Kinetics and Catalysis, Vol. 41, No. 6, 2000, pp. 753–755. Translated from Kinetika i Kataliz, Vol. 41, No. 6, 2000, pp. 831–833.

Methanol Decomposition in a Water–Methanol Equimolar Mixture on a Nickel-Promoted Copper–Zinc–Cement Catalyst

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Received September 30, 1999

Abstract—Methanol decomposition in a water–methanol equimolar mixture is studied in the presence of a nickel-promoted copper–zinc–cement catalyst. Methanol decomposition at 200–300°C on the oxide and reduced forms of the catalyst yields a gas with an H_2/CO ratio close to two. The use of an equimolar CH_3OH–H_2O mixture under analogous conditions enables obtaining gaseous products with a hydrogen concentration up to 75 vol %.

INTRODUCTION

The catalytic decomposition of methanol in its equimolar mixture with water leads to the formation of hydrogen-containing gaseous mixtures. These processes can be used to obtain the mixtures of hydrogen and carbon monoxide, which are supplied to internal combustion engines when methanol is used as a fuel [1, 2]. Methanol decomposition is also a promising method for the preparation of syngas, which can further be used in small-scale technologies and research studies. Finally, water–methanol mixtures can be a source of virtually pure hydrogen after the removal of carbon oxides from resulting gaseous mixtures using adsorption by monoethanolamine or selective adsorption under pressure [3].

Methanol decomposition in its aqueous solutions can be carried out in the presence of metallic catalysts (platinum-group metals) [4] or metal oxide catalytic systems containing Cu, Ni, Cr, Fe, or Mn supported on alumina, silica, or other materials [5–7]. The highest selectivity in methanol steam reforming is observed in the case of copper-containing catalysts with an activity depending on the choice of support and a preparation procedure.

EXPERIMENTAL

Catalytic decomposition of methanol and a water–methanol equimolar mixture was carried out in a quartz reactor (with an inner diameter of 20 mm) within a flow-type setup at an atmospheric pressure and 200–450°C. The catalyst volume was 10 ml. The space velocity of liquid starting materials (w) was 0.6–20.0 h^{-1}. The catalyst composition was 5% NiO, 35% CuO, 32% ZnO, and talum (aluminocalcium cement consisting of calcium mono- and dialuminates). A 1–2-mm fraction was taken. The samples were calcined in a flow of air at 400°C for 5 h. In major cases, the catalyst was treated at 200°C for 3 h by reagent vapors (by methanol or a water–methanol equimolar mixture) before runs (sample K1). In some cases, the same catalyst was treated with hydrogen at 450°C at a space velocity of 1000 h^{-1} for 3 h (sample K2). Each run lasted 2 h. Gaseous products were analyzed by chromatography using an LKhM-8MD chromatograph with a katharometer and a 2.2-m column packed with activated carbon AR-3 (0.250–0.315-mm fraction). The temperature was 140°C. Liquid products were analyzed by GLC using an LKhM-8MD chromatograph with a 1.7-m column packed with 10% Tween-6.0 on Polychrome-1 at 70°C.

RESULTS AND DISCUSSION

Methanol Decomposition

Data presented in Tables 1 and 2 show that, with an increase in temperature, the methanol conversion increases for both oxide (K1) and reduced (K2) catalysts. Sample K1 treated with the vapors of starting materials at 200–250°C shows a noticeable activity. At 250°C, K1 and K2 are almost equally active. At 300°C, the conversion reaches 100%. With an increase in temperature, the concentrations of H_2 and CO in gases decreases in both cases, while the concentrations of CO_2 and CH_4 grow (Tables 1 and 2). The concentrations of dimethyl ether (DME) and methyl formate (MF) decrease, and they become undetectable in the products at 300°C. The product composition substantially depends on the pretreatment procedure. As can be seen from Table 1, at temperatures above 300°C, the concentrations of water, carbon dioxide, and methane in the reaction products substantially increase in the

Table 1. Composition of the products of methanol decomposition on the oxide sample K1 (the space velocity is $w = 0.6$ h^{-1})

