Dehydrogenation of methanol on low Cu and Re—Cu catalysts supported on sibunite

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The activity and selectivity of mono- and bimetallic catalysts containing copper and rhenium on sibunite were studied in the decomposition of methanol to methyl formate (MF), water, H₂, CO, and CO₂ at 200–400 °C. Methane is also formed on rhenium-containing catalysts at 300–400 °C. The dehydrogenating activity and selectivity to form MF are higher on the copper-sibunite catalysts than on the rhenium-sibunite samples. The introduction of 0.25% Re into the 4% copper-containing catalyst enhances its total activity and stability.

Key words: supported monometallic copper- and rhenium-containing catalysts, bimetallic rhenium,copper-containing catalysts, methanol, methyl formate, dehydrogenation, sibunite.

Catalytic dehydrogenation of methanol is a preparative method for the synthesis of methyl formate (MF), which is a starting product for such valuable compounds as formic and acetic acids, formamide, and DMF.

The copper-containing catalytic systems based on aluminacalcium cements¹ with an optimum content of copper of 40 wt.% manifest a high activity in the dehydrogenation of methanol to MF. However, at high temperatures the catalyst activity decreases probably because of sintering of copper.² The system containing copper, zinc, aluminum, and alkaline metal oxides is also an active and selective catalyst for the synthesis of MF.³ The introduction of promoting additives, such as zirconium dioxide,⁴ into the copper-containing catalysts improves their time-on stream behavior.

The nature of the support has a great effect on the activity and selectivity of catalytic systems. A new class of supports, *viz.*, sibunites, is of considerable interest. They are prepared by introducing the pyrolytic carbon layer on the surface of technical carbon.⁵ The Cu(1%)/Sib catalyst (Sib is sibunite) is active in the dehydrogenation of isopropyl alcohol to acetone. The introduction of 1% rhenium into the same catalyst enhances its activity and selectivity.⁶

In this work an attempt is made to develop a selective low copper catalyst supported on sibunite for the dehydrogenation of methanol to MF and to estimate the influence of rhenium additives on its characteristics.

Experimental

The reaction was carried out in a flow-type quartz reactor $(450 \times 12 \text{ mm})$ at 150-400 °C and atmospheric pressure. The weight of the catalyst sample was 0.7 g. Methanol (reagent grade, n_D^{20} 1.3288, d_4^{20} 0.7912) was supplied to the reactor using an automated plunger-type dosing system with a space velocity $v = 7.5 \text{ h}^{-1}$. The duration of each run was 30 min.

Liquid products were analyzed by an LKhM-8MD chromatograph with a thermal conductivity detector (column 2 m×3 mm packed with 10% Tween-60 on Polychrom-1). The internal standard method was used to estimate the quantitative composition of the liquid products with an accuracy of 4 rel.%. Gaseous products were analyzed by gas adsorption chromatography on three packed columns using a thermal conductivity detector. Column A (3 m×3 mm) was packed with the SKT carbon, column B (1.7 m×3 mm) was packed with molecular sieves 5 Å, and column C (2 m×3 mm) was packed with Polisorb. Argon served as the carrier gas in column A, and helium was used in columns B and C. The gas composition was determined with an error not higher than 3 rel.%.

Sibunite was used as the support for the catalysts. Its filled mass was 0.6 g cm⁻³, and the specific surface measured by nitrogen adsorption was $680 \text{ m}^2 \text{ g}^{-1}$ and that estimated by phenol adsorption was $230 \text{ m}^2 \text{ g}^{-1}$. The granules were 2–3 mm in size (see Ref. 5).

Samples of the monometallic copper- and rhenium-containing catalysts were prepared by the impregnation of the support with aqueous solutions of copper salts and ammonium perrhenate, respectively. The combined impregnation of sibunite with aqueous solutions of the copper salts and ammonium perrhenate was used to obtain bimetallic copper-rhenium cata-

