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Kinetics of Methanol Decomposition on $Cu/ZnO/ZrO_2$ Catalysts

by R. Grabowski[*] and A. Kozłowska

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,
ul. Niezapominajek 8, 30-239 Kraków, Poland

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Interaction of methanol with $Cu/ZnO/ZrO_2$ (with different copper content) has been investigated by gravimetric and TPD methods. The TPD measurements of methanol adsorption on these catalysts show that it forms the complexes of two types. The first complex (I) decomposes at low temperature (453 K) yielding H_2 and CO_2 and second (II) decomposes at the temperature (573 K) giving CO and H_2. In the process of the decomposition of the complex (I) takes part water which is adsorbed on the surface of the catalyst and the decomposition of the complexes (II) occurs without participation of adsorbed water. Gravimetric measurements of methanol adsorption show that Cu facilitates adsorption of methanol and that an increase of copper content leads to the changes in the kinetics of methanol adsorption and its decomposition. On the basis of gravimetric measurements a model of methanol adsorption and decomposition on $Cu/ZnO/ZrO_2$ catalyst has been proposed and the rate constants of methanol adsorption (k_a) and decomposition with and without participation of water (k_1 and k_2) have been determined.

Key words: methanol decomposition, methanol adsorption, kinetics model

Recently the $Cu/ZnO/ZrO_2$ catalysts have been intensely studied, because of their activity in the synthesis of methanol from CO_2 and H_2 [1–13] and in the steam reforming of methanol [14–17]. The former reaction is of interest, because it opens a perspective of processing CO_2, in particular contained in biogases, in which also hydrogen is present. The steam reforming is considered currently as an alternative source of hydrogen for fuel cells [18–20].

The active catalyst is obtained by reducing CuO, contained in the oxide precursor, usually in the stream of 5% H_2 in nitrogen. As it was found, the catalyst containing copper and zirconia behave in bifunctional manner, with Cu and zirconia having different but complementary roles [21,22]. Copper serves to dissociate molecular hydrogen and supply atomic hydrogen by spillover to the reactive intermediates located on zirconia.

Previous studies of methanol adsorption and decomposition on Cu/SiO_2 [23,24], ZrO_2 [25–29], CuO/ZrO_2 [29] and $Cu/ZrO_2/SiO_2$ [30] showed that the forms of adsorption and nature of adsorbed species depend strongly of the nature of the catalyst,

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[*] Corresponding author.

but in the case of $Cu/ZrO_2/SiO_2$ catalyst the decomposition of methanol occurred primarily on ZrO_2, while the primary function of copper was the removal of hydrogen.

In this paper, we examine the kinetics and the mechanism by which the methanol is decomposed over $Cu/ZnO/ZrO_2$ catalyst with different content of copper, using gravimetric and TPD methods.

EXPERIMENTAL

The $CuO/ZnO/ZrO_2$ precursors were obtained by adding into water small portion of sodium carbonate solution and a solution containing nitrates of Cu and Zn, and $ZrOCl_2$ at a constant pH = 7 and at 338 K. The precipitated residue was aged for 24 h, repeatedly washed with demineralised water, filtered and dried for 3 h at 383 K and subsequently calcined on air for 3 h at 623 K. The specific surface area of the oxide precursors was determined with the BET method using an Autosorb-1 Quantachrome apparatus with nitrogen as adsorbate at 77.5 K. ChemBet-3000 Quantachrome was used for the reduction of the catalyst samples *in situ* to determine the surface of the reduced catalysts.

The gravimetric measurements of the rate of the methanol adsorption were carried by a vacuum microbalance S3DV from Sartorius, placed in a chamber with volume 2415.1 cm^3 linked to a standard vacuum system. A sample of an oxide precursor (around 0.5 g) was outgassed at 523 K, and then oxidized under gaseous O_2 at a pressure of about 2 kPa, cooled down to 473 K and outgassed again under vacuum until constant mass was attained. Next the sample was reduced in hydrogen at 523 K under 4–5.3 kPa, until a constant mass. Water formed was removed from the system by a cold trap, cooled by liquid nitrogen. After reduction the samples were outgassed under the pressure of 10^{-5} kPa. The measurements of methanol adsorption and decomposition were carried out isothermally at 473 K for three different pressures of methanol. Pressure of the gas adsorbate was measured by a membrane manometer-122A Baratron from MKS Instruments.

