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Mechanistic Study of Ethanol Dehydrogenation over Silica-Supported Silver

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A silica-supported Ag catalyst has been shown to be an efficient heterogeneous catalyst for the oxidant-free dehydrogenation of ethanol into acetaldehyde. The reaction mechanism has been investigated by in situ FTIR spectroscopy. The kinetic isotope effects for proton and hydride abstraction have been studied by using CH₃CD₂OH and CH₃CH₂OD as labeled reactants. The results indicate that O–H bond activation and the

Introduction

The selective dehydrogenation of alcohols into carbonyl compounds has attracted attention as aldehydes and ketones are important intermediates for the synthesis of various valuable products, such as acetals, plastics, and perfumes.^[1] This class of reaction is increasingly important for the conversion of biomass-derived feedstocks such as bioethanol, which can be produced from carbohydrates and can contribute to the decreased use of fossil fuels.

The traditional route for alcohol dehydrogenation uses stoichiometric inorganic oxidants in environmentally undesirable chlorinated solvents, which produce large amounts of toxic waste. To achieve environmental and economical acceptability, efforts have been devoted to the development of a catalytic oxidation route with environmentally friendly oxidants (such as O₂ and H₂O₂) that avoids the use of a large excess of toxic and expensive metal-based oxidants. Therefore, a large number of papers have been devoted to the oxidative dehydrogenation of alcohols with O₂ over different heterogeneous catalysts.^[2] Ru, Pd, and Au nanoparticles supported on different oxides (mostly alumina and silica) have demonstrated high catalytic activities and selectivities to the target carbonyl compounds.^[3] In addition, $Ni^{[4]}$ and $Cu^{[5]}$ supported on hydrotalcite (HT) have shown promising results in the liquid-phase oxidative dehydrogenation of alcohols.

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formation of a hydrogen-bonded complex take place on the silica support and that the Ag particles are necessary for the activation of the C–H bond. The kinetic isotope effect (k_H/k_D) is 1.9 for CH₃CD₂OH and 1.8 for CH₃CH₂OD. The concerted mechanism of C–H cleavage on the Ag sites and proton abstraction on the silica sites is proposed to account for the results of the spectroscopic and kinetic experiments.

However, the presence of O_2 may cause overoxidation and explosion or combustion of the organic solvents or alcohol reactants. This safety problem becomes particularly serious for the practical large-scale application of oxidative dehydrogenation. Thus, the oxidant-free dehydrogenation of alcohols is a challenging goal, from both a practical and environmental point of view. This route provides the following advantages with respect to oxidative dehydrogenation:

- It suppresses the overoxidation of substrates to carboxylic acids and thus leads to a higher selectivity to carbonyls;
- It eliminates the formation of water as a byproduct, which often deactivates catalysts and complicates the purification of products;
- 3) It produces H₂, which is an attractive feedstock for energy generation;
- 4) It is tolerant towards alcohols that have O₂-sensitive functional groups.

The first studies of the oxidant-free dehydrogenation of ethanol were performed over Cu-based catalysts, which showed a good selectivity to acetaldehyde.^[6] The doping of Cu-based catalysts with Cr, Mn,^[7] or Zn^[8] improved their activity and stability with time on-stream.

More recent studies of ethanol dehydrogenation have been devoted to Au-containing catalysts. Gazsi et al. demonstrated that Au nanoparticles deposited on various supports are active catalysts for the dehydrogenation of ethanol into acetalde-hyde.^[9] The product distribution depended significantly on the nature of the support. The application of silica, alumina, and titania as supports for the Au particles led to a high ethanol conversion but low acetaldehyde and hydrogen yields, and the major products were methane and CO. The highest rate of H₂ evolution was observed for Au deposited on CeO₂, which showed stable activity with time on-steam.

Guan and Hensen,^[10] and Zheng and Stucky,^[11] investigated the effect of the Au particle size on ethanol dehydrogenation. A series of Au catalysts with increasing particle sizes was synthesized on various silica supports from different Au precursors. Ordered mesoporous silica was used to control the Au particle size. Au particles of approximately 6–8 nm were much more active than smaller or larger particles. The authors proposed that this effect can be accounted for by the formation of step sites on the Au surface, which have a favorable geometry for the rate-limiting β -H elimination of the adsorbed alcoholate.

