

CHEMICAL KINETICS
AND CATALYSIS

Activity of Calcined Ag, Cu, Au/TiO₂ Catalysts
in the Dehydrogenation/Dehydration of Ethanol

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Abstract—The catalytic activity of the anatase TiO₂ and M^{z+}/TiO₂ with supported ions M^{z+} = Ag⁺, Cu²⁺, Au³⁺ in vapor phase conversions of ethanol is investigated at temperatures of 100–400°C. It is shown that the yields of acetaldehyde and ethylene decline for the most active catalyst Cu²⁺/TiO₂ but increase for TiO₂ and Ag/TiO₂. The drop in the activation energy of the dehydrogenation reaction over calcined samples is linearly correlated with the one in the reduction potential of M^{z+} to Cu⁺, Au⁰, Ag⁰ and the ionic radius of M^{z+} in the crystal. The energies of activation for ethylene formation change in the series TiO₂ > Au³⁺ > Cu²⁺ > Ag⁺ and TiO₂ ≈ Cu²⁺ ≈ Ag⁺ > Au³⁺ for the calcined samples. The rate of pyridine adsorption, considered as an indicator of the activity of acid sites, is a linear function of ion charge +z = 1, 2, 3, and slows by two-thirds after calcination.

Keywords: M^{z+}/TiO₂ catalyst, ethanol dehydrogenation/dehydration, catalytic activity.

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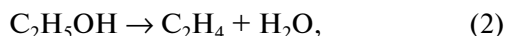
INTRODUCTION

The environmentally friendly wasteless processing of raw plant materials into valuable energy products include catalytic ethanol conversion. Supported catalysts are convenient systems whose composition and preparation can be easily varied in order to change the direction of the reaction. Calcination of the catalyst is an important procedure with a choice of conditions: temperature, duration, medium [1, 2]. The active phase is generated on the support surface during the thermolysis of precursor salt, but the activity often passes through a maximum as the calcination temperature rises in a stream of oxygen or air. Upon the dehydrogenation of ethanol, the yield of aldehyde grows after the calcination of copper containing Sibunit-based catalysts [3]. In [4], it was noted that thermal treatment and the introduction of Cu²⁺ and Ag⁺ ions increases the photocatalytic activity of TiO₂.

In [5, 6], we studied the conversion of ethanol over supported M^{z+}/TiO₂ (anatase) catalysts exposed to UV radiation. The products of transformation were acetaldehyde, ether, and ethylene formed by the dehydrogenation reactions



and dehydration



In this work, calcination was selected for the pretreatment of M^{z+}/TiO₂.

The aim of this work was to determine the effect calcination has on the activity of TiO₂ with supported ions of silver, copper, and gold in the catalytic conversion of ethanol in the vapor phase.

EXPERIMENTAL

Silver, copper, and gold ions were deposited by impregnating TiO₂ (anatase) (Aldrich, Canada) with aqueous solutions of AgNO₃, CuCl₂, and AuCl₃ (all of reagent grade) and keeping it for 24 h at room temperature. The concentration of the precursor solutions was calculated for monolayer deposition of the support surface $S_{\text{sp}} = 10 \text{ m}^2/\text{g}$ with metal ions of (wt %) 0.9 Ag, 0.55 Cu, and 1.65 Au by weight of the carrier. After impregnation, the samples of series I were dried for 2 h at 100°C. Samples of series II, further subjected to calcination, were heat treated in air at 450°C for 1 h. The catalytic properties of M^{z+}/TiO₂ were tested in a flow-type setup with gas-chromatographic analysis under the conditions elevated temperature when the constant activity of a sample was achieved for each preset temperature. The time required to attain a steady state was no greater than 15 min. The standard pretreatment was used before each experiment: catalyst with mass $m = 0.03 \text{ g}$ was heated in a microreactor in a stream of helium at 400°C for 0.5 h; a mixture of