TPD measurements were carried out in a microreactor coupled to a mass spectrometer VG/Fision Quartz-200D. About 0.5 g of a sample was reduced by 3 h in the stream of the mixture of He + 5% H_2 at the temperature 523 K. After reduction the sample was flushed in He for 30 min and a stream of a mixture of methanol or water vapour and He was introduced at 523 K for 0.5 h. The system then was cooled down to 333 K and again flushed with helium for several minutes. The desorption was performed from 333 K to 873 K in a stream of helium (30 cm^3/min at 8 deg/min). The mass peaks were registered as follows: CO_2 = 44, CO = 28, H_2O = 18, methanol = 32, H_2 = 2.

RESULTS AND DISCUSSION

The TPD profile for adsorbed water on the reduced $Cu/ZnO/ZrO_2$ catalyst (Fig. 1b) shows two peaks: first with the maximum at about 370 K and the second very broad and complex peak at ~ 430 K. A similar TPD profile of adsorbed water is observed for ZnO/ZrO_2 support (Fig. 1a). Figure 1c shows a TPD profile, which has been done directly after the reduction of $Cu/ZnO/ZrO_2$ catalyst at 523 K in the flow of Ar + 5% H_2. The amount of water, which desorbs from the surface of the freshly reduced catalyst, is about 60–70% of that on reduced catalyst (Fig. 1b).

TPD studies of the methanol adsorption on reduced $Cu/ZnO/ZrO_2$ catalyst containing 62.5% of Cu (Fig. 2a) show that methanol adsorbs and decomposes on the surface of the catalyst. As can be seen in Fig. 2a, the quantity of the methanol, which desorbs without a decomposition, is small (methanol profile ~410 K) and the main part of adsorbed methanol desorbs as a product of its decomposition (H_2, CO and CO_2). The hydrogen profile shows two peaks – at ~460 K and at ~580 K. The first maximum on hydrogen profile is accompanied by the maximum on CO_2 profile, and the second maximum is connected with the maximum on the CO profile. The water profile shows no maximum in the temperature range, where are observed the maxima for CO, CO_2 and H_2 and a small peak of desorbed water appears above ~723 K, what hints to the participation of adsorbed water in the process of methanol decomposition.

In the case of the methanol adsorption on the support ZnO/ZrO_2 (Fig. 2b), the methanol adsorption/desorption process and its decomposition occur differently than in the case of the $Cu/ZnO/ZrO_2$ catalyst. Methanol desorbs from the surface of the support without the decomposition up to ~ 560 K with the maximum on the profile of methanol desorption at 370 K. At 510 K the peaks corresponding to H_2, CO_2 and CO appear, indicating the decomposition of methanol. The amount of desorbed water in this temperature region abruptly decreases what hints to its participation in the reaction of the methanol decomposition. This process attains the maximum at 580 K. As can be seen from the Fig. 2b, the methanol decomposition with the participation of water and generation of CO_2, CO and H_2 on the support occur at the same time at a higher temperature than for $Cu/ZnO/ZrO_2$ catalyst. At ~670 K the process of the methanol decomposition is practically finished and the strongly adsorbed water remaining on the ZnO/ZrO_2 surface is desorbed. These facts allow to write down the reactions, which describe the process of methanol adsorption and its decomposition on the support and on the catalyst

$$CH_3OH_a \Leftrightarrow CH_3OH_g \qquad k_a, k_d \qquad (1)$$

$$CH_3OH_a + H_2O_a \rightarrow CO_2 + 3H_2 \qquad k_1 \qquad (2)$$

$$CH_3OH_a \rightarrow CO + 2H_2 \qquad k_2 \qquad (3)$$

where (g) and (a) denote gaseous and adsorbed phase respectively and k_a, k_d, k_1 and k_2 are the respective rate constants.

