ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2011, Vol. 85, No. 7, pp. 1140–1144. © Pleiades Publishing, Ltd., 2011.
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CHEMICAL KINETICS AND CATALYSIS

Synthesis of Dimethyl Ether from CO and H_2

N. I. Kosova, L. N. Kurina, and L. P. Shilyaeva
Tomsk State University, Tomsk, 634050 Russia
e-mail: kosova@mail.tsu.ru

Received August 5, 2010

Abstract—Thermodynamic conditions for synthesizing dimethyl ether from synthesis gas are determined. The optimum conditions of the process are as follow: $T \sim 300°C$ at $p = 3$ MPa for two catalysts loaded into the reactor: methanol synthesis catalyst (Katalco-58) and catalyst of methanol dehydration to dimethyl ether (γ-Al_2O_3). The changes that occur with the catalysts during this process are demonstrated by electron scanning microscopy.

Keywords: synthesis of dimethyl ether, thermodynamic conditions, catalysis.
DOI: 10.1134/S0036024411070168

INTRODUCTION

Ecological problems and the depletion of oil reserves are forcing researchers to seek alternative energy resources. The synthesis of dimethyl ether (DME) from CO-containing gas is considered as possible way of replacing oil stock. DME has been widely used as a refrigerant, extractant, propellant, and intermediate product in organic synthesis. Its low boiling temperature (–25°C) allows us to accelerate the processes of mixture formation and combustion, reducing the ignition delay period and ensuring good engine start at low ambient temperatures. The high oxygen content in DME (35%) ensures the smokeless combustion of fuel without formation of solid particles, preventing the atmosphere from being polluted with exhaust gases [1].

There are two technologically possible ways of synthesizing DME from synthesis gas: (1) in two series rectors for methanol synthesis and its dehydration; (2) in one reactor over a bifunctional catalyst, due to the simultaneous occurrence of both methanol synthesis reaction and its dehydration to DME. The catalysts used are an oxide catalyst for methanol synthesis and Al_2O_3 or zeolites for dehydration of the resultant methanol to dimethyl ether. Even though hybrid catalysts have been designed, research continues into commercial methanol synthesis catalysts, such as SNM-1 [2] and ICI, KTM, SüdChemi [3] as components for methanol synthesis followed by dehydration into DME on an acid catalyst. In this work, we study the process of producing DME from synthesis gas from a mixture of methanol catalyst Katalco-58 and γ-Al_2O_3.

EXPERIMENTAL

Commercial catalyst Katalco-58 (Johnson Mattley Catalysts), referred to below as R-1, was used for methanol synthesis, and γ-Al_2O_3 (Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk) was used as a catalyst for methanol dehydration. The phase composition of the samples was determined on a Shimadzu XRD 6000 X-ray diffractometer with a copper anode (CuK_α). The obtained data were compared with the tabulated values according to the ASTM card file using the Match software (Phase Identification from Powder Diffraction, Version 2.1). R-1 was shown to have a composition of $CuO/ZnO/Al_2O_3$; alumina was used as the γ form.

The porous structure and specific surface area of the samples prior to and after conducting catalytic studies were determined by BET using a TriStar II (3020) automated gas adsorption analyzer. The distribution of acid sites was obtained by ammonium desorption (table).

Prior to the experiment, the catalyst was reduced in a hydrogen–nitrogen mixture (10 vol % $H_2 + N_2$) at 300°C for 3 h. The recovery procedure was selected

Characteristics of R-1 and γ-Al_2O_3 catalysts prior to and after catalysis

Catalyst		s_{spec}, m^2/g	V, cm/g	R, Å	β
R-1	prior to	110	0.29	81	0.064
	after	87	0.27	125	–
γ-Al_2O_3	prior to	250	0.71	77	0.254
	after	311	0.68	87	–

Note: S_{spec} is specific surface area, V is pore volume, R is pore radius, and β is catalyst acidity, mmol NH_3/g.