Table 1. Total ethanol conversion (W , %) and selectivity toward aldehyde (S , % values in parentheses) over M^{z+}/TiO_2 (I) without and (II) with calcination of the samples

Sample	Series	Reaction temperature, °C				
		200	250	300	350	400
TiO ₂	I	0.4 (100)	2.2 (100)	7.0 (88)	15.7 (74)	31.1 (36)
	II	0.6 (100)	2.9 (100)	8.5 (89)	14.8 (70)	24.5 (42)
Ag/TiO ₂	I	4.7 (100)	8.8 (100)	15.3 (100)	17.5 (93)	22.9 (71)
	II	0.5 (100)	4.6 (92)	11.2 (91)	18.3 (77)	18.6 (53)
Cu/TiO ₂	I	2.3 (88)	14.0 (80)	22.2 (65)	28.0 (47)	26.1 (24)
	II	1.1 (100)	9.1 (100)	21.0 (100)	24.2 (84)	24.9 (65)
Au/TiO ₂	I	2.3 (100)	4.5 (100)	9.2 (84)	19.8 (65)	27.6 (50)
	II	3.0 (100)	5.5 (100)	10.7 (91)	17.0 (86)	17.7 (82)

Table 2. Experimental activation energy (E_a , kJ mol⁻¹) and pre-exponential factor ($\ln N_0$ in parentheses) of the formation of products from ethanol (I) without and (II) with calcination of the samples.

Sample	Series	Aldehyde	Ethylene	Ether
TiO ₂	I	44 (1.6)	163 (22.5)	82 (6.5)
	II	47 (2.9)	141 (18.8)	81 (6.7)
Ag/TiO ₂	I	27 (-1.4)	105 (10.8)	No
	II	48 (-3.0)	139 (17.7)	51 (0.4)
Cu/TiO ₂	I	58 (6.5)	111 (14.4)	59 (4.2)
	II	92 (13.7)	144 (18.3)	132 (15.5)
Au/TiO ₂	I	28 (-1.4)	136 (18)	67 (3.6)
	II	26(-2.0)	81 (6.0)	80 (5.8)

alcohol vapor and helium was then fed in and the temperature of the reactor was lowered to 100°C.

(1) Acetaldehyde, (2) ethylene, and (3) diethyl ether were among the products of alcohol conversion at the temperatures marking the onset of formation on a control sample of TiO₂: (1) 150°C and (2 and 3) 300°C before calcination; (1) 190, (2) 280, and (3) 270°C after calcination. The deposition of M^{z+} had little effect on their value. In the absence of oxygen, carbon oxides were present in the products in small amounts and only at $T > 360^\circ\text{C}$. The yield of dehydrogenation and dehydration products (N , g mol⁻¹ h⁻¹) was calculated using the formula

$$N = Wc_0wk/m \times 22.4,$$

where W is the depth of alcohol conversion, c_0 is the initial content of alcohol in the mixture, w is the flow rate (1.1 L h⁻¹), and k is a calibration coefficient that depends on the nature of a substance. Alcohol conver-

sion (W , %) and product selectivity (S , %) were determined using N values.

The acidic activity on the surface of M/TiO_2 samples of series I and II was analyzed by comparing the rate of in situ pyridine adsorption from octane via spectrophotometry (analytic a.b., 251 nm; extinction $\epsilon = 1742 \text{ L cm}^{-1} \text{ mol}^{-1}$).

RESULTS AND DISCUSSION

Temperature regions for the reactions of (1) dehydrogenation and (2, 3) dehydration differed, and the introduction of ions did not affect the nature of $T-N$ dependences. However, yields N of products was dependent on the nature of M^{z+} and the calcination of the sample, as can be seen from Fig. 1. Most active was the sample with copper; least active was the sample with gold (Figs. 1c, 1d). Only the activity of TiO₂ increased after calcination; it fell for M^{z+}/TiO_2 samples, as is evident from the data in Table 1 and Fig. 1.