On the $Cu/ZnO/ZrO_2$ catalyst, the reactions (1), (2) and (3) occur separately at different temperatures, while on the support reaction (1) plays the main role, and reactions (2) and (3) occurs simultaneously (Figs. 2a and 2b).

These reactions are similar to those proposed by Rozowskii *et al.* [33–35] for the methanol adsorption and decomposition on the surface of the reduced $Cu/ZnO/Al_2O_3$ catalyst.

At the conditions of the reaction (T, V = const), reaction (1) leads to a decrease of the pressure in the measurement chamber and the reactions (2) and (3) are associated with an increase of the pressure.

Kinetics experiments of methanol adsorption on the catalysts with the different content of copper were carried out at 473 K on prior reduced catalyst at 523 K. After the reduction, practically all weakly adsorbed water (peak with maximum at 370 K in

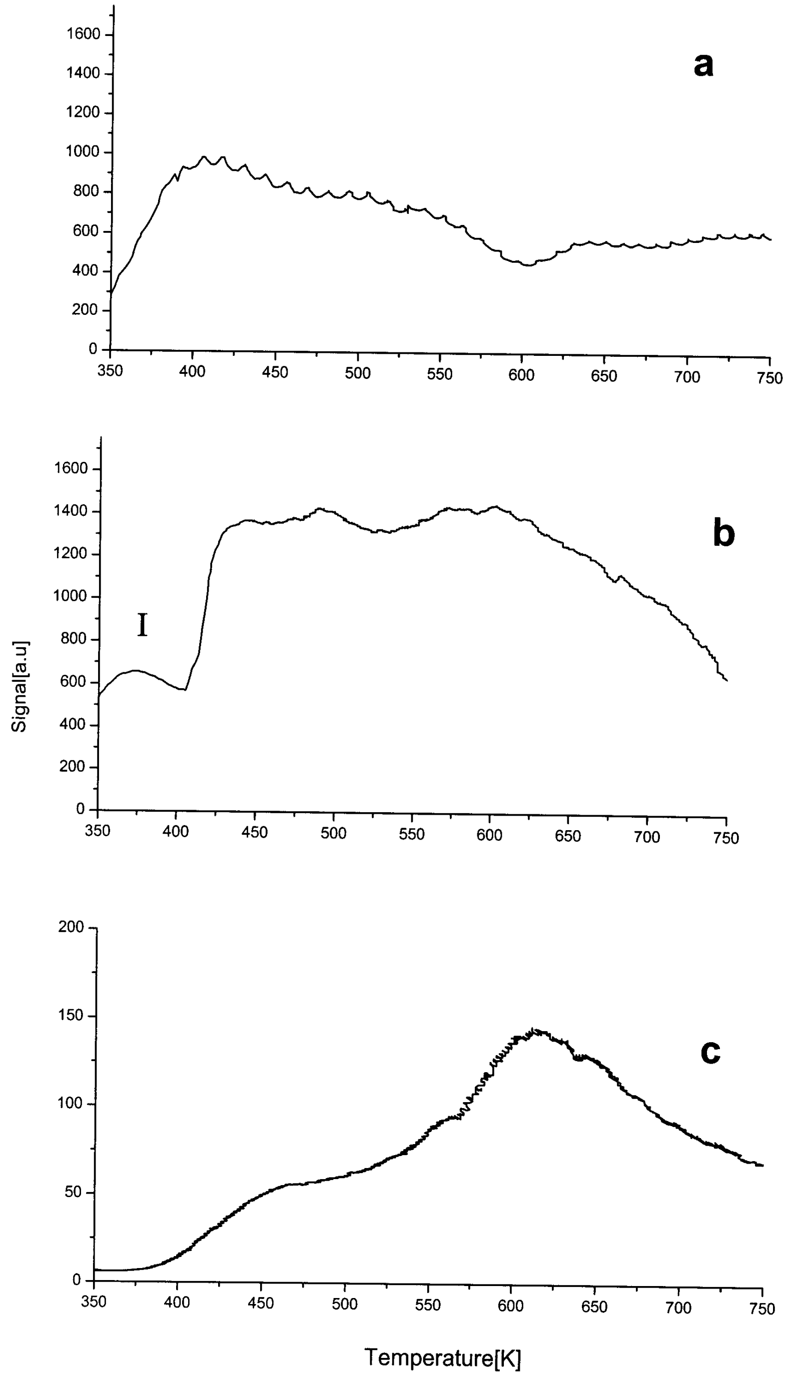

Figure 1. **a**. Evolution of water in TPD experiments after sorption of water on support ZnO/ZrO_2.
b. Evolution of water in TPD experiments after sorption of water on $Cu/ZnO/ZrO_2$ catalyst.
