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Comparison of activities of bulk and monolith $Mn–Na_2WO_4/SiO_2$ catalysts in oxidative coupling of methane

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The monoliths were prepared by coating of Al_2O_3 and SiO_2 on the FeCrAl alloy foil and by introducing appropriate catalytically active oxides on the supports. It was found that, for both catalytic systems of monolith and bulk catalysts of $Mn–Na_2WO_4/SiO_2$, the dependences of methane conversion to C_2 products on the contact time virtually coincide if the normalized quantities of the active component are considered.

Oxidative coupling of methane (OCM) is one of the challenges in natural gas processing, and all the problems of oxidation catalysis are revealed in the catalyst design, especially for the extremely high OCM temperatures, 700–900 °C. During OCM the heterogeneous catalytic reaction of methane activation is accompanied by gas-phase reactions, and the interplay of the homogeneous and heterogeneous stages of OCM has substantial significance in this reaction.[1,2]

The oxide catalysts supported on metal foams or foils (*i.e.*, monoliths) have the essential advantages over bulk or granulated oxide catalysts, which provide an opportunity for the high temperature OCM reaction because of the low pressure drop as well perfect heat and mass transfer for the monolith.

An appropriate material of monolith catalysts for the OCM reaction can be a foil made from the FeCrAl alloy having high thermal stability and nearly the same thermal expansion coefficient as alumina and silicates. In order to prepare monolith catalysts, a foil surface is covered with a thin film of the catalytically active oxide. The most attractive way to obtain an oxide coating on the metal surface is the electrophoretic deposition method (EPD).[3,4] This is based on deposition of colloidal particles on the surface of an electrode under the influence of the electric field.

Application of monolith catalysts for the methane reforming is connected to the comparison of activity of the monolith catalyst with that of the bulk catalysts. It is very important for both preparation method of the monolith catalyst and methane reforming performance.

In some works,[5–9] a major characteristic of the monolith activity was either the temperature for the sufficient conversion of the initial reactant or the dependence of the reactant conversion on the temperature at equal amounts of the catalysts and equal feed gas velocities. This method gives an opportunity for qualitative comparison of monolith activities, but it does not allow obtaining a quantitative ratio of activities of the studied monoliths.

In order to compare catalytic activities of grains and monoliths in methane oxidation, the values of the reaction rate constants were measured.[10] The normalized rate constants per amount of an active component of the both monolith and granulated catalysts were almost the same in the kinetic region.

Slovetskaya *et al.*[11] compared the activity of the granulated Mn–Cu oxide catalyst in methane oxidation with that of the monolith catalyst produced from the FeCrAl foil having a thin coating of the same oxide catalyst. Catalyst activities were compared on the basis of the space velocity of the methane–air mixture at definite methane conversions on both catalyst systems under identical conditions. The reaction rate constants as well as the feed gas space velocity for the specified conversion were normalized to the active oxide component and were found to be the same for both types of the catalysts.

The purpose of the present study is the comparison of activities in OCM process of the bulk $Mn–Na_2WO_4/SiO_2$ catalyst and monoliths with this catalyst supported on the FeCrAl foil. The research is focused on the optimization of the coating procedure of the metal foil with catalytically active component, *i.e.*, $Mn–Na_2WO_4/SiO_2$ by the EPD method.[†]

Three catalyst samples were prepared: the bulk catalyst, monolith 1, which was made by EPD followed by impregnation, and monolith 2, which was made by EPD using the ready (bulk) catalyst.[‡]

The thermally stable base of monoliths was a 50 μm thick FeCrAl foil. The preparation of the monolith catalysts consisted of the following stages: (1) preliminary treatment of the foil

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[†] Oxidative coupling of methane over bulk catalysts was carried out in a quartz reactor of 40 cm length, 8 mm i.d. with a fixed catalyst bed mounted inside a cylindrical furnace. The weighted catalyst sample (0.25–0.50 mm fraction) was placed in the central part of the reactor. The free space in the reactor was filled with quartz chips (2.0–3.0 mm). The initial gas mixture containing 61.0 vol.% of CH_4, 8.2 vol.% of O_2 and 30.8 vol.% of N_2 was prepared by mixing methane with air.

Testing of monolith catalysts in OCM was carried out in a quartz reactor of 40 cm length, 20 mm i.d. The monolith samples with 3 cm length, 20 mm i.d. were placed in the central part of the reactor. To suppress homogeneous reactions outside of the monolith, the void volume in the reactor upstream and downstream was filled with quartz chips (2.0–3.0 mm).