The only product of the catalytic process was aldehyde, while alcohol dehydration began above 300°C. The amount of ethylene grew sharply as the temperature rose, and the diethyl ether yield passed through a maximum, indicating two routes of ethylene formation: a single stage (reaction (2)) and two stages occurring via the intermediate formation of ether (reaction (3)) and its decomposition $C_2H_5OC_2H_5 \rightarrow 2C_2H_4 + H_2O$. In series II, the selectivity toward aldehyde was higher than in series I over the samples with Cu^{2+} and Au^{3+} .

Experimental activation energies E_a and the pre-exponential factors N_0 of product formation (Table 2) were determined from the Arrhenius plots.

From the data in Fig. 2 and Table 2, it can be seen that the values of E_a increase in the series of products alde-

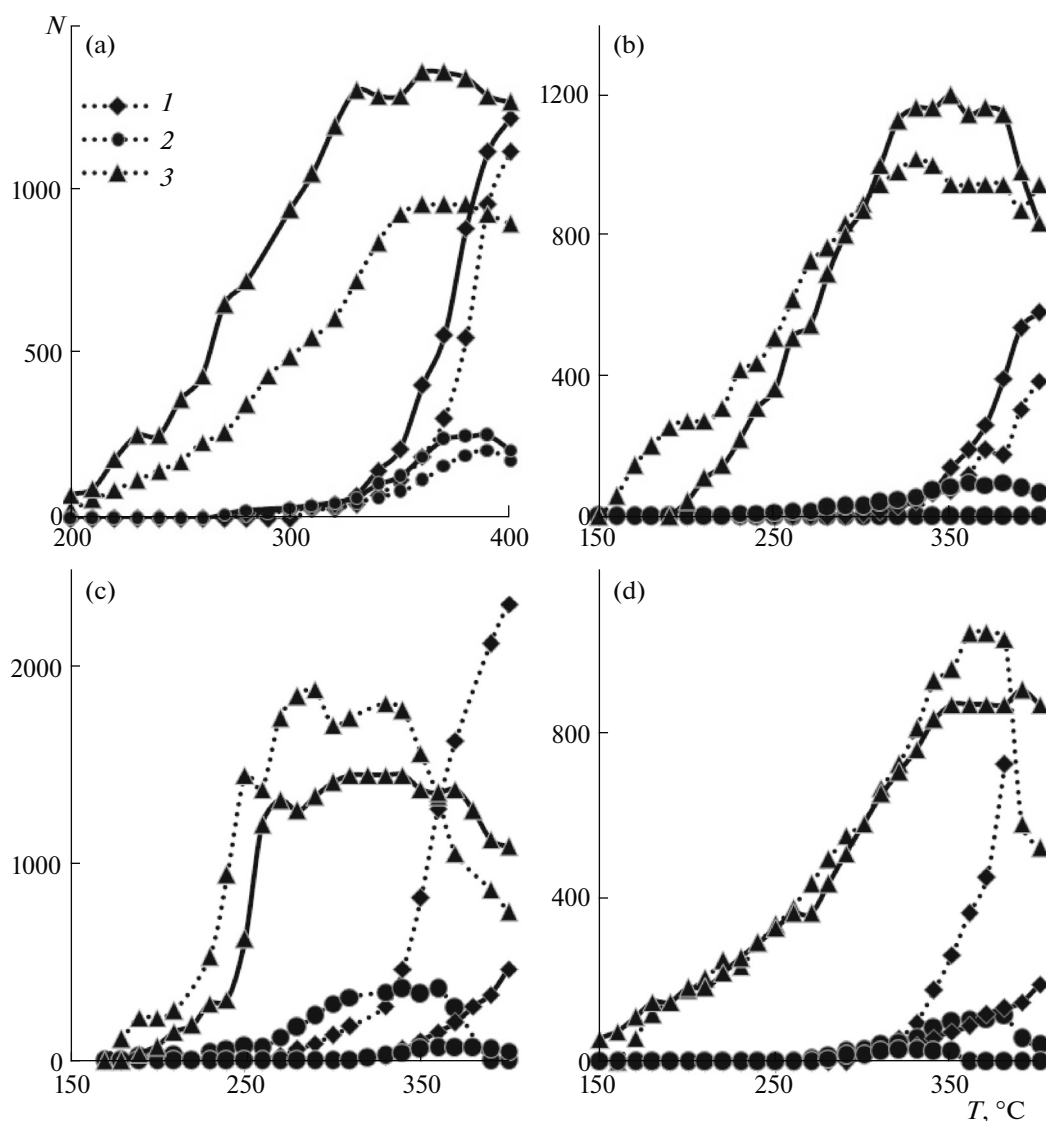


Fig. 1. Temperature dependence for the yields of products from ethanol conversion (N , $\mu\text{mol mol}^{-1} \text{h}^{-1}$). Solid lines denote calcined samples; dotted lines, those without calcination: (1) olefin, (2) ether, (3) aldehyde; (a) TiO_2 , (b) Ag, (c) Cu, (d) Au.

hyde \rightarrow ether \rightarrow ethylene. The high values of $E_{a,2}$ are compensated for by that of the pre-exponential factor. The series $E_{a,1} \leq E_{a,3} < E_{a,2}$ testifies to the different nature of the centers of (1) dehydrogenation and (2, 3) dehydration of alcohol. Reaction (1) occurs via an oxidation-reduction mechanism over centers containing oxygen vacancies, while the active center (an acid mechanism) in dehydration is the ion pair $\text{M}-\text{O}$ [7].