c. Evolution of water in TPD experiment on reduced $Cu/ZnO/ZrO_2$ catalyst after reduction at 523 K.

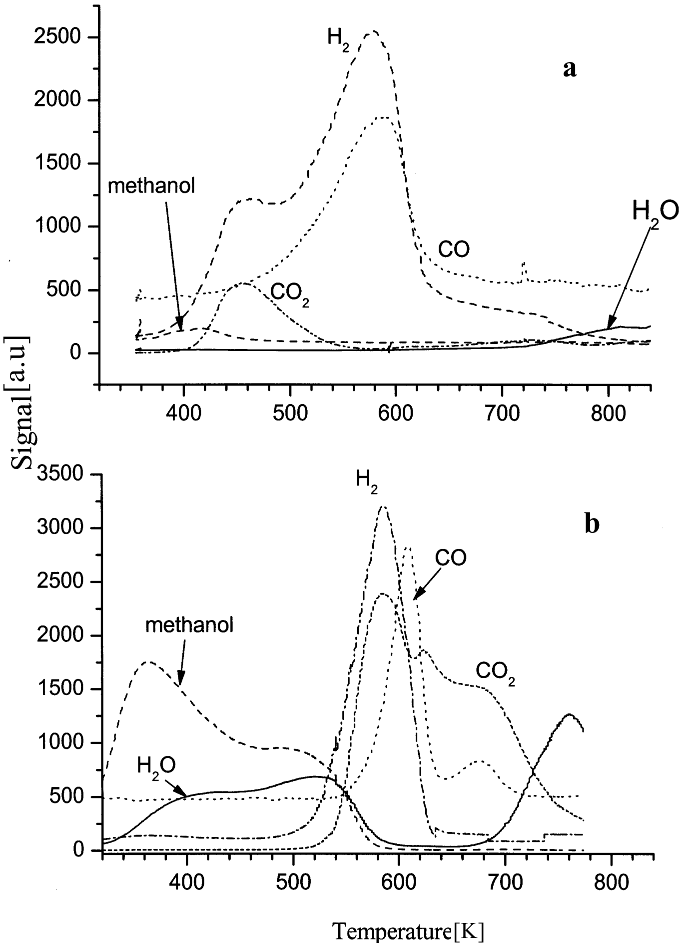

Figure 2. **a**. Evolution of methanol, CO, CO_2 and H_2 after adsorption of methanol on reduced 62.5% $Cu/ZnO/ZrO_2$ catalyst at 473 K. **b**. Evolution of methanol, CO, CO_2 and H_2 after sorption of methanol on support at 473 K.

Fig. 1b) and a significant part of more strongly adsorbed water is desorbed, and the remaining part of adsorbed water can react with the adsorbed methanol (Eq. 2) giving CO_2 and hydrogen. The amount of the adsorbed water on the surface of the catalyst, which can react with methanol, is limited and after its depletion methanol can only decompose according to (3). On the basis of the TPD results, one can propose a model of methanol adsorption and its decomposition over $Cu/ZnO/ZrO_2$ catalyst. Assuming that the rate of the of change in the surface coverage by methanol is proportional to the difference between the rates of methanol adsorption and methanol consumption in the reaction of its decomposition described by (2) and (3), one can write