T, °C	Methanol conversion, %	Product composition, mol %						
		H_2	CO	CO_2	CH_4	DME	MF	H_2O
200	38.7	66.9	27.8	0.9	0.2	0.3	3.8	0.1
250	67.0	67.4	30.7	1.0	0.3	0.2	0.3	0.1
300	100	66.4	28.9	2.4	2.1	0	0	0.2
350	100	20.1	3.9	18.8	37.1	0	0	20.1
400	100	18.9	1.9	20.4	39.0	0	0	19.8

Table 2. Composition of the products of methanol decomposition on the reduced sample K2 (the space velocity is $w = 0.6$ h^{-1})

T, °C	Methanol conversion, %	Product composition, mol %						
		H_2	CO	CO_2	CH_4	DME	MF	H_2O
200	6.3	67.1	25.2	1.2	0.1	0.1	5.9	0.4
250	72.4	66.9	29.9	1.9	0.5	0.1	0.4	0.3
300	100	64.4	26.5	4.3	4.7	0	0	0.1
350	100	60.5	19.1	10.3	9.6	0	0	0.5
400	100	43.3	8.2	17.1	26.9	0	0	4.5

presence of K1. This is probably due to the fact that the NiO phase is reduced at these temperatures [8]:

$$NiO + H_2 = Ni + H_2O, \qquad (I)$$

$$NiO + CO = Ni + CO_2. \qquad (II)$$

Due to these reactions, the concentration of metallic nickel increases in the surface layer of a catalyst and nickel favors the methanation reaction:

$$CO + 3H_2 = CH_4 + H_2O. \qquad (III)$$

Changes in the concentration of gas-mixture components observed at 300–400°C is probably due to the structuring of the catalyst surface layer with the participation of surface nickel (Table 1). Another important question is the composition of the gaseous mixture. Methanol decomposition results in the formation of carbon monoxide and hydrogen:

$$CH_3OH = CO + 2H_2. \qquad (IV)$$

CO_2 formation is explained by the fact that CO methanation (III) yields water, which then reacts with CH_3OH (methanol hydrolysis) and CO (water-gas shift):

$$CH_3OH + H_2O = CO_2 + 3H_2, \qquad (V)$$

$$CO + H_2O = CO_2 + H_2. \qquad (VI)$$

Indeed, an increase in the yield of methane is accompanied by an intensive formation of CO_2 and a decrease in the concentration of CO. Note that reaction (III) consumes hydrogen. This agrees with experimental data according to which the concentration of hydrogen in the mixture decreases at temperatures higher than 300°C. However, we should take into account that hydrogen is also consumed for the reduction of the NiO–CuO phase. When the preliminarily reduced sample K2 is used, changes in the component concentrations are smooth (Table 2). As in the case of oxide catalyst sample K1, methanation is intensified at temperatures higher than 300°C. The hydrogenation of carbon dioxide (VII) is also possible with further reactions of water (V) and (VI):

$$CO_2 + 4H_2 = CH_4 + 2H_2O. \qquad (VII)$$

Thus, additional amounts of hydrogen are formed by reactions (V) and (VI).

Equimolar Water–Methanol Mixture Decomposition

To obtain hydrogen-rich gas, we carried out a series of experiments on the study of the properties of catalyst K1 in the process of the decomposition of the equimolar methane–water mixture (V). Data presented in the figure and Table 1 suggest that