Calcination of the support raises the aldehyde yield by a factor of 2–3 due to an increase in the pre-exponential factor (the number of active centers), while the activation energy $E_{a,1}$ of the dehydrogenation reaction remains the same. The increase in the olefin yield is in contrast associated with a drop in $E_{a,2}$. The parameters

of the intermolecular dehydration of alcohol (ether formation) are not affected by TiO_2 calcination.

Among the samples of $\text{M}^{z+}/\text{TiO}_2$, the catalyst containing Cu has the highest activity, which falls after calcination. The maximum of the aldehyde yield is 100°C lower than the one given in [3].

Based on the yield of aldehyde, the activities of series I and II Au/TiO_2 are identical. For the products of alcohol dehydration, however, they fall upon calcination. Only $\text{Ag(II)}/\text{TiO}_2$ sample, similarly to $\text{TiO}_2(\text{II})$, showed activity increase at temperatures of catalytic process above 350°C .

A linear correlation of experimental activation energy $E_{a,1}$ of aldehyde formation with reduction potential M^{z+} and ion radius R is observed for the cal-

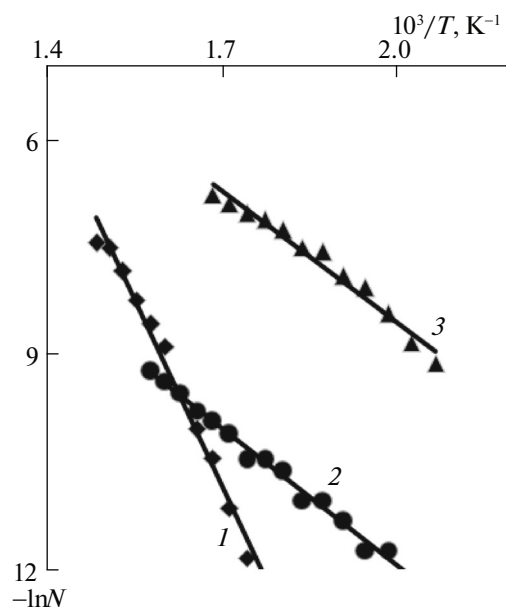


Fig. 2. Arrhenius plots for the yields of products from ethanol conversion over the surface of Ag/TiO₂ with calcination: (1) olefin, (2) ether, (3) aldehyde.

cined samples (Fig. 3a) [8, 9]. Note that the reduced form in the case of copper is Cu⁺, while for gold it is Au⁺; this is consistent with straight line E_a-R . This indicates a change in the charge of M under the conditions of the dehydrogenation reaction. An analysis of the activity of M^{z+} centers before catalysis revealed a

linear relationship between the rate of adsorption of pyridine as a probe molecule and the charge of ions Ag⁺-Cu²⁺-Au³⁺ (Fig. 3b). It can be seen that calcination reduces the adsorption activity of M^{z+}/TiO₂, maintaining this linearity.