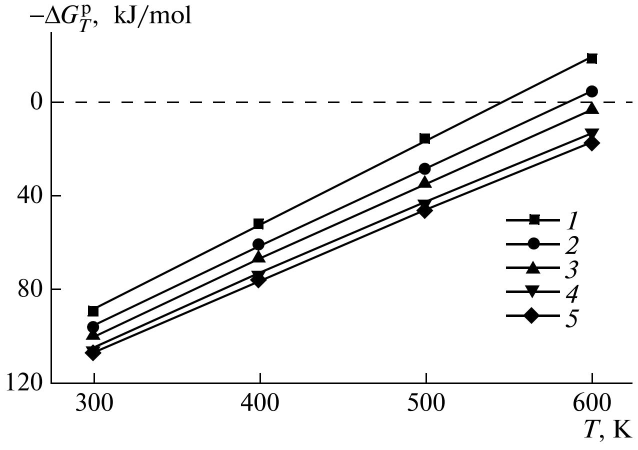

Fig. 1. The calculated Gibbs energy values (ΔG_T^p) of reaction (3) over the 300–600 K temperature range at (*1*) 1, (*2*) 2, (*3*) 3, (*4*) 5, and (*5*) 6 MPa.

from the results of temperature-programmed reduction (TPR) of the original catalyst for methanol synthesis, which showed reduction peaks in the 150–300°C temperature range. TPR spectra were obtained on a Chemisorb 2750 chemisorption analyzer. A weighed portion of the sample was reduced in a mixture flow (10% H_2 in Ar); the linear heating rate was 10 K/min to 350°C. The signal was measured using a thermal conductivity detector. Water vapor was frozen out in a trap; this eliminated the error contributed to the measurement of the mixture's thermal conductivity from the water formed in the reaction and released from the sample.

A setup enabling us to perform the process under elevated pressure was used for our catalytic studies. The volume of the loaded catalysts (1–0.5 mm fraction) was 5 cm^3. Hydrogen and carbon monoxide were fed from gas bottles. The purity of the outgoing gases and the composition of the resultant products were determined chromatographically. The investigation of morphological features of the samples prior and after the catalytic experiments was performed by scanning electron microscopy (SEM) on a VEGA II LMU electron microscope with a primary electron beam energy of 20 keV.

RESULTS AND DISCUSSION

Thermodynamics. DME synthesis from the CO+ H_2 mixture comprises the following key reactions: synthesis of methanol, its dehydration, direct DME syn-

