PILLAR STRUCTURAL BENTONITE
FOR OBTAINING DIMETHYL ETHER FROM NATURAL GAS

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ABSTRACT

The development of a catalyst for obtaining dimethyl ether is considered. Pillar structural bentonite clay is used as its carrier. The latter structure is based on interlayers of bentonite clay intercalated by polyhydroxocomplexes of molybdenum. The specific surface of the samples defined after heat treatment at 160°C amounts to 220 m²/g - 260 m²/g, while upon calcination at 540°C - 560°C these values decrease to 160 m²/g - 180 m²/g.

Keywords: pillar structure, dimethyl ether, selectability, one-stage synthesis, catalyst.

INTRODUCTION

The inordinate use of oil-based fuels for transportation purposes is one of the major reasons of the rapid depletion of petroleum causing major environmental problems. These issues have necessitated the development of clean non-petroleum based alternative transportation fuels. In recent years, the application of dimethyl ether (DME) as a potential diesel substitute used in compression ignition engines has attracted considerable attention [1, 2]. DME is a volatile substance which forms a liquid phase when pressurized above 0.5 MPa; therefore, it is commonly handled and stored as liquid (see the physical property of DME in Table 1). Burning with a visible blue flame and with similar properties as propane and butane, DME may hence be used as liquefied petroleum gas (LPG) for heating and home cooking [3].

Dimethyl ether (DME) is a new fuel that could help address environmental and fuel security issues. DME can be produced from a variety of feedstocks, including natural gas or bio-methane. Current production is focusing on methane-containing feedstocks, but gasification of any suitable organic source can lead to the syngas chemistry products with DME as one of the more

energy efficient options. DME is a gas under ambient conditions with properties similar to those of LPG and can thus be stored as a liquid under moderate pressure. DME produced from bio-methane (from landfill gas or the decomposition of manure, for example) would be a non-fossil, renewable fuel [4].

At present, dimethyl ether is the only synthetic fuel that provides a complete replacement of traditional diesel fuel. The fuel offered as an alternative must meet several requirements [5 - 7] - first, availability of raw materials, secondly, the technology and the equipment for fuels production in commercial quantities should ensure its high cost, including the process of transportation, storage and distribution. Thirdly, the fuel should provide the car with high consumer qualities, in particular, power and economic parameters of the engine. And, finally, the fuel must be environmentally safe for production, transportation, storage, refueling and combustion in engines. Motor fuels, obtained from natural gas, do not contain aromatic hydrocarbons, sulfur and are characterized by the completeness of combustion. There are numerous technologies for the production of dimethyl ether, but getting it at some point with a good yield remains an urgent problem. In this respect, the direct oxidation of

natural gas or methane to dimethyl ether will help to increase the efficiency of diethyl ether production. At the same time, the production of dimethyl ether from natural gas will ensure a complete replacement of the traditional diesel fuel from oil [8, 9]. Along with this, the fuel offered as an alternative must meet international standards and norms [6]. However, the technology of methane direct oxidation to dimethyl ether is not available on an industrial scale. In industry, DME is produced from the dehydration of methanol.

Providing real-time data this article treats the direct oxidation of natural gas to dimethyl ether. Its specific aim is to develop a carrier of the synthesized catalytic system.

EXPERIMENTAL

The bentonite clay used as a supported catalyst carrier was collected in South Kazakhstan. The mass (%) chemical composition referred to: (SiO_2) 54.0 - 60.0, (Al_2O_3) 13.0 - 16.0, (Fe_2O_3) 4.0 - 6.0, (MgO) 2.0 - 3.0, (Na_2O) 1.0 - 2.0, (H_2O) 8.0 - 11.0, other ingredients 6.0-9.0. The cation-exchange used was 66.4 mmol/100.0 g clay. Molybdenum (II) chloride and sodium hydroxide were of an analytical grade. They were used without further purification to prepare molybdenum polyhydrocomplexe. The other chemical reagents- HCl, H_2SO_4, H_3PO_4, and $CuCl_2·4H_2O$ were of an analytical grade. The environment's acidity was supervised by a digital pH meter OP-208/1. The acids concentration varied from 0.5 mol/L to 3.0 mol/L.

The crystal phase composition of the carrier prepared at 20^0C was determined by

X-ray diffraction using a Rigaku D/Max 2200 VPC powder diffractometer with CuK_α radiation, an accelerating voltage of 40 kV, an emission current of 30mA, and a scanning speed of 10^0/min.

The textural properties of the support catalysts were evaluated on the ground of the N_2 adsorption-desorption isotherms obtained at 77K over the whole range of relative pressures, using a Micromeritics ASAP-2000 apparatus. The catalysts specific surfaces calculated from these isotherms using the BET method were in the 0.005 P/P_0 - 0.25 P/P_0 range. The temperature–programmed study of the catalysts was carried out in a semiautomatic Micromeritics TPD/TPR 2900 apparatus interfaced to a computer. Cu and Ag amounts on the support catalysts

were determined using an Analytic Jena ContrAA 300 atomic absorption spectrophotometer.

The preparation of the pillared clays was carried out as in correspondence with procedure described in refs. [11 - 12]. A suspension of bentonite clay was prepared through mixing with water for 4 h. The pH value of the water extract of the clay was 8-9. The polyhydroxocomplex of molybdenum was obtained by adding gradually a solution of sodium hydroxide to an aqueous solution of molybdenum (II) chloride. The concentration of chloride molybdenum changed from 6.0 mmol to 34 mmol Mo^{2+} per gram clay. The solution of molybdenum polyhydroxocomplexes was slowly added to the clay suspension aiming coagulation exclusion. The system obtained was left undisturbed for 14 h. Then the deposit was washed by water and condensed to a paste. The latter was dried for 14 h at the room temperature, then for 3h at 120^0C and finally for 6h at 180^0C. After cooling off to the room temperature the firm mass obtained was powdered and sifted to different fractions of certain particles sizes. The pillar structural bentonite of a particles size less than 2.0 mm was subsequently impregnated by aqueous solutions of $CuCl_2·2H_2O$ and $AgNO_3·4H_2O$ at room temperature. The water was then evaporated at mixing and the paste obtained was dried for 6 h at 120^0C in air. It was finally calcinated in air for 4 h at 300^0C. The Cu and Ag content in pillar structural bentonite changed from 1.0 mass % to 20 mass %, while the molar ratio Cu:Ag varied from 1:1 up to 9:1.

The analysis of the reaction products was carried out using Chrom-4 chromatograph of «Chromaton-N» (a column length of 3 m; a diameter of 3 mm; liquid polyethylenglycol adipate as a carrier (15 mass % of the carrier); argon as a carrier gas with a velocity of 50 cm^3/min; a column temperature of 373K; an evaporator temperature of 423K).

RESULTS AND DISCUSSION

The selectivity of DME reaction is studied varying the nature of the promoters used. Some of the data obtained is listed in Table 1.

The data of Table 1 shows that the metal reduction is 35.3 %, while the methane conversion reaches 3.2 % in presence of 1 % Ag/Al_2O_3. The addition of a second metal to the catalyst leads to an increase in the selectivity of the process from 15 % to 20 %. The introduction

Table 1. Effect of the nature of the promoters (5 mass %) on the selectivity of DME reaction. Process temperature 250⁰C - 280⁰C; P (CH$_4$)/P (O$_2$) = 10:1 P (N$_2$)/P (O$_2$) = 20:1. General = 3 MPa.

Sample	Specific surface area, m^2/g	Degree of restoration, %	Conversion of methane, %	DME selectivity, %
1 % Ag/Al$_2$O$_3$	1.7	35.3	3.2	15.0
5 % CuAg/ Al$_2$O$_3$	2.7	44.7	4.3	11.0
5 % CuAg(V$_2$O$_5$)/ Al$_2$O$_3$	4.8	60.2	10.0	40
5 % CuAg(Cr$_2$O$_3$)/ Al$_2$O$_3$	4.0	54.0	8.0	34
5 % CuAg(Fe$_2$O$_3$)/ Al$_2$O$_3$	3.4	48.0	7,0	32
5 % CuAg(Co$_2$O$_3$)/ Al$_2$O$_3$	3.0	46.0	6.0	28
5 % CuAg(TiO$_2$)/ Al$_2$O$_3$	4,9	66.4	11.0	41

of copper into Ag/Al$_2$O$_3$ results in an increase of the degree of recovery from 35.2 % to 44.7 %. The introduction of vanadium oxide promoter (V) leads to an even greater recovery rate of 60.2 %. The active surface also increases from 1.7 m^2/g for Ag/Al$_2$O$_3$ to 2.7 m^2/g and 4.8 m^2/g for CuAg/Al$_2$O$_3$ and CuAg (V$_2$O$_5$)/Al$_2$O$_3$ samples, respectively (Table 1). The greatest promoter effect is provided by vanadium oxide and titanium. The degree of metal reduction in this case is 60.2 %, while the process selectivity is 40 %. However, the DME yield does not exceed 4.0 % using this catalyst.

Natural bentonite clay has a little specific surface of about 40 m^2 per gram. It loses its porosity at heating above 383K to 20 m^2/g. The bentonite clay thermograms show three endothermic effects observed in the ranges of 120°C - 180°C, 560°C - 580°C and 820°C - 850°C. They are mainly inherent for the montmorillonite mineral present in the bentonite clay (Fig.1). The first endothermic effect (120°C - 180°C) corresponds to the release of adsorbed water, the second endothermic effect (560°C - 580°C) refers to the separation of chemically bound water from the crystalline lattice structure of montmo-
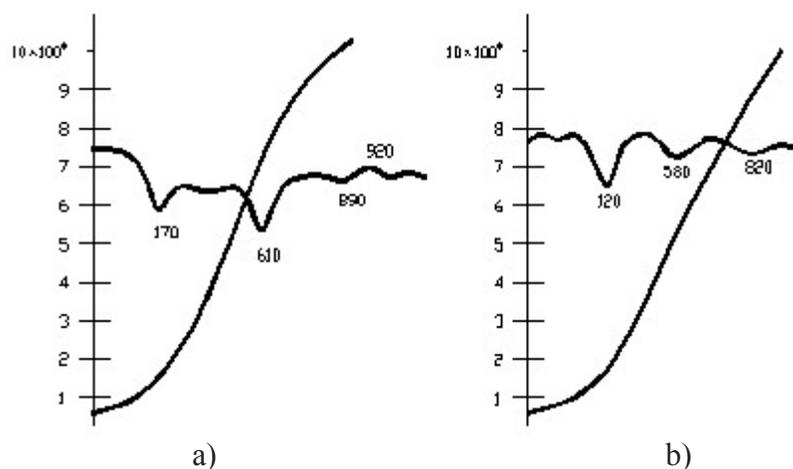

Fig. 1. Thermograms of South Kazakhstan's bentonite: a) clay (depth - 1 m); b) clay (depth - 2 m).
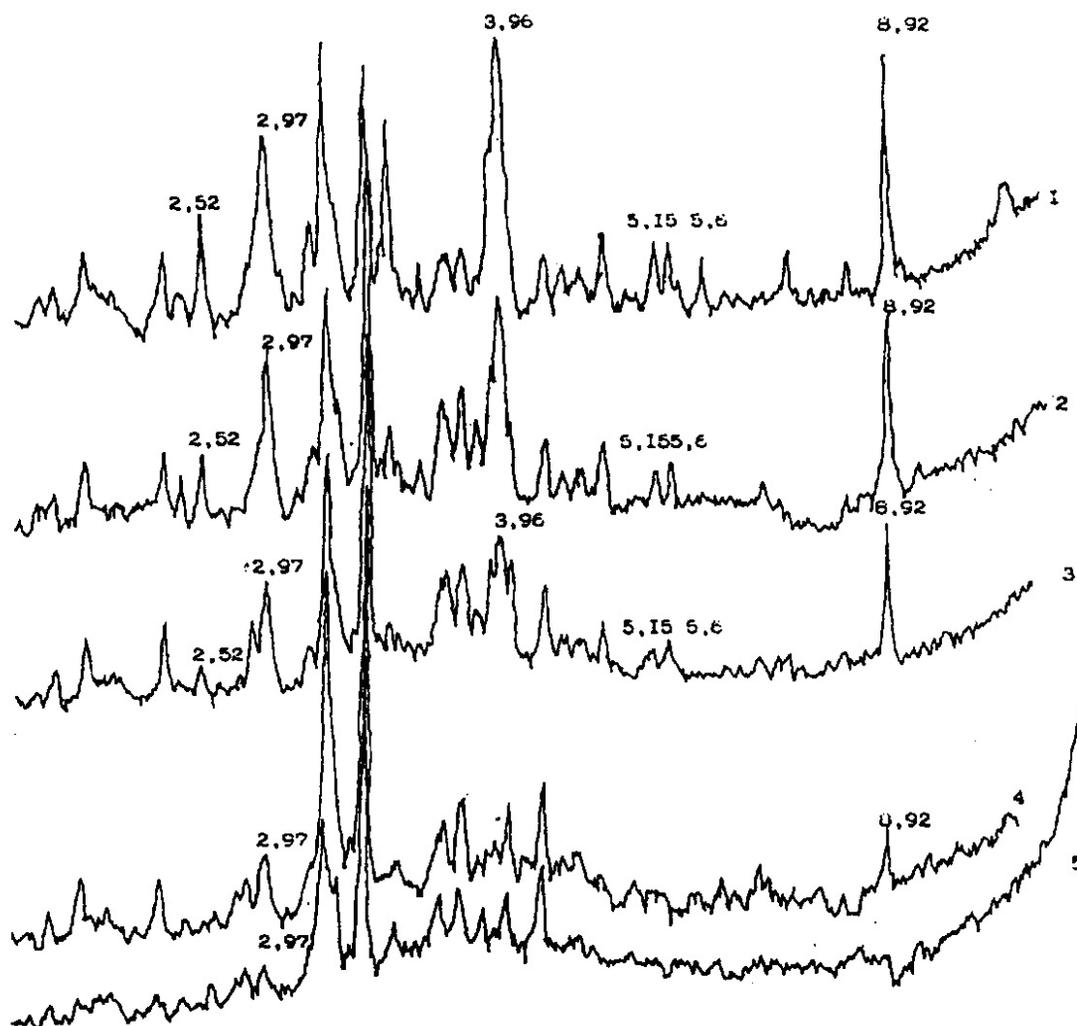
Fig. 2. X-ray grams of bentonite treated by hydrochloric acid. 1 - natural bentonite clay; 2 - bentonite treated with 0,5M HCl; 3 - bentonite treated with 1,0M HCl; 4 - bentonite treated with 2.0M HCl; 5 - bentonite treated with 3,0M HCl.

rillonite [13], while the endothermic effect observed at 820°C - 890°C can be attributed to the destruction of the montmorillonite crystalline lattice structure.

The preliminary experiments connected with bentonite clay treatment with HCl, H_2SO_4 and HNO_3 show that the hydrochloric acid effect is the greatest - the SiO_2/Al_2O_3 ratio changes from 3.8 up to 14.6 in case of using 3.0 mol/l HCl. This suggests a transformation of aluminum from the crystalline lattice structure of montmorillonite (Fig. 2).

X-ray diffraction data referring to bentonite treated by hydrochloric acid solutions of a varying concentration is illustrated in Fig. 2. It is evident that the signal at 8.92Å decreases with the acid concentration increase.

The variation of the peaks at 3.3Å and 8.92Å (Fig. 2) indicates a change of the state and the cation composition of the mineral lattice (Fig. 2). Table 1 lists the structural and adsorption characteristics of natural bentonite clay (test 1) juxtaposed to those of bentonite samples treated with 2M HCl (test 2).

The acidic treatment increases the specific surface, the porosity, the total pore volume and the static activity of bentonite clay but decreases the stability to temperature treatment. The porosity is also decreased at heating above 140°C. Molybdenum polyhydrocomlex intercalates into bentonite.

Polyhydroxocomplexes of Cr, Ti, Al, Zr and Fe are used for natural clays modification aiming a pillar

Table 2. Structure adsorption characteristics of bentonite clay.

Physicochemical character	Layer					
	I (depth -1m)		II (depth - 2m)		III (depth - 3m)	
	test 1	test 2	test 1	test 2	test 1	test 2
Powder density(0.5mm), g/cm^3	1.24	1.04	1.24	1.04	1.20	1.06
Density, g/cm^3	2.74	1.86	2.76	2.10	2.86	1.98
Porosity, %	23	36	25	38	26	38
Total pore volume, cm^3/g	0.14	0.36	0.17	0.34	0,16	0.36
Static activity, cm^3/g:						
by water	0.11	0.27	0.13	0.29	0,11	0.30
by benzene	0.14	0.28	0.19	0.20	0,13	0.31
Specific surface, m^2/g	61	120	58	120	60	130
Specific surface after heating at 140^{0}C, m^2/ g	18	26	19	28	19	26

structural form. They also provide thermostability at temperature values of 500^{0}C - 600^{0}C [14, 15]. Using such materials in catalytic and adsorption processes is an incitement for development of synthesis methods on the ground of a natural clay. In this work bentonite clay is modified by molybdenum polyhydroxocomplexes.

Table 2 shows some physical characteristics of the system studied. Modifying bentonite clay by polyhydroxocomlexes of Mo(II) leads to increase of the specific surface from 40 m^2/g up to 280 m^2/g. The values of specific area depend on molybdenum polyhydroxocomplex amount. They are also affected by the temperature - thermostability is observed up to 500^{0}C - 540^{0}C, while the further temperature increase up to 600^{0}C brings about decrease of the specific area to 160 m^2/g - 180 m^2/g. The pillar structural bentonite has a total pore volume of 0.44 cm^3/g - 0.58 cm^3/g, the interlaminar distances amount to 1.34 nm - 2.16 nm. The values of natural bentonite are 0.16 cm^3/g and 0.91 nm, correspondingly. The maximal value of the total pore volume is 0.58 cm^3/g, while that of the interlaminar distance (d$_{0.01}$) is 2.14 - 2.16 nm. In fact, these values refer to a molybdenum concentration of about 15 mmol - 22 mmol per gram of clay (polyhydroxocomplex molybdenum ions are settled down

Table 3. Some parameters of bentonite intercalated by molybdenum polyhdroxocomplexe.

Amount of molybdenum, mmol/g. clay	S$_{sp}$, m^2/g	d$_{001}$, nm	Total pore volume, cm^3/g	Top stability temperature and S$_{sp}$	
				°C	S$_{sp}$, m^2/g
-	40	0,91	0,16	140	20
5-6	140	1,34	0,44	420	110
11-12	240	1,84	0,51	500	160
15-16	270	2,14	0,56	520	180
20-22	280	2,16	0,58	540	180
30-31	260	1,94	0,54	540	160

between the clay layers). The increase of molybdenum concentration above 20 mmol per gram of clay does not lead to further distance increase. This is probably due to the lack of hydrolized forms of molybdenum chloride which affect pillar structures formation. Similar phenomena are also observed [12] with polyhydroxocomplex ions of iron (III).

CONCLUSIONS

The modification of montmorillonite minerals contained in bentonite clay by molybdenum ions poly-hydroxocomplex provides heat resistance. The specific surface of samples containing 15 mmol - 22 mmol Mo^{2+} defined after heat treatment at 180°C amounts to 220 m^2/g - 260 m^2/g. The further temperature increase up to 500°C - 540°C brings about this value decrease to 160 m^2/g - 180 m^2/g. The bentonite clay lacking intercalation loses its porosity at 110°C, while its specific surface is about 20 m^2/g.

The modified bentonite clay is used for the preparation of support catalysts containing copper and silver. A 5% CuAg bimetallic catalyst using bentonite modified by molybdenum compounds as a carrier exhibits selectivity to dimethyl ether of 40 % with at a total methane conversion. The increase of the molybdenum ions poly-hydroxocomplex content above 30 mmole per gramm clay does not significantly affect the process selectivity for dimethyl ether as a target product.

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