollandite [12, 13]. It was shown that, in ethanol oxidation over the Fe-containing catalyst at 300ºC, the highest ethanol conversion is 71.5% at 78.9% acetaldehyde selectivity [12]. Note that the oxidation reaction was carried out using a 1% O_2 + He mixture. At higher oxygen concentrations, the dominant reaction in this system is total ethanol oxidation to CO_2.

The manganese oxide–supported Ag-containing catalysts showed fairly high activity: at 230°C, the ethanol conversion was 82% and the acetaldehyde selectivity was 95% [13]. The O_2 content of the reaction mixture was 10%. However, raising the temperature to 270°C caused a dramatic decrease in acetaldehyde selectivity (down to 30%) because of total ethanol oxidation.

Thus, the individual Fe-containing and Ag-containing supported systems are efficient in ethanol oxidation to acetaldehyde. However, both systems afford

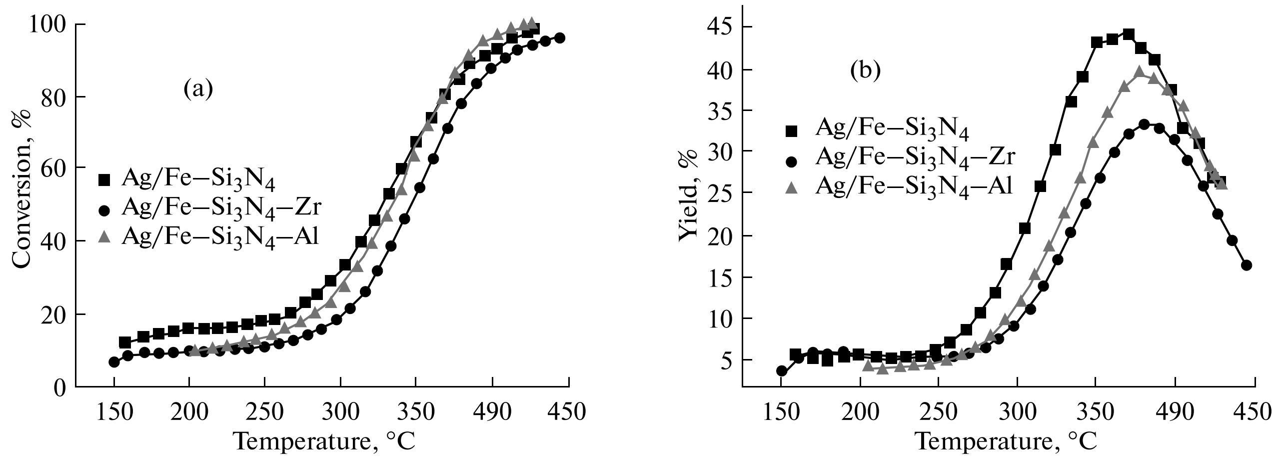

Fig. 4. (a) Ethanol conversion and (b) acetaldehyde yield as a function of temperature in the dehydrogenation process.

a high acetaldehyde yield only in narrow temperature and reaction mixture composition ranges. This circumstance impedes commercialization of the process.

CONCLUSIONS

We have investigated Ag-containing catalytic systems supported on ceramic materials with high thermal conductivity—zirconium- and aluminum-modified silicon nitride—by deposition of silver trifluoroacetate from toluene solution. The introduction of the active component into the system yields a silver trifluoroacetate film that reproduces the morphology of the support surface. The silver metal particles are obtained on the support surface by silver trifluoroacetate decomposition in air atmosphere in a narrow temperature range of 250–350°C.

It was demonstrated by TPR that the simultaneous presence of silver and iron on the support surface increases the hydrogen oxidation activity of the catalyst.

The Ag-containing catalyst supported on silicon nitride shows high catalytic activity in the selective gas-phase oxidative dehydrogenation of ethanol to acetaldehyde. Dehydrogenation can also take place under anaerobic conditions, but much less efficiently than oxidative dehydrogenation does. In view of the availability and environmental friendliness of the oxidizer (dioxygen or air), the rapid growth of the production of bioethanol (renewable, environmentally friendly feedstock), and simplicity of scaling up gas-phase processes, the catalytic reactions reported here are expected to find use in new, "green" technologies for partial oxidation of ethanol and other alcohols.

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