$$\frac{d\theta_{\mathrm{meth}}}{dt} = k_a(1 - \theta_{\mathrm{Meth}} - \theta_{\mathrm{W}})p_{\mathrm{Meth}} - k_1\theta_{\mathrm{Meth}}\theta_{\mathrm{W}} - k_2\theta_{\mathrm{Meth}} \tag{4}$$

where θ_{Meth} and θ_{W} are the surface coverages by methanol and water respectively, and p_{Meth} is the partial pressure of methanol in the measurement cell. k_a is the rate constant for the methanol adsorption (1), k_1 and k_2 are the rate constants corresponding to the methanol decomposition, according to (2) and (3) respectively. As the volume of the measurement cell is big, pressure changes are small in the course of the measurements and, thus, the mean value of pressure was taken in the calculations.

The rate of the change in the coverage of the catalyst surface by the adsorbed water is given by

$$\frac{d\theta_{\mathrm{W}}}{dt} = -k_1\theta_{\mathrm{Meth}}\theta_{\mathrm{W}} \tag{5}$$

The coverages by methanol and water can be defined as

$$\theta_{\mathrm{Meth}} = \frac{N_{\mathrm{Meth}} \cdot \sigma_{\mathrm{Meth}}}{S_{\mathrm{BET}}} \tag{6}$$

and

$$\theta_{\mathrm{W}} = \frac{N_{\mathrm{W}} \cdot \sigma_{\mathrm{W}}}{S_{\mathrm{BET}}} \tag{7}$$

where N_{W} and N_{Meth} are numbers of molecules of adsorbed water and methanol respectively. S_{BET} is the specific surface area of the reduced catalyst and σ_{W} and σ_{Meth} are cross sections of water and methanol molecules respectively. From (6) and (7) the mass of the adsorbed methanol can be calculated as

$$m_{\mathrm{Meth}} = \frac{N_{\mathrm{Meth}} M_{\mathrm{Meth}}}{N_A} = \frac{\theta_{\mathrm{Meth}} \cdot S_{\mathrm{BET}}}{\sigma_{\mathrm{Meth}}} \cdot \frac{M_{\mathrm{Meth}}}{N_A} = \alpha \cdot \theta_{\mathrm{Meth}} \tag{8}$$

and similarly the mass of the adsorbed water

$$m_{\mathrm{W}} = \frac{N_{\mathrm{W}} M_{\mathrm{W}}}{N_A} = \beta \cdot \theta_{\mathrm{W}} \tag{9}$$

At a given moment the mass of a sample is given by

$$m = m_o + m_{Meth} + m_W \tag{10}$$

where m_o is the initial mass of the sample, m_{Meth} is the mass of the adsorbed methanol and m_W is the mass of water present on the catalyst surface after the reduction and prior to the adsorption experiment. Substituting expressions for m_{Meth} and m_W from (8) and (9) to (10) one obtains

$$m - m_o = \alpha \cdot \theta_{Meth} + \beta \cdot (\theta_o - \theta_W) \tag{11}$$

where α and β are constants and θ_o is the initial coverage of the surface of the reduced catalyst by water.

(11) describes the rate of change of the mass of the catalyst as a function of time. By solving (4) and (5), combining with (11) and next fitting (11) to experimental results, one can calculate rate constants k_a, k_1 and k_2. As it is showed by the TPD results (Fig. 2b), some amount of adsorbed water is present on the surface of the catalyst after the reduction. The initial coverage by water θ_o, corresponding to the amount of the water present prior to the adsorption experiments, is unknown and can be determined in the frame of the above presented model. This water is responsible for the decomposition of methanol according to (2).

The experimental results of the methanol adsorption at 473 K on three different catalysts and on the support are shown in Fig. 3 for three different pressures of methanol (3, 12, 50Tr). As one can see, the increase of the copper content in the studied catalysts brings about the increase in the rate of the methanol decomposition. This effect (Fig. 3a) is observed as a decrease of the mass of the catalyst with time and additionally as an increase of the pressure in the measurement cell (Fig. 4a). In the case of the support, a decrease of the pressure over the sample is observed at this temperature (Fig. 4b) and the methanol adsorption is not accompanied by the decomposition (Fig. 3d). For catalyst containing 2% of Cu the kinetic and adsorption properties are more similar to the properties of the support than to those of the catalyst with higher content of copper.