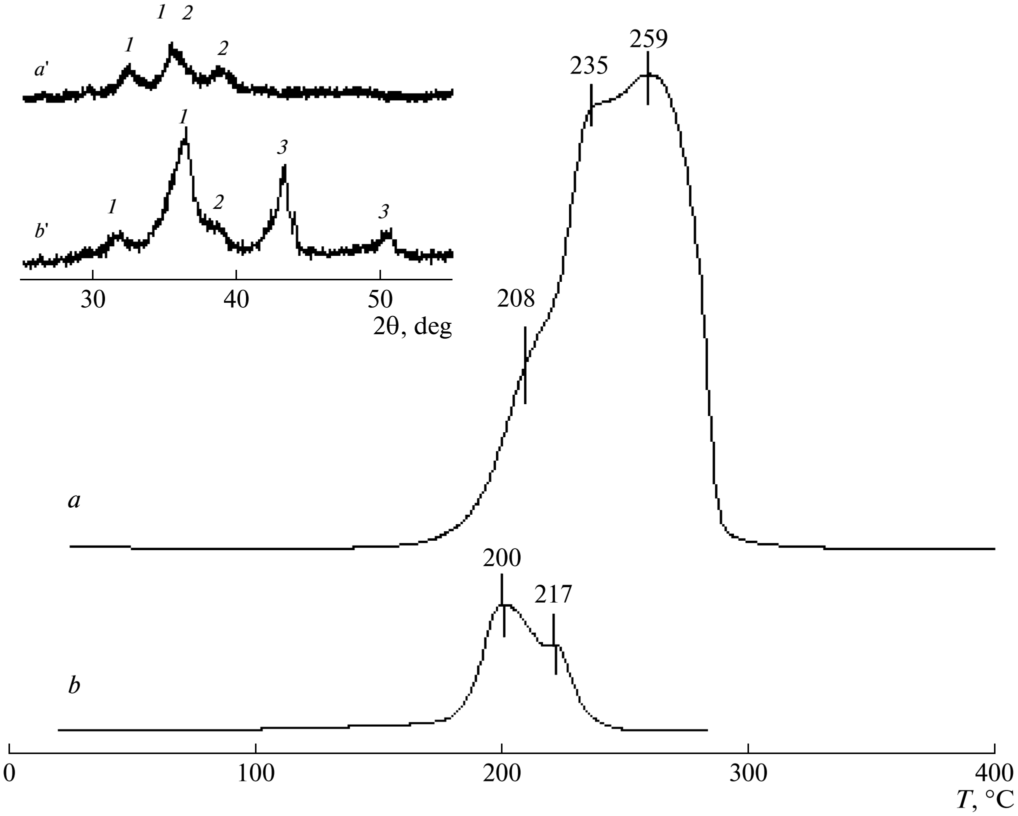

Fig. 2. The TPR spectrum of the initial (*a*) catalyst R-1 reduced in a hydrogen–argon mixture (17 vol % H_2 + Ar) at 300°C for 3 h, and (*b*) after a catalytic experiment. The XRD patterns of (*a*') the initial R-1 sample and (*b*') after catalysis: (*1*) ZnO, (*2*) CuO, and (*3*) Cu.

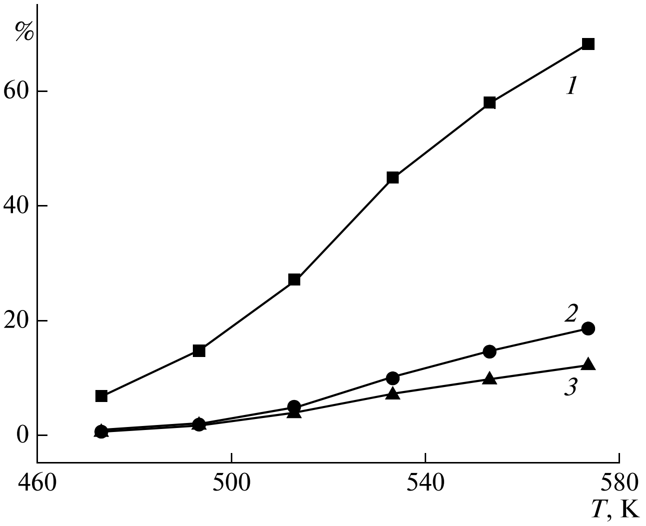

Fig. 3. The effect of temperature on (*1*) CO conversion and (*2*) DME yield. Experimental conditions: $p = 3$ MPa, $H_2/CO = 2$, $\tau_{cont} = 6$ s; (*3*) concentration of CO_2, vol %.

thesis from synthesis gas, and a steam conversion reaction:

$$CO + 2H_2 \rightarrow CH_3OH, \quad \Delta H = -90.7 \text{ kJ/mol}, \qquad (1)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O, \quad \Delta H = -23.4 \text{ kJ/mol}, \qquad (2)$$

$$2CO + 4H_2 \rightarrow CH_3OCH_3 + H_2O, \quad \Delta H = -207.4 \text{ kJ/mol}, \qquad (3)$$

$$H_2O + CO \rightarrow CO_2 + H_2, \quad \Delta H = -41.2 \text{ kJ/mol}. \qquad (4)$$

The production of dimethyl ether directly from synthesis gas (3) is accompanied by heat release and a reduction in the number of moles; this process is therefore likely to be efficient at low temperatures and high pressures.

The changes in the Gibbs energy (ΔG_T^p) for the direct production of dimethyl ether from synthesis gas were calculated on the basis of Eq. (5) [4]:

$$\Delta G_T^p = \Delta G_T^0 + \Delta n RT \ln(p/p_0), \qquad (5)$$

where ΔG_T^p is the Gibbs energy at specified pressure p (Pa) and temperature T (K), kJ/mol; ΔG_T^0 is the change in the Gibbs energy calculated using the Temkin–Schwartzman equation [5] at specified temperature, kJ/mol; Δn is the change in the number of moles in the course of the reaction; and p_0 is the standard pressure (1.013×10^5 Pa). As can be seen from Fig. 1, the change in the Gibbs energy becomes more negative with increasing pressure; i.e., reaction (3) is allowed over the 300–600 K range, the pressure in the system starting from 3 MPa. At pressures below 2 MPa, the occurrence of the reaction is possible below 550–575 K.