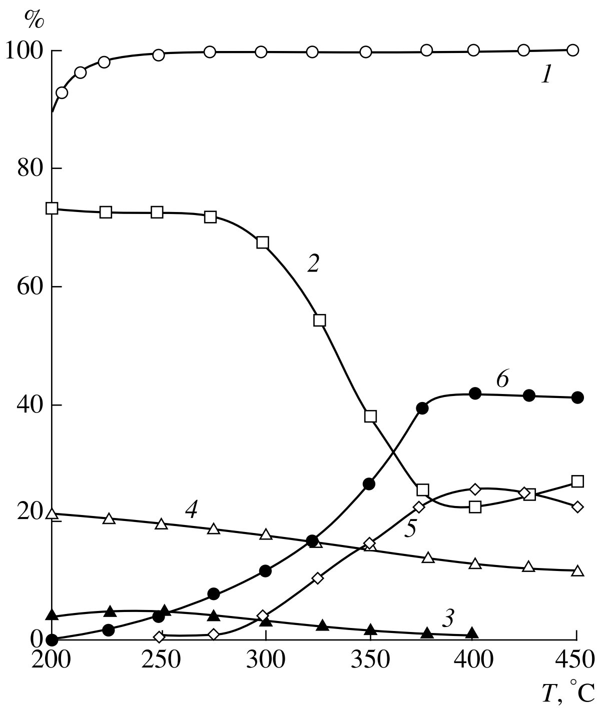
(a) Water belonging to the equimolar mixture completely suppresses methanol dehydrogenation that could form MF;

(b) Complete methanol conversion is achieved at as low a temperature as 225°C;

(c) The concentration of CO_2 decreases with an increase in the temperature;

(d) The concentration of CO_2 in the gaseous products is higher than the concentration of CO at all temperatures studied;

(e) The hydrogen concentration in the mixture decreases similarly to the concentrations of water and



Effect of temperature on the conversion of (*1*) methanol and the product composition in the course of the decomposition of the equimolar methanol–water mixture (w = 0.6 h^{-1}): (*2*) H_2, (*3*) CO, (*4*) CO_2, (*5*) CH_4, and (*6*) H_2O.

methane; and the concentrations of H_2O, H_2, and CH_4 are virtually constant at temperatures higher than 350°C.

On this basis, we conclude that there are two schemes for the conversion of the equimolar methanol–water mixture: (1) immediate hydrolysis by reaction (V) and (2) the stepwise decomposition by reactions (IV) and (VI). The first scheme (reaction of CH_3OH and H_2O) is preferable. Hydrogen is consumed for the hydrogenation of CO and CO_2 with the formation of methane and water. Experiments on the effect of the space velocity of starting materials on the decomposition of the equimolar water–methanol mixture in the presence of catalyst K1 showed that an increase in the space velocity from 0.6 to 20.0 h^{-1} results in a decrease in the methanol formation to 91.5% at 300°C. Because of a decrease in the contact time, side processes become less intensive, and the concentration of CH_4 decreases to 0.5 vol %, while the concentration of hydrogen increases to 75 vol %.

CONCLUSION

Thus, we showed that the nickel-promoted copper–zinc–cement catalyst is highly active in the processes of methanol decomposition in the equimolar water–methanol mixture at 200–300°C. These processes produce syngas with an H_2/CO ratio close to 2 (from methanol) or with an H_2 concentration of up to 75% (from the equimolar water–methanol mixture). Both on oxide (K1) and reduced (K2) forms of the catalyst, the methanation process, methanol steam reforming, and a water-gas shift reaction occur.

REFERENCES

1. Smal', F.V. and Aksenov, E.E., *Perspektivnye topliva dlya avtomobilei* (Promising Fuel for Cars), Moscow: Transport, 1979, p. 41.
2. *Kataliz v C1-khimii* (Catalysis in C1 Chemistry), Kaim, W., Ed., Leningrad: Khimiya, 1987, p. 97.
3. Janda, Z., *Hutnik*, 1987, no. 8, p. 317.
4. Bond, G.C., *Catalysis by Metals*, New York: Academic, 1962.
5. Amphlett, J.C., Evans, M.J., Jones, R.A., *et al.*, *Can. J. Chem. Eng.*, 1981, vol. 59, p. 720.
6. Tada, A., Yoshino, T., and Iton, H., *Chem. Lett.*, 1987, vol. 2, p. 419.
7. Gel'man, V.N., Karvovskaya, A.A., Golosman, E.Z., and Nechugovskii, A.I., *Khim. Prom-st.*, 1994, no. 12, p. 22.
8. Ismailov, T.S., Galsekov, T.Sh., and Ismailova, E.Sh., *Zh. Obshch. Khim.*, 1974, vol. 44, no. 12, p. 2738.