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Catalyst	<i>T</i> /°C	Composition of products (mol.%)							X*	<i>S</i> _{MF} **
		MF	MeOH	H ₂ O	H ₂	CO	CH ₄	CO ₂	%	
Cu(1%)/Sib	200	0.4	97.7	0.2	1.4	_	_	0.3	2.3	34.8
	225	0.8	96.1	0.2	2.7	Traces	_	0.2	3.9	41.0
	250	1.0	95.7	0.2	3.0	0.1	_	Traces	4.3	46.5
	300	0.5	96.8	0.2	2.2	0.3	_	Traces	3.2	31.3
	400	0.2	92.3	0.2	6.7	0.6	_	_	7.7	5.2
Re(1%)/Sib	200	Traces	99.4	0.2	0.4	_	_	Traces	0.6	0
	225	0.2	98.7	0.2	0.9	Traces	_	Traces	1.3	30.8
	250	0.4	97.6	0.2	1.7	0.1	Traces	0.1	2.4	33.3
	300	0.7	95.6	0.2	3.0	0.4	Traces	0.1	4.4	31.8
	400	0.4	79.6	0.2	14.8	4.5	0.1	0.4	20.4	3.9
Cu(2%)/Sib	200	0.6	98.4	Traces	1.0	Traces	Traces	Traces	1.6	69.0
	250	1.3	95.7	Traces	2.6	0.4	Traces	Traces	4.3	59.1
	300	1.2	94.1	Traces	3.0	1.4	0.2	0.1	5.9	42.1
	400	0.1	97.0	0.1	2.3	0.5	Traces	Traces	3.0	6.7
Re(2%)/Sib	200	0.2	99.2	Traces	0.6	Traces	_	Traces	0.8	50.0
	250	0.6	97.2	Traces	2.0	0.2	Traces	Traces	2.8	42.9
	300	1.1	92.3	Traces	3.7	2.7	Traces	0.2	7.7	28.6
	400	0.4	73.9	Traces	14.5	10.6	0.2	0.4	26.1	3.1
Cu(1%)+	200	0.2	98.8	0.1	0.9	Traces	_	Traces	1.2	33.3
+Re(1%)/Sib	250	0.6	95.6	0.1	3.3	0.3	Traces	0.1	4.4	27.3
	300	0.6	88.1	0.1	8.8	2.0	Traces	0.4	11.9	10.1
	400	Traces	72.0	0.1	20.1	6.6	0.3	0.9	28.0	0
Cu(2%)+	200	0.3	98.9	0.1	0.5	0.1	Traces	0.1	1.1	59.2
+Re(2%)/Sib	250	0.6	96.6	0.1	1.9	0.6	Traces	0.2	3.4	35.1
	300	0.4	92.9	0.1	3.0	3.0	0.1	0.5	7.1	12.5

Table 1. Composition of products of methanol transformation on the sibunite-supported mono- and bimetallic catalysts $(p = 0.1 \text{ MPa}, v = 7.5 \text{ h}^{-1})$

* Total conversion of MeOH.

** Selectivity for MF formation.

lysts. The samples were dried at 120 $^{\circ}\mathrm{C}$ and reduced in a hydrogen flow at 400 $^{\circ}\mathrm{C}.$

The sibunite-supported monometallic catalysts containing 1, 2, and 4% Cu or 1 and 2% Re and bimetallic samples with the Cu content from 1 to 4% and the Re content from 0.25 to 2% were used (Table 1).

The degree of methanol conversion was taken as a measure of the catalytic activity. The selectivity to form MF ($S_{\rm MF}$) was estimated from the content of MF in the reaction products.

Results and Discussion

Sibunite alone does not decompose methanol at 150-400 °C, and at temperatures >400 °C CO and H₂ are formed in the 1 : 2 molar ratio due to the thermal decomposition.

Liquid products of methanol transformation formed at 200–400 °C on monometallic catalysts containing 1% and 2% Cu or Re and on the corresponding bimetallic samples contain the unreacted alcohol, MF, and water (see Table 1). Gaseous products contain hydrogen, carbon monoxide, and carbon dioxide. At temperatures >300 °C methane is formed on the rhenium-containing samples. The fraction of MF in the liquid products increases as the temperature increases from 200 to 250–300 °C. However, side reactions resulting in the formation of CO and CH₄ begin to occur simultaneously. According to the available data,^{7,8} MF formation on the copper-containing catalysts proceeds *via* dehydrogenation of methanol

 $2 \text{ MeOH} \rightarrow \text{HCOOMe} + 2 \text{ H}_2. \tag{1}$

In addition, the following reactions can occur:

decarbonylation of the MF that formed^{1,9}

$$\mathsf{HCOOMe} \to \mathsf{MeOH} + \mathsf{CO},\tag{2}$$

decomposition of MF to CO and hydrogen¹⁰

$$\text{HCOOMe} \rightarrow 2 \text{ CO} + 2 \text{ H}_2, \tag{3}$$

decomposition of MF to carbon dioxide and methane⁸

$$\mathsf{HCOOMe} \to \mathsf{CO}_2 + \mathsf{CH}_4,\tag{4}$$

water-gas shift reaction¹¹

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{5}$$

and steam conversion of methanol^{12,13}

$$MeOH + H_2O \rightarrow CO_2 + 3 H_2. \tag{6}$$

Based on the thermodynamics of methanol dehydrogenation,¹⁴ equilibrium concentrations of MF are in the range from 20 to 50%. Methanol and MF are capable of forming intermediates, which are tightly bound to the surface.^{15,16}

The conversion of methanol to MF on the monometallic copper- and rhenium-containing sibunite-supported catalysts increases as the temperature increases from 200 to 250–300 °C. Higher temperatures decrease the dehydrogenating activity.

An increase in the rhenium content from 1 to 2% increases $S_{\rm MF}$ from 33.3 to 42.9% at 250 °C. A similar increase in the copper content in the monometallic sample increases the selectivity from 46.5 to 59.1%.

The decomposition of MF was studied on the Cu(1%)/Sib and Re(1%)/Sib samples (Table 2). At 200 °C the amount of methanol formed on the copper-containing sample is ~3 times greater than that formed on the rhenium-containing sample. On the Re(1%)/Sib catalyst the CO : H_2 ratio is equal to 1, which corresponds to the stoichiometry of reaction (3), whereas on the copper-sibunite catalyst it is ~2. The decomposition of MF has previously been studied in detail¹³ on the CuO/ZnO/Al₂O₃ catalyst. A kinetic analysis of this process showed that the formation of CO was mainly caused by reaction (3). According to the published results,¹³ the data in Table 1 indicate that the change in the selectivity of MF conversion is antiparallel to the conversion of methanol, and this determines a low yield of MF.

Methanol dehydrogenation occurs as a successive reaction through stages (2) and (3).¹⁴ At high conversions the selectivity with respect to MF decreases rapidly due to the decomposition of MF in reaction (3). The kinetics and mechanism of MF transformations on the coppercontaining catalysts were considered in detail in several works.^{15–17}

Bimetallic samples containing 1 or 2% Cu and Re exhibit similar dehydrogenating activities at 200 and 250 °C (see Table 1). The data on the influence of the rhenium additives to the copper-containing catalysts on their dehydrogenating activity are presented in Table 3.

Table 2. Decomposition of methyl formate on the sibunitesupported monometallic catalysts (p = 0.1 MPa, v = 7.5 h⁻¹)

Cata-	T/°C	Con	Composition of products (mol.%)							
lyst		HCOOMe	MeOH	H ₂ O	H_2	CO	CO ₂			
Cu(1%)/Sib	200	83.8	6.4 3.1	0.1	3.0	6.3	0.4			
	250	93.7	2.5	0.2	1.0	2.4	0.2			
Re(1%)/Sib	200 225 250	95.3 94.1 92.6	2.0 1.9 1.4	0.2 0.6 0.9	0.2 1.2 2.5	0.2 1.2 2.4	2.2 1.0 0.3			

Table 3. Influence of the rhenium content in the sibunitesupported copper-containing catalysts on the total conversion (X (%)) and selectivity of methyl formate formation $(S_{\rm MF} (\%))$ in the dehydrogenation of methanol* at 200 (I), 250 (II), and 300 °C (III)

Initial	<i>C</i> **		Х			S _{MF}		
sample		Ι	Π	III	Ι	Π	III	
Cu(2%)/Sib	0	1.6	4.3	5.9	69.0	59.1	42.1	
	0.25	1.5	4.1	6.2	66.4	52.5	36.0	
	0.5	1.4	3.7	6.4	62.5	49.9	28.4	
	1.0	1.3	3.5	6.9	60.0	42.4	17.1	
	2.0	1.1	3.4	7.1	59.2	35.1	12.5	
Cu(4%)/Sib	0	1.3	2.2	3.1	65.8	55.6	20.0	
. ,.	0.25	1.5	5.8	8.7	63.5	52.6	28.2	
	0.5	2.7	5.2	8.4	62.3	52.5	25.5	
	1.0	2.3	4.7	8.6	53.5	44.3	20.8	

* p = 0.1 MPa, v = 7.5 h⁻¹.

** Content of Re (wt.%).

When the reaction temperature increases from 200 to 300 °C, the dehydrogenating activity of the monometallic samples containing 2 and 4% Cu changes insignificantly. The introduction of Re (from 0.25 to 1%) into the Cu(4%)/Sib sample enhances the total conversion of methanol at 300 °C almost threefold, whereas an increase in selectivity is insignificant. The Cu(4%)+Re(0.25%) sample on sibunite exhibits the highest dehydrogenating activity.

It can be assumed that at high temperatures copper sintering occurs more intensely on the samples without a rhenium additive. The time-on stream behavior of these two samples was studied for 24 h of the continuous operation at 250 °C and $v = 7.5 \text{ h}^{-1}$. On the monometallic Cu(4%)/Sib sample the total conversion of methanol after operation for 1 h was 11%. It decreased to 8% after 24 h on stream, and the selectivity of MF formation decreased from 55 to 49%. The total conversion of methanol on the Cu(4%)+Re(0.25%)/Sib sample was twice as high (~23%) and remained virtually unchanged. The selectivity for MF formation (41±2%) also remained unchanged.

The strong interaction of the metal with the oxide support suppressing the reduction of the metal on the surface can be observed in conventional supported catalysts.^{18–20} In metal-carbon catalysts, unlike metal-oxide catalysts, there is no strong interaction of the metal with the support, and that facilitates the reduction of the active component on the surface.²⁰

Thus, our study shows that the introduction of rhenium into the copper-sibunite catalyst enhances its activity in methanol dehydrogenation and time-on stream behavior. These properties are characteristic of rheniumcontaining catalytic systems.²¹

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