Recently, Mitsudome et al.^[12] and Shimizu et al.^[13] found that Ag-containing catalysts supported on basic or acidic oxides are very active in the nonoxidative dehydrogenation of secondary alcohols. In particular, Ag/HT (hydrotalcite-supported Ag nanoparticles) was the most active and selective catalyst in the dehydrogenation of aliphatic, benzylic, and heterocyclic secondary alcohols into the corresponding ketones. The comparison of Ag/HT with Pd/HT and Ru/HT indicated that the Ag-based catalyst showed significant advantages in alcohol dehydrogenation with respect to Pd/HT and Ru/HT in terms of activity and selectivity. However, practically no information is available on the dehydrogenation of primary aliphatic alcohols over Agcontaining catalysts. The only indication given in Ref. [12] concerns 1-octanol, which was not dehydrogenated efficiently over Ag/HT under the conditions studied.

Here we report on the application of Ag/SiO_2 as a catalyst for the oxidant-free dehydrogenation of ethanol, which is considered to be among the most promising renewable chemicals. We aimed to investigate the mechanism of the reaction over Ag/SiO_2 , which is important for the design of practical heterogeneous catalysts for the oxidant-free dehydrogenation of ethanol into acetaldehyde. In situ FTIR spectroscopic studies and the investigation of kinetic isotope effects for O–H and C–H bond cleavage were used to achieve this goal.

Results and Discussion

Catalyst structure and composition

 N_2 sorption-desorption experiments confirmed that the silica support selected has a high surface area (340 m²g⁻¹ by the BET method) and narrow pore size distribution (100 Å). FTIR spectra of the silanol groups are shown in Figure 1. Before activation, almost all of the silanol groups are hydrogen bonded to adsorbed water, which is reflected by the broadening and blueshift of the H–O stretch from 3740 cm⁻¹ to approximately 3300 cm⁻¹. After heating in a flow of He, the adsorbed water was removed from the surface of the silica, and only a narrow band at 3740 cm⁻¹, attributed to isolated silanol groups, is observed in the spectrum.

Analysis of the Ag content by atomic absorption spectrometry (AAS) gives 10.3 wt.%, which is in a good agreement with the amount calculated for the insipient wetness impregnation. TEM images show that the Ag particles are 2–4 nm in size (Figure 2).



Figure 1. IR spectra of silanol groups.



Figure 2. TEM image of Ag/SiO₂.

Catalyst evaluation in ethanol dehydrogenation

The main reaction products observed during ethanol conversion over Ag/SiO_2 are acetaldehyde, ethyl acetate, ethylmethylketone, butanal, and butan-1-ol. Plots of the yields of these products versus ethanol conversion are shown in Figure 3.

Acetaldehyde is the only product observed at low conversions, which suggests that it is the only primary product of the



Figure 3. Yield of products versus ethanol conversion.

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reaction. Ethylmethylketone and ethyl acetate are formed at ethanol conversions higher than 20% and can be attributed to secondary reaction products formed from acetaldehyde. The direct product of acetaldehyde condensation (3-hydroxybutanal) is not observed in the reaction mixture, most probably because of its high reactivity and fast conversion into ethylmethylketone, butanal, and butan-1-ol. Small amounts of butanal and butanol are detected at ethanol conversions higher than 40% (Figure 3).

A reaction pathway is shown in Scheme 1. The main reaction pathway involves ethanol dehydrogenation to acetaldehyde, which can be further converted through two reaction routes. The Cannizarro reaction leads to ethyl acetate, whereas aldol condensation gives 3-hydroxybutanal. The isomerization of 3-hydroxybutanal gives 1-hydroxybutan-3-one, the sequential dehydration and reduction of which results in ethylmethylketone. The dehydration of 3-hydroxybutanal into crotonaldehyde and the reduction of the C=C bond in crotonaldehyde lead to butanal, which can be converted into butan-1-ol by a further hydrogenation reaction.