Note that there is a linear correlation between the parameters of the Arrhenius equation and the Constable ratio $\ln N_0 = A + BE_a$ for all of our catalysts; this is known as the linear compensation effect (LCE) [10]. Values A and B are identical for the reactions of (2) intramolecular and (3) intermolecular dehydration of ethanol, so ethylene and ether form on the same centers. The straight line of the LCE for acid-type reactions (2) and (3) does not coincide with the one for reaction (1) that occurs on the electron acceptor centers. Some are also of the opinion that the selective conversion of ethanol to aldehyde over oxides involves O-H groups and highly dispersed particles M in the mechanism considered by the authors for the Ag/SiO₂ system [11].

CONCLUSIONS

The deposition of Ag⁺, Cu²⁺, Au³⁺ ions leads to an increase in TiO₂ activity in the conversion of ethanol, while calcination leads to a reduction. The experimental energy of activation for the formation of products increases in the series aldehyde → ether → ethylene. In the dehydrogenation reaction over calcined samples, it correlates linearly with the growth of reduction potential Cu²⁺/Cu⁺ → Ag⁺/Ag⁰ → Au³⁺/Au⁺ and the ion radius in the series Cu²⁺ → Ag⁺ → Au⁺.

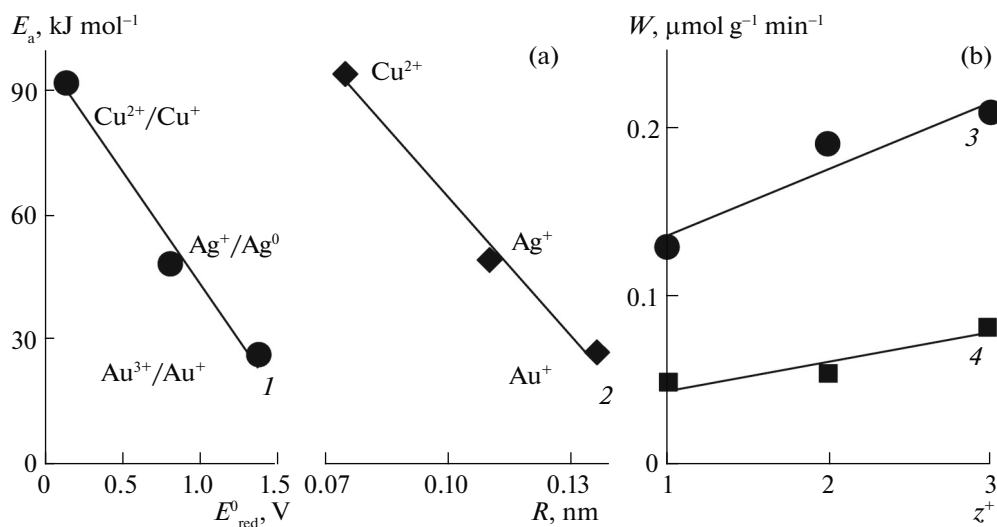


Fig. 3. Linear correlation between the experimental activation energy of ethanol dehydrogenation over calcined M^{z+}/TiO₂ and (1) the reduction potential and (2) ion radius. Linear correlation of the rate of pyridine adsorption and the charge of a supported ion (3) before and (4) after the calcination of M^{z+}/TiO₂, where M^{z+} = Ag⁺, Cu²⁺, Au³⁺.

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