Temperature-programmed reduction (TPR). Figure 2 shows the results from TPR of the methanol catalyst R-1 prior to and after catalysis. As can be seen, the original sample is reduced over the 150–300°C range. Since the sample contains copper, the reduction peaks with $T = 208$, 235, and 259°C (Fig. 2, curve *a*) are probably associated with the reduction of copper from the oxidized to the metallic state: Cu^{2+}–Cu^{+}–Cu^0 [6]. The amount of hydrogen absorbed was 0.003533 mol/g. A considerably smaller amount of hydrogen (0.000562 mol/g) was required for the reduction of the sample after catalysis; two peaks with $T = 200$ and 217°C were observed (Fig. 2, curve *b*).

It is likely that a small amount of copper remained in the oxidized state within the catalyst during catalysis. The XRD data presented in Fig. 2 provide support for this assumption; according to Fig. 2, the initial catalyst R-1 (Fig. 2, curve *a*') consists mainly of copper and zinc oxides, while two new peaks characteristic of metallic copper (Fig. 2, curve *b*') and negligible peaks of copper oxide are detected on the XRD pattern after the catalytic experiments.

Catalysis. The catalytic studies were performed with a hydrogen : carbon (II) oxide ratio of two. In order to ensure the complete reaction of the initial mixture with the catalyst surface, the following method for catalyst loading was used:

First bed: copper-containing catalyst R-1 for methanol synthesis;

Second bed: a mixture of methanol catalyst R-1 and γ-Al_2O_3 for methanol dehydration and conversion of the nonreacted CO and H_2;

Third layer: alumina γ-Al_2O_3 for methanol dehydration into dimethyl ether.

Figure 3 shows the effect of temperature on the yield of dimethyl ether, CO conversion, and formation of by-product CO_2 under pressure of 3 MPa, H_2/CO ratio = 2, contact time of 6 s. These conditions were selected in the course of the experiment as the optimum conditions. As can be seen, CO conversion and the yield of dimethyl ether attain their maximum values (68 and 18%, respectively) upon a single pass of the CO–H_2 mixture through the reactor at 300°C. The main contribution to the formation of carbon dioxide as a by-product is made by the reaction of steam conversion (4), since H_2O under these conditions interacts with CO, yielding hydrogen and carbon dioxide. The accumulation of CO_2 in the system can be regarded as a partial loss of carbon as well [7].

The catalytic data obtained coincide with the results from thermodynamic calculations; the reaction range lies below 600 K. With increasing temperature, however, the yield of DME and CO conversion under constant pressure increase, unlike the data presented in Fig. 1. In this case, reaction (3) occurs via a path

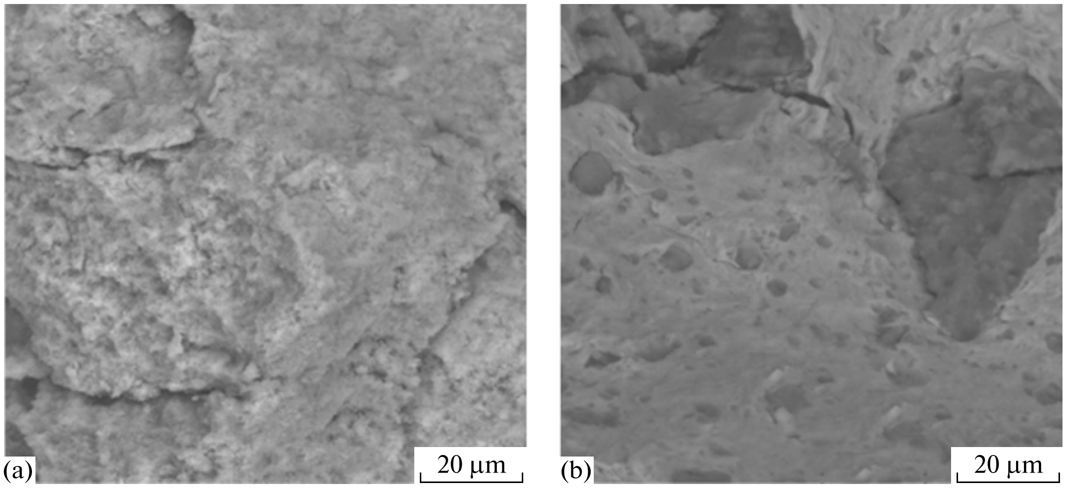

Fig. 4. Microimages of R-1 (a) prior to and (b) after catalytic experiments lasting 70 h.