The reaction rate estimated from the initial slope of the kinetic curve for ethanol conversion over Ag/SiO_2 at 573 K is 0.63 mmolg⁻¹s. Taking into account that the average Ag particle size is approximately 3 ± 1 nm and assuming that the Ag



Scheme 1. Reaction pathway.

particles have a crystalline structure with a bulk Ag lattice constant of $a_0 = 0.4086$ nm,^[14] the turnover frequency (TOF) per surface Ag site is estimated to be 3.4 ± 0.8 s⁻¹. This value is higher than those reported for supported Au catalysts,^[10] which suggests that less-expensive Ag catalysts can be competitive for ethanol dehydrogenation.

Mechanism of ethanol dehydrogenation over Ag/SiO₂

To understand the nature of the active sites responsible for the conversion of ethanol into acetaldehyde and their role in the overall reaction pathway, the mechanism of ethanol transformation was studied over Ag/SiO_2 by using in situ FTIR spectroscopy.

It is generally accepted that the mechanism of alcohol dehydrogenation over metal-containing catalysts involves the following steps: 1) cleavage of the O-H bond in alcohol to form a surface alkoxide, 2) cleavage of the C-H bond to form a carbonyl compound and a metal hydride, and 3) H₂ recombination and desorption.^[9,10,13,15-21] Recently, it has been proposed that both the metal and support can take part in the reaction over supported metal catalysts, in which the active sites of the support are usually responsible for O-H cleavage and the metal sites play a key role in C-H cleavage and H₂ recombination and desorption.^[9,13,15] The latter processes can be also assisted by the active sites of the support.^[13] However, there is no general consensus on the rate-limiting step of alcohol dehydrogenation: most reports suggest that C-H cleavage is the rate-limiting step.^[9, 10, 15, 16, 19, 21] However, in some contributions, it is proposed that proton abstraction^[16, 17, 20] or H₂ recombination and desorption^[18] can determine the reaction rate. Generally, the rate-limiting step is dependent on the structure of the alcohol, the type of metal and support, and the reaction conditions. Therefore, the key factor to understand the mechanism of alcohol dehydrogenation is the determination of the ratelimiting step and the active sites responsible.

In situ FTIR spectroscopy was performed to answer these questions. The surface species formed during the reaction of ethanol over Ag/SiO₂ (1 mmol per g of catalyst) at 373 K are revealed in the spectra shown in Figure 4. Immediately after the introduction of ethanol onto the catalyst, an intense negative peak at approximately 3740 cm⁻¹ appears in the O–H stretching region as a result of the interaction of the surface Si–OH groups with ethanol.^[22,23] A broad band centered at approximately 3400 cm⁻¹ in the O–H stretching region is also observed. This band is characteristic of the O–H stretching vibration of hydrogen-bonded Si–OH groups^[22–25] and suggests that the ethanol molecules are hydrogen bonded to the surface.

In the C–H bond vibration region, the following bonds are observed: 2980 (methyl asymmetric stretching), 2935 (methyl symmetric stretching), 2902 (methylene asymmetric stretching), 1448 (methyl asymmetric deformation), 1398 (methyl symmetric deformation), and 1339 cm⁻¹ (CH₂ deformation). These bands are typical of the ethyl groups of adsorbed ethanol.^[22,26]

No bands that correspond to ethoxy species were detected as a result of the rather weak interaction between ethanol and

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Figure 4. IR spectra recorded at 373 K after exposure of Ag/SiO $_{\rm 2}$ to CH $_{\rm 3}CH_{\rm 2}OH.$

silica. The question of ethoxy formation over silica has been addressed in detail,^[22] and it was concluded that ethanol is adsorbed on silica through the formation of hydrogen bonds. Therefore, small amounts of ethoxy species can be observed only after evacuation at 573 K.

The results of our FTIR spectroscopic study indicate that in the very early stages of the reaction at 373 K, ethanol forms a hydrogen-bonded complex with the silica support (Figure 5).