The space velocity of the methane–air mixture was varied from 70 to 420 cc min^{-1}. The temperature was ranged in the 650–800 °C interval.

Reaction products were analyzed by gas chromatography using two chromatographic columns packed with Polysorb and 5 Å molecular sieves. The carrier gas was helium.

[‡] The bulk 1.9% Mn–5% Na_2WO_4/SiO_2 catalyst was prepared by a method described by Wang *et al.*[13] To prepare a catalyst sample, commercial silica (S-120, Russia, $S_{sp} = 120\ m^2\ g^{-1}$) was first impregnated by a $Mn(NO_3)_2$ solution at 80 °C, dried at 140 °C for 3 h and then impregnated by a Na_2WO_4 solution at 80 °C and dried again. The sample was calcined for 8 h in air at 800 °C.

Figure 1 The monolith blocks produced from the FeCrAl foil and prepared for deposition of oxide coating by the EPD method.

surface; (2) coating the surface with Al_2O_3 or SiO_2; (3) preparation of the monolith support; (4) impregnation of the monolith support with a solutions of $Mn(NO_3)_2$ and Na_2WO_4; (5) calcinations. In one case, instead of stage of impregnation (stage 4) a coating of the support with the ready bulk catalyst from its suspension was carried out.[§]

In order to produce the coated foil, bare foil was placed into the appropriate sol solution where it served as a negative electrode (cathode) in the EPD procedure.

It was found that SiO_2 coatings are very sensitive to the calcination conditions and less stable than Al_2O_3 coatings. In order to reach the necessary thickness of the oxide layer, it is optimal to carry out multiple deposition stages with the intermediate stages of drying and calcination. Besides, SiO_2 coatings on the foil pre-covered with Al_2O_3 as an intermediate layer are obtained more uniform.

To prepare a monolith block, plain and corrugated foil ribbons were rolled (Figure 1).

Two samples of monoliths were prepared.[¶]

The bulk 1.9% Mn–5% Na_2WO_4/SiO_2 catalyst was characterized by XRD analysis and XPS spectra.[††] It was found by XRD that the prepared sample contained highly crystalline α-cristobalite (intensive reflections at $2\theta = 22.1°$, 28.6°, 33.2°, 36.3°) and trydimite-like phases (a shoulder at 21.3° in Figure 2).

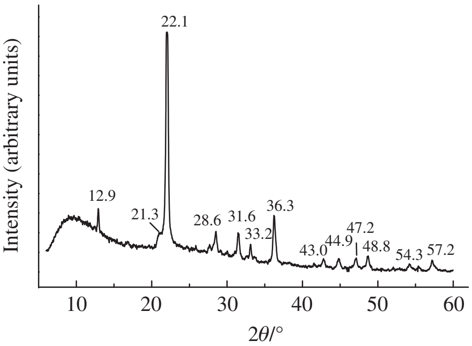

Figure 2 XRD patterns of the 1.9% Mn–5% Na_2WO_4/SiO_2 catalysts after calcination at 800 °C.

The XPS data showed that two samples of the 1.9% Mn–5% Na_2WO_4/SiO_2 catalyst have very similar surface compositions.

Usually, the activities of the catalysts can be compared by measuring the feed gas flow rate, V_0, corresponding to the same conversions of the reactants. The flow rate of the reactant mixture at a specified conversion is proportional to the reaction rate constant per unit weight of the catalyst. Since the volume of monoliths is determined by the reactor size and not by the volume of the active component directly, it is difficult to determine the real volume of the active component. Therefore, for the kinetic study of the catalysts, we used the effective contact time $\tau' = m/V_0$ (s g cm^{-3}) instead of the contact time $\tau = v_c/V_0$ (s). Here v_c is the catalyst volume, V_0 is a space velocity of the gas flow, m is the weight of the active component ($Mn–Na_2WO_4/SiO_2$).

The obtained activities were independent of the size of reactors. Using the effective contact time, the activities of various samples of catalysts can be compared irrespective of design and amount of inactive components in the samples.