Values of the rate constants calculated for the model described above are given in Table 1. Values of k_2 for the support are close to those calculated for the catalyst containing 2% of Cu and they increase with increasing copper content, which means that the reaction of the methanol decomposition according to (3) occurs mainly with the participation of copper. In the case of the methanol decomposition according to (3), the mean value of rate constant k_2 attains ~1 with the decrease of the content of coper. It is due to the fact that in (4), the rate constant describing the methanol decomposition according to (3), is in fact the sum of the rate constants of the proper decomposition of methanol – k_{2p} and the methanol desorption – k_d.

$$k_2 = k_{2p} + k_d \tag{12}$$

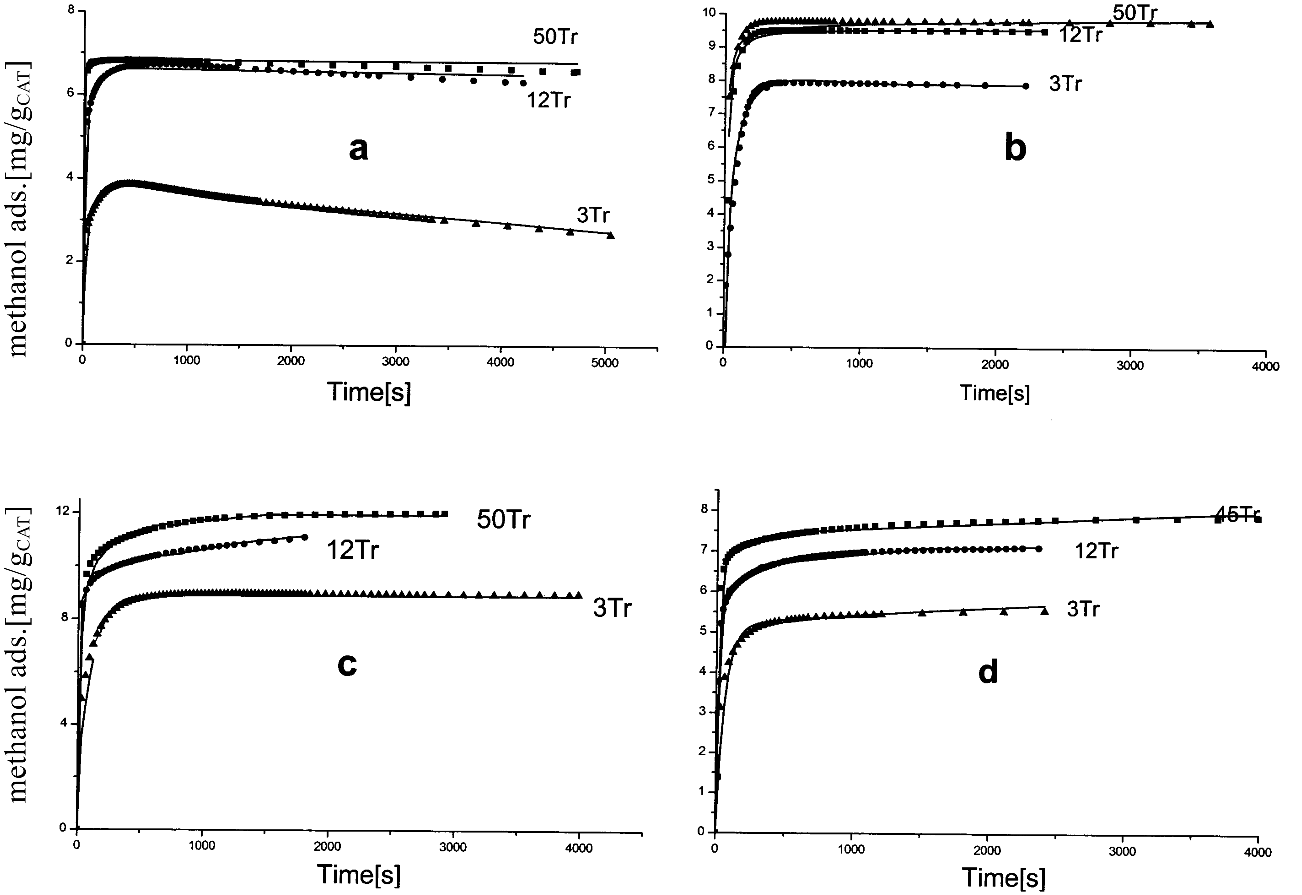

Figure 3. Experimental data and calculated results for adsorption of methanol on Cu/ZnO/ZrO_2 catalysts with different content of copper (**a**, **b**, **c**) and on support ZnO/ZrO_2 (**d**) for three different pressures of methanol (50, 12, 3Tr) at 473 K.