Further heating to 373 K reveals the appearance of a new

Figure 5. Ethanol hydrogen bond complex.

band at 1726 cm⁻¹ (Figure 4), which is typical of the C=O stretching vibration in acetaldehyde.^[26-29] The intensity of this band increases with time, which suggests that ethanol undergoes continuous C–H cleavage to form acetaldehyde. Importantly, the formation of the surface complex of ethanol with the Si– OH groups is very fast, whereas its conversion into acetaldehyde is much slower.

To elucidate the role of Ag in this reaction, an experiment was performed on Ag-free

silica (Figure 6). After the adsorption of ethanol on pure silica, a set of bands similar to that observed over Ag/SiO_2 was detected, which indicates the formation of the same adsorbed complex. However, no band at 1726 cm^{-1} , attributed to acetal-dehyde, is observed even after 5 min of the reaction.

These observations suggest that although surface silanol groups are responsible for the O–H bond activation in ethanol, Ag particles are necessary for the activation of the C–H bonds (Figure 7).

Cleavage of the C–H and O–H bonds of alcohol may occur by stepwise or concerted mechanisms. The stepwise mechanism includes the sequential cleavage of the O–H bond on the active sites of the support, cleavage of the C–H bond on a metal site, recombination of H⁺ and H⁻, and desorption of H₂. The rate-limiting step depends on the types of alcohol, support, and metal.



Figure 6. IR spectra recorded at 373 K after exposure of SiO₂ to CH₃CH₂OH.

In the case of a concerted mechanism, cleavage of the O–H and C–H bonds can occur simultaneously and can determine the rate of the overall reaction.

To distinguish between the stepwise and concerted mechanisms, we tried to determine the rate-limiting step of the reaction. For this purpose, experiments with ethanol spe-



Figure 7. Silver activation of the C–H bond

cifically labeled with deuterium were performed and the kinetic isotope effects were studied. In the first experiment, the reaction of CH_3CD_2OH over Ag/SiO_2 was investigated and in the second, the reaction of CH_3CH_2OD over deuterated with D_2O Ag/SiO₂ was studied.

The FTIR spectra observed during the reaction of CH_3CD_2OH over Ag/SiO₂ are shown in Figure 8. The bands that correspond to the vibrations of the methyl group of CH_3CD_2OH are observed at 2975 (methyl asymmetric stretching), 2937 (methyl symmetric stretching), 1449 (methyl asymmetric deformation), and 1405 cm⁻¹ (methyl symmetric deformation). The slight shift of these bands with respect to those observed for unlabeled ethanol (Figure 4) can be explained by the influence of the neighboring deuterium atoms. The bands assigned previ-



Figure 8. IR spectra recorded at 373 K after exposure of Ag/SiO_2 to CH_3CD_2OH .

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ously to the CH₂ group of ethanol (Figure 4) are not observed in Figure 8. However, new bands at approximately 2757, 2214, 2118, and 1381 cm⁻¹ appear, which are assigned to the vibrations of the α -deuterated methylene group of CH₃CD₂OH. The band at 1726 cm⁻¹ can be attributed to the C=O stretching vibration in acetaldehyde, which is also seen in the spectrum of the unlabeled reaction mixture (Figure 4), and the intensity of this band increases with time.

The spectra obtained during the reaction of CH_3CH_2OD over deuterated Ag/SiO₂ are presented in Figure 9. In the region of the C–H vibrations, the spectra are very similar to those observed for unlabeled ethanol (Figure 4). The slight shift of the



Figure 9. IR spectra recorded at 373 K after exposure of deuterated Ag/SiO₂ to CH_3CH_2OD .

bands can be explained by the interaction with the deuterated silica surface. The band that corresponds to the C=O stretching vibration in acetaldehyde is again observed at 1726 cm⁻¹ (Figures 4 and 8). No bands are detected in the region of the O–H stretching vibrations. Instead, an intense negative peak at approximately 2755 cm⁻¹ and a broad band centered at approximately 2615 cm⁻¹ are observed in the O–D stretching region as a result of the interaction of the surface Si–OD groups with CH₃CH₂OD.

The results of the kinetic analysis of the conversion of ethanol into acetaldehyde are shown in Figure 10. The relative amount of acetaldehyde species formed is estimated from the changes in the area of the IR band observed at 1726 cm⁻¹. This band is observed in all the spectra (Figures 4, 8, and 9), it does not overlap with the other bands, and, therefore, it is the most suitable for quantitative analysis. The first-order plots for acetaldehyde formation from CH₃CH₂OH, CH₃CD₂OH, and CH₃CH₂OD give fairly straight lines in all cases (Figure 10). The first-order rate constants for acetaldehyde formation at 373 K are estimated to be $4.28 \times 10^{-4} \pm 0.26 \times 10^{-4} \text{ s}^{-1}$ for CH₃CH₂OH, $2.24 \times 10^{-4} \pm 0.19 \times 10^{-4} \text{ s}^{-1}$ for CH₃CD₂OH, and $2.38 \times 10^{-4} \pm 0.11 \times 10^{-4} \text{ s}^{-1}$ for CH₃CD₂OH and CH₃CH₂OD is 1.9 and 1.8, respectively. This result indicates the limitation of both the C–



Figure 10. First-order plots for the formation of the acetaldehyde on Ag/ SiO₂ for CH₃CH₂OH (\Box), CH₃CD₂OH (\bullet), and CH₃CH₂OD (\triangle).

H and O–H cleavage during ethanol dehydrogenation over Ag/SiO $_2$.

The same values of the rate constants for acetaldehyde formation from CH₃CD₂OH and CH₃CH₂OD suggest that the cleavage of the α -C–H bond and the proton abstraction proceed simultaneously, which is an argument in favor of a concerted mechanism for the dehydrogenation of ethanol over Ag/SiO₂. The recombination and desorption of H₂, which usually proceeds over metal species, is unlikely to be the rate-limiting step as no AgH was detected in our in situ FTIR spectra. Therefore, we suppose that the later steps proceed at a higher rate than the concerted α -cleavage and proton abstraction. This conclusion is in agreement with the results of Mitsudome et al.^[12] who observed the facile release of H₂ from Ag particles.

A reaction mechanism based on the results of spectroscopic and kinetic experiments is presented in Scheme 2. The first step is the interaction of ethanol with the surface Si–OH



Scheme 2. Mechanism for ethanol dehydrogenation over Ag/SiO2.

groups to yield a hydrogen-bonded complex on the silica surface. The next step involves concerted C–H bond cleavage on the Ag site and proton abstraction on the silica site to form H_2 adsorbed on Ag and acetaldehyde adsorbed on silica. This step is the rate-determining step of the reaction, which is evidenced by the observation of primary isotopic effects for the conversion of specifically deuterated ethanol into acetaldehyde (Figure 10). The last step is the desorption of H_2 and acetalde-

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hyde, which regenerates the active sites (Scheme 2). Although this mechanism is consistent with the data reported, more studies are needed to confirm all the reaction steps. Additional insight can be obtained by the investigation of the reaction over Ag catalysts with different Ag dispersions and different supports.

Although the mechanism proposed is somewhat speculative, it provides useful information for the further design of efficient catalysts for ethanol dehydrogenation. In particular, it implies that such catalyst should exhibit the following features: 1) a high density of Si–OH groups in silica, 2) a high Ag dispersion on the silica surface, and 3) a close proximity of the Si–OH and Ag sites.

Work is in progress for the development of such catalysts.

Conclusions

A silica-supported Ag catalyst has been shown to be an efficient heterogeneous catalyst for the oxidant-free dehydrogenation of ethanol into acetaldehyde. The catalyst shows a higher activity (TOF = $3.4 \pm 0.8 \text{ s}^{-1}$) than more expensive supported Au catalysts.

A mechanism for the oxidant-free dehydrogenation of ethanol into acetaldehyde over the silica-supported Ag catalyst is proposed based on the results of in situ FTIR spectroscopic studies and kinetic experiments. The first step involves the activation of ethanol on silica to yield a hydrogen-bonded surface complex. The next step is concerted C–H bond cleavage on a Ag site and proton abstraction on a silica site. This step is the rate-determining step of the reaction as evidenced by the observation of the primary isotopic effects for the conversion of CH_3CD_2OH and CH_3CH_2OD . The final step of the reaction includes desorption of H_2 and acetaldehyde, which regenerates the active sites.

The mechanism proposed suggests that an efficient Ag catalyst for ethanol dehydrogenation should have a high density of Si–OH groups on the silica support, a high Ag dispersion, and it should be characterized by the close proximity of the Si–OH and Ag sites. The results demonstrate that less expensive catalysts than Pt- or Au-based catalysts can be designed by the optimization of the acid–base properties of the support, Ag particle size, and by control of the distance between the metal and the active sites of the support.

Experimental Section

Catalyst preparation

The Ag/SiO₂ catalyst was prepared by the incipient wetness impregnation of SiO₂ (Karpov Chemical Plant) with an aqueous solution of AgNO₃ to attain a Ag content of 10 wt.%. After impregnation, the catalyst was dried at 393 K and calcined at 773 K for 3 h in a flow of air.

Catalyst characterization

The chemical composition of the sample was determined by AAS. $N_{\rm 2}$ sorption–desorption isotherms were measured at 77 K by using

an automated porosimeter (Micrometrics ASAP 2000). The surface OH groups were characterized by FTIR spectroscopy in the region of $3000-4000 \text{ cm}^{-1}$. TEM images were obtained by using a JEOL 1200 EX II electron microscope operated at 100 kV. Samples were placed on a microgrid carbon polymer supported on a Cu grid by deposition of a few droplets of a suspension of the ground sample in ethanol on the grid followed by drying under ambient conditions.

Catalyst evaluation

The Ag/SiO₂ catalyst was tested for ethanol dehydrogenation under atmospheric pressure. Catalytic experiments were performed in flow-type fixed-bed reactor. In a typical experiment, the catalyst (2 g, fraction 0.5–1 mm) was loaded into the quartz tubular reactor, which was purged with N₂ at 873 K for 0.5 h followed by reduction under a H₂ flow at 573 K for 0.5 h. Ethanol was fed in to the reactor by using a Razel syringe pump. He (20 mL min⁻¹) was used as a carrier gas, and methane was used as an external standard. The reaction temperature was 573 K, and the weight hourly space velocity (WHSV) was varied within 2.0–6.0 h⁻¹. The reaction products were analyzed online by using GC (Crystal 2000 M) equipped with a 50 m capillary column with SE-30.

In situ spectroscopic studies

In situ IR spectra were recorded by using a Nicolet Protégé 460 instrument fitted with a stainless-steel IR cell with CaF₂ windows connected to a conventional flow-reaction system. The sample was pressed into a self-supporting wafer (20 mg) and placed in the IR cell. Spectra were recorded with an accumulation of 64 scans at 4 cm⁻¹ optical resolution. Before each experiment, the catalyst disk was heated in a He flow (40 mLmin⁻¹) at 573 K for 2 h and reduced in a H₂ flow (20 mLmin⁻¹) at 573 K for 0.5 h followed by cooling to 373 K and purging with He for 20 min. Ethanol was dosed to a flow of He by using a microsyringe pump, and the adsorption time was 30 s at 373 K. After adsorption, the weakly bonded ethanol was purged with a He flow (20 mLmin⁻¹) for 50 s. Then the He flow was stopped, and the spectra were recorded every 20 s. A reference spectrum of the catalyst wafer under He recorded at 373 K was subtracted from each spectrum.

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Keywords: dehydrogenation • IR spectroscopy • silver • reaction mechanisms • supported catalysts

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FULL PAPERS

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Mechanistic Study of Ethanol Dehydrogenation over Silica-Supported Silver



Every mechanism should have a silver lining: Ethanol is selectively converted into acetaldehyde over Ag supported on silica. The Ag particles and SiOH groups of silica act in a complementary manner in a concerted mechanism, which is proposed based on in situ FTIR spectroscopic studies and kinetic experiments with specifically deuterated ethanol. The proposed mechanism shows the way for the design of efficient supported Ag catalysts.