As mentioned above, three samples of the $Mn–Na_2WO_4/SiO_2$ catalyst were made by different methods. One was prepared with bulk $Mn–Na_2WO_4/SiO_2$ catalysts and two $Mn–Na_2WO_4/SiO_2$ catalysts were made with monolith catalysts and different in the coating method of the metal support as the catalytic layer. That is, one monolith sample was prepared by wet impregnation of silica film on the FeCrAl foil surface using the solutions of $Mn(NO_3)_2$ and Na_2WO_4 while the other was prepared by depositing of the ready-made $Mn–Na_2WO_4/SiO_2$ catalyst on the foil. The results of their testing at 700, 750 and 800 °C and 70 ml min^{-1} of gas flow rate are summarized in Table 1. The main products were CO_2, C_2H_4 and C_2H_6. Carbon monoxide was present in trace quantities. With increasing reaction temperature, the selectivity rises from 32 to 64%.

Monolith 1 was prepared by wet impregnation of the silica coating. Monolith 2 was prepared by EPD from suspension of the ready 1.9% Mn–5% Na_2WO_4/SiO_2. From these data the activity of monolith 2 is essentially inferior to the bulk catalyst only at first sight. But it must be taken into account that the weight of the bulk sample was 300 mg, while the weight of the same catalyst sample supported on the foil was only 50 mg. Then, according to caculations, productivities of the bulk catalyst, monolith 1 and monolith 2 samples in formation of C_2 products at 800 °C are 8.2, 4.2, 16.7 μmol s^{-1} (g cat.)$^{-1}$, respectively. Hence, performance of the monolith 2 under reaction conditions is better than those of two other samples, *i.e.*, the bulk catalyst and monolith 1.

[§] Preliminary treatment of the foil surface included chemical cleaning of the surface by the electrochemical method at 5 V voltage in a solution containing 40 g dm^{-3} NaOH, 40 g dm^{-3} Na_2CO_3 and 40 g dm^{-3} Na_3PO_4 at 80 °C for 3 min and followed by etching in a solution containing 100 g dm^{-3} H_2SO_4 and 200 g dm^{-3} NaCl at 80 °C for 1 min.

Alumina coatings were obtained by the EPD method using the same procedure as applied earlier to prepare gauze catalysts.[3] For deposition of oxide coatings, alumina sol was used. The alumina sol was prepared by hydrolysis of aluminum isopropoxide. The concentration of AlO(OH) in the prepared sol was 33 g dm^{-3}, pH 4.5.

Silica coatings were obtained by the EPD method from a solution of silica sol. The latter was prepared by acid-catalyzed hydrolysis of tetraethoxysilane (TEOS).[14] Before deposition, the silica sol was diluted with an equal volume of ethanol.

The coated with colloidal particles foils were dried at 20 °C for 24 h and then calcined at 550 °C for 1 h. To prevent destruction and peeling of coatings, deposition was performed in several stages with drying and calcination between them.

[¶] *Sample* **1**. The foil surface was pretreated as described above. To coat the silica layer on the FeCrAl foil, the EPD from a silica sol was used. The coat was deposited at a voltage of 10 V for 60 s. Then, the monolith was calcined in air at 600 °C for 3 h. To prepare the catalyst, a monolith with the SiO_2 coating was first impregnated with a solution of $Mn(NO_3)_2$ and then dried at 140 °C. Then, it was impregnated with a solution of Na_2WO_4, dried and calcined similarly to the bulk catalyst. The resulting monolith contained 190 mg of the catalytic coating.

Sample **2**. The monolith was prepared by coating the ready bulk $Mn–Na_2WO_4/SiO_2$ catalyst on the FeCrAl foil. We used a 10 g dm^{-3} suspension of a finely ground bulk $Mn–Na_2WO_4/SiO_2$ catalyst in acidic SiO_2 sol diluted with ethanol (1:1). The coat was deposited at a voltage of 10 V for 60 s. After deposition, the sample was dried at 140 °C and calcined at 800 °C. The resulting monolith contained 170 mg of the oxide coating and 50 mg of the $Mn–Na_2WO_4/SiO_2$ catalyst.

[††] XPS spectra of the catalysts were recorded with an XSAM-800 X-ray photoelectron spectrometer using AlKα radiation. X-ray diffraction patterns were obtained using a DRON-2 diffractometer with CuKα radiation. Scanning was performed over the 2θ region from 6 to 60° at 2° min^{-1}. SEM images were obtained with a JEOL JSM-5300LV scanning electron microscope.