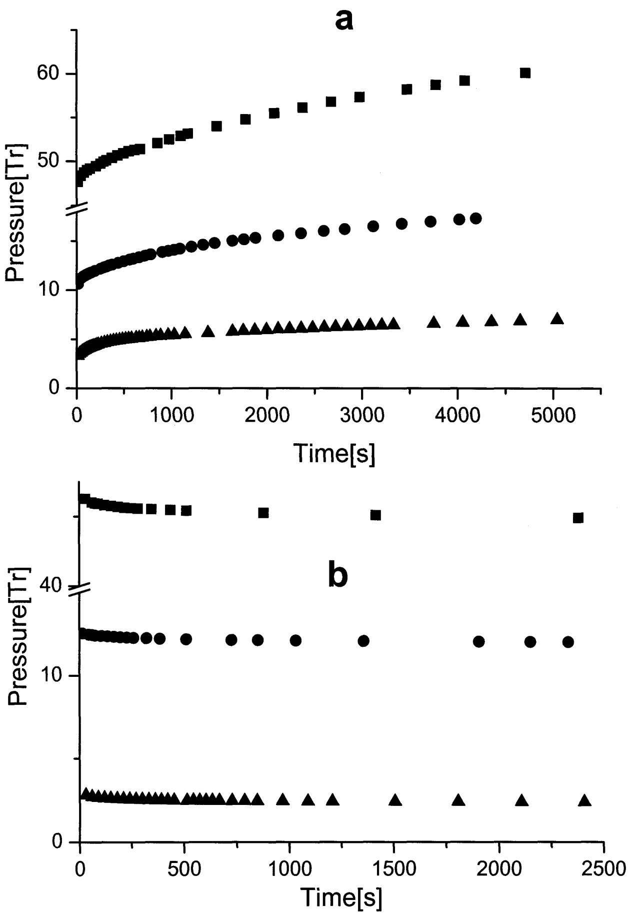

Figure 4. Changes of the pressure in the measurement cell in time of the kinetic experiments for the Cu/ZnO/ZrO$_2$ catalyst (**a**) and for the support (**b**) at 473 K.

As a result of the decrease of the copper content in the catalyst, k_{2p} approaches zero and the limit value of k_2 becomes k_d. When the content of copper is small, the desorption of methanol, not accompanied by the decomposition, begins to play the main role. For the catalysts with higher contents of copper, rate constant k_2 is several times higher than k_{DES} and is mainly responsible for the methanol decomposition according to (3).

The same is valid of k_1. For the support and for the catalyst containing 2% of Cu, values of k_1 are close to zero and the corresponding reaction practically does not occur. This means that the presence of copper is decisive for the decomposition of methanol with the participation of water.

Table 1. Kinetic parameters for methanol adsorption.