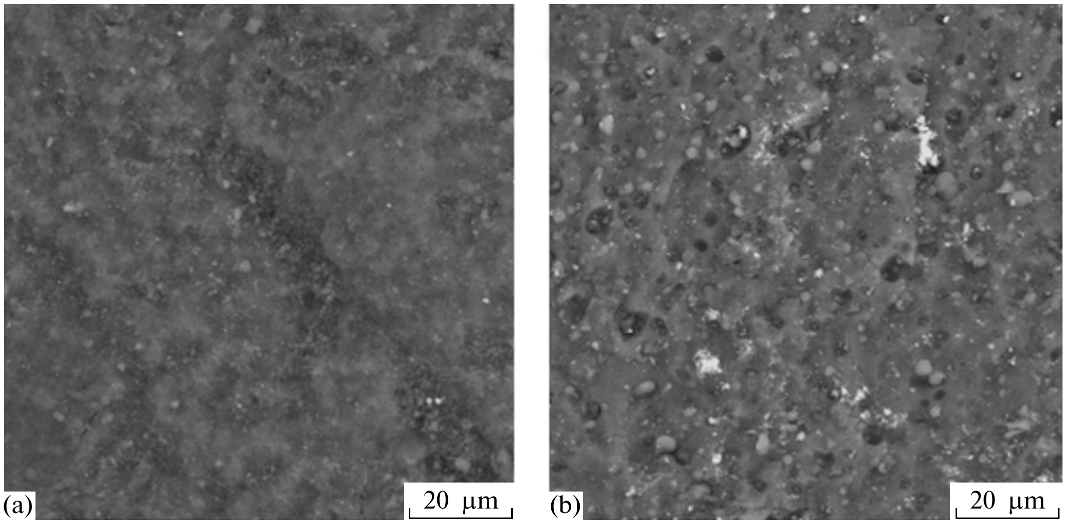

Fig. 5. Microimages of γ-Al_2O_3 (a) prior to and (b) after catalytic experiments lasting 70 h.

that does not obey the laws of thermodynamics. This could be due to the complexity of the process, since reactions (1)–(4) proceed simultaneously.

Surface morphology of the catalysts. Figure 4 presents microimages of the R-1 sample prior to and after the catalytic experiments. As can be seen, the surface of the initial methanol catalyst (Fig. 4a) is heterogeneous, uneven, and covered with fractures without the formation of any isolated particles. After the catalytic experiments with temperature and pressure varied from 200 to 300°C and from 1 to 5 MPa, respectively, there was a change in the catalyst morphology (Fig. 4b): the surface coalesced with the formation of individual dark cleavages. The average size of these formations varies from 1 to 40 μm. Even though the operating time of the catalyst was ~70 h, no carbon deposits were observed on its surface, as was supported by the data from differential thermal analysis.

Figure 5 shows microimages of γ-Al_2O_3 prior to and after the catalytic experiments. While the surface of the initial sample (Fig. 5a) is homogeneous, the surface of the dead catalyst (Fig. 5b) is covered with craters with an average diameter of 2 μm and individual particles with dimensions of ~1 μm. The formation of such holes is probably due to changes in the alumina volume under pressure; i.e., the crystalline form is likely to undergo a transformation due to the rearrangement of the electron shell of alumina [8]. The pore size increases simultaneously, (table), leading to the formation of holes on the surface.

CONCLUSIONS

When synthesis gas passes once over sequentially loaded R-1 and γ-A_2O_3 catalysts at 300°C, 3 MPa, $H_2/CO = 2$, and a contact time of 6 s, the DME yield is 18%, with CO conversion of 68%. The composition and structure of the catalysts for DME synthesis undergo changes under the influence of pressure and temperature. Copper oxide within the methanol catalyst R-1 is reduced in the course of catalysis to the metallic state, the surface coalesces, and the pore size of the alumina increases.

ACKNOWLEDGMENTS

This work was supported by the Federal Target Program, state contract no. 02.523.12.3023.

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