Table 1 Results of catalytic tests of the Mn–Na_2WO_4/SiO_2 samples (flow rate is 70 $cm^3 min^{-1}$).

T/°C	Catalyst weight in the sample/mg	Yield (%)			O_2 conversion (%)	C_2 selectivity (%)	C_2H_4 in C_2 (%)
		CO_2	C_2H_4	C_2H_6			
1.9% Mn–5%Na_2WO_4/SiO_2 – bulk							
700	300	2.03	0.32	0.65	33.5	32.3	33.2
750	300	3.48	2.55	1.86	66.4	55.9	57.8
800	300	4.47	5.43	2.34	91.2	63.5	69.9
1.9% Mn–5%Na_2WO_4/SiO_2 – monolith (impregnation of deposited SiO_2)							
700	184	0.35	0.10	0.20	7.4	46.2	33.3
750	184	0.48	0.25	0.34	9.3	55.2	42.2
800	184	1.17	1.68	0.78	26.4	67.8	68.3
1.9% Mn–5%Na_2WO_4/SiO_2 – monolith (deposition of the ready catalyst)							
700	50	0.22	0.06	0.10	5.2	36.4	38.2
750	50	0.48	0.33	0.37	11.3	59.7	47.1
800	50	1.42	1.67	0.96	29.3	65.0	63.5

In Figure 3, dependences of the C_2 yield and C_2 selectivity on the effective contact time for all three samples are presented. The experimental curves indicate that lower activity is exhibited by monolith sample that was obtained by wet impregnation. At the same time, a good coincidence of the curves for the bulk catalyst and a monolith 2 was observed. The data show that the catalyst, which was introduced in monolith by the EPD method, keeps its original activity. Noteworthy, the selectivities of all three samples were very close. The obtained results are close to the published data[15] on the reaction of deep oxidation of methane. In our work, we found that a bulk catalyst and a monolith prepared from the same catalyst material have equal specific activities.

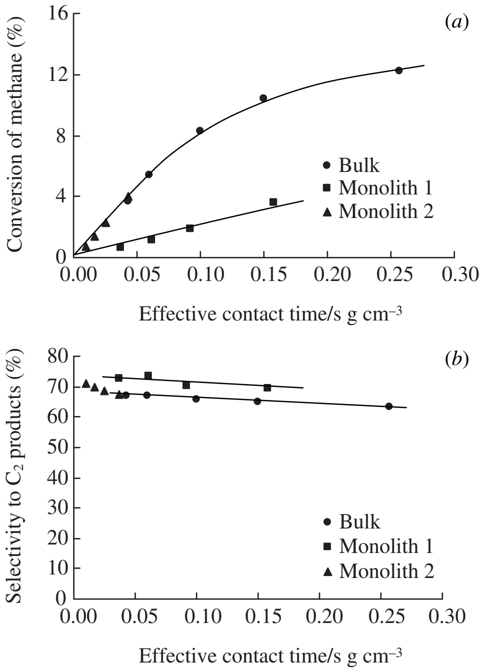

Figure 3 Dependences of (*a*) methane conversion and (*b*) selectivity to C_2 products on effective contact time in OCM on the bulk and monolith 1.9% Mn–5% Na_2WO_4/SiO_2 catalysts at 800 °C. Monolith 1 was prepared by wet impregnation of silica coating, monolith 2 was prepared by EPD from suspension of the ready-made 1.9% Mn–5% Na_2WO_4/SiO_2 catalyst.

The results of our research show that the catalytic activity of the monolith prepared by impregnation of the electrophoresis-deposited secondary supports (Al_2O_3 or SiO_2) is essentially inferior compared to the activity of the bulk catalyst. It is supposed that the presence of the metal carrier and oxide layer of the secondary carrier deposited by EPD makes it impossible to obtain a catalytically active phase. Probably, it is related to the non-uniformity of oxide coatings in depth and the formation of active centers near to the metal surface.

The most important result is that the activity of the deposited catalyst retains on the high level in case of covering the surface with the ready catalyst, and the activity of a monolith depends on the amount of the introduced catalyst. The coincidence of the activities of the bulk and monolithic catalysts allow us to suppose that interplay of homogeneous and heterogeneous stages of OCM is not affected by the large ratio of the monolith volume to the catalyst volume. It is likely, the gas-phase reactions with participation of free radicals occur in the area that is very close to the catalyst surface.

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