Catalyst	Specific surface area after reduction $[m^2/g]$	k_a $[s^{-1}\ kPa^{-1}]$	k_1 $[s^{-1}]$	k_2 $[s^{-1}]$	θ_o
62.5% $CuZnOZrO_2$	52				
50Tr of methanol		1.4	12	9	0.05
12Tr of methanol		1.8	10	6	0.20
3Tr of methanol		2.0	12	5	0.15
10% $CuZnOZrO_2$	85				
50Tr of methanol		2	9	6	0.28
12Tr of methanol		2	4	7	0.15
3Tr of methanol		0.6	3	7	0.11
2% $CuZnOZrO_2$	85				
50Tr of methanol		1.7	0.6	1.4	0.20
12Tr of methanol		0.8	0.02	1.2	0.20
3Tr of methanol		1.0	0.05	0.4	0.20
$ZnOZrO_2$	91				
45Tr of methanol		0.2	0.01	1.3	0.15
12Tr of methanol		0.4	0.02	1.3	0.15
3Tr of methanol		0.5	0.02	0.7	0.15

In [36] the adsorption of the reactants has been studied for the catalyst reduced at 473 K and standardized at 623 K (activation in the mixture of the reactants). On the basis of these experiments surface coverages by water molecules were calculated for the catalysts and they were 0.28 and 0.2 respectively. As one can calculate from Table 1, the mean value of θ_o, determined on the basis of the model described above, is around 0.17, which is in good accordance with values calculated from the independent static adsorption experiments and which additionally support the proposed model of the methanol adsorption and decomposition.

The results supporting the important role of copper in the methanol adsorption and decomposition have been obtained in the experiments investigating the interaction of methanol with Cu/SiO_2, ZrO_2/SiO_2 and $Cu/ZrO_2/SiO_2$. The experiments involved *in situ* infrared spectroscopy, as well as programmed desorption and reaction [21,22,30]. The authors have shown that, in the presence of copper, surface complexes formed during the adsorption process decompose to CO, CO_2 and H_2, whereas in the absence of Cu these complexes decompose very slowly. The quoted papers postulate that Cu provides sites on which hydrogen atoms formed during the dehydrogenation of species located on zirconia can recombine efficiently and desorbed as H_2. Thus, the methanol decomposition over the $Cu/ZrO_2/SiO_2$ catalyst occurs primarily on ZrO_2, while the primary role of Cu is the removal of hydrogen.

Similar results were obtained by Chan *et al.* [31]. Using different surface techniques the authors have revealed an important role of copper in the process of the methanol adsorption and decomposition by increasing the intensity of the CO_2 desorption.

Studies of the methanol adsorption on zirconia supported methanol aerogel catalysts [29] have shown that the decoposition of methanol takes place during the TPD experiments, with the production of CO_2, H_2 and CO on the surface of Cu/ZrO_2 and

CuO/ZnO/ZrO$_2$ catalyst. The decomposition is parallel to the desorption of the non-decomposed methanol. The progressive oxidation of methoxy groups occurs around 473 K on the copper containing catalysts during the TPD process. In contrast, on coppperless catalysts, the methoxy groups are stable up to 623 K, hydrogen is not released and remains stored on the surface of the catalyst in the form of OH groups.

CONCLUSIONS

1. Water is strongly adsorbed both on the support and the catalyst, and stays on the surface up to 773 K. The amount of water, which remains after the reduction of the catalyst at 523 K, is smaller and is equal ~70% of the water, which is adsorbed on the freshly reduced catalyst.

2. Methanol is adsorbed in reversible and irreversible form on the surface of the catalyst as well as of the support. The amount of methanol reversibly adsorbed on the catalyst is small in comparison with that adsorbed on the support.

3. Both the TPD results and the kinetic calculations show that the reaction of methanol decomposition to CO_2 and H_2 described by k_1 is more sensitive to the presence of copper than the reaction of methanol decomposition to CO and H_2 described by k_2. For the support, the onset of the peak corresponding to the decomposition of the irreversible adsorbed methanol to CO, H_2 and to CO_2 and H_2 is observed at 623 K. The onset of the methanol decomposition to CO_2 and H_2 is lowered about 120 K, and to CO and H_2 by only about 20 K, in the presence of copper on the catalyst.

4. The presence of copper in the studied catalyst leads to changes of its adsorptive properties: (i) it increases the amount of adsorbed methanol, (ii) it changes the rate and the temperature of the methanol decomposition, both in the reaction to CO and H_2 and CO_2 and H_2.

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