Deep oxidation of methane on granulated and monolith copper—manganese oxide catalysts

K. I. Slovetskaya, A. A. Greish, M. P. Vorob'eva, and L. M. Kustov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: greish@ioc.ac.ru

Deep oxidation of methane on the granulated Cu—Mn-mixed oxide catalyst and metallic monolith catalysts coated with the same oxide was studied. The experimental kinetic curves for both monolith and granulated catalysts are satisfactorily described by the first-order rate law. The values of activation energies, reaction rate constants, and feed flow rates for the specified conversion almost coincide for both types of the catalysts. The data obtained confirm the possibility of a quantitative comparison of the activities of the granulated and monolith catalysts. The activity of the monoliths is proportional to the concentration of the active component.

Key words: methane, oxidation, kinetics, Cu—Mn-mixed oxide catalyst, monolith catalyst.

Monolith catalysts[1] have a lower gas-dynamic resistance than granulated catalysts. In addition, in monolith catalysts cross sections of heat and mass flows are uniform and that decreases the probability of the formation of "hot" zones and improves the time-on stream behavior of the catalyst and process selectivity. Finally, when the active component is supported on the monolith surface as the secondary coating, its fraction in the reaction space unit is 0.01—0.25, which is much lower than 0.5—1 characteristic of granulated catalysts.

Thus, the volume of monolith catalysts exceeds that of granulated catalysts by several times at a lower content of the active component. All this impedes strongly to compare activities of granulated and monolith catalysts under identical conditions.

In several works, activities of monolith catalysts are compared comparing the reaction temperature T_α at which the conversion has a set value α or the temperature dependence of the conversion (α_T) at a set catalyst volume and a set feed gas space velocity.[2—5] These methods do not allow the quantitative comparison of activities.[6] In addition, the reaction volumes of monolith and granulated catalysts differ so strongly that their activities cannot be compared when experiments are carried out under identical conditions.

The authors[7] compared the adsorption properties of CuZSM-5 zeolite and the related monolith catalyst using the TPD. To compare the catalytic properties of these catalysts, the activation energy was used that was determined in the kinetic and internal-diffusion regimes. Catalytic activity was measured in a flow-type reactor with a vibrofluidized bed catalyst on different fractions of grains obtained by grinding of the starting monolith catalyst. Comparison of activities of the grains and monolith fragments using reaction rate constants showed that the rate constants of CH_4 oxidation per unit volume of the active component (La—Mn—O—perovskite) were identical for the monolith and granules when the process was controlled by kinetics. The method for comparison of activities of granulated and monolith catalysts is applicable for ceramic monoliths only, which can be subjected to crashing with fractionation. For metallic monoliths, the preparation of similar fractions by crashing or grinding of the starting catalyst is completely impossible and, hence, another method for comparison of activities is necessary.

The purpose of this work is under identical conditions and compare the activities of the granulated oxide catalyst based on Mn and Cu oxides (Carulite-200) and monolith metallic catalyst with supported Carulite as an active component.

Experimental

The starting granulated catalyst Carulite-200 with a specific surface area of 273 $m^2\ g^{-1}$ contained 52.7 wt.% manganese oxide and 11.40 wt.% copper oxide. To obtain monolith catalysts, the foil of the Fe—Cr—Al alloy 80 μm thick was coated with a thin layer of Carulite. The oxide coating was supported by the electrophoretic deposition[9] of a suspension containing finely ground Carulite (8.2 g L^{-1}, particle size 5—10 μm) in a solution of aluminum hydroxide sol in ethanol (the content of AlO(OH) was 8.2 g L^{-1}). After deposition the samples obtained were dried in air for 36 h at 20 °C and then calcined in an air flow for 2 h at 500 °C. The smooth and corrugated foil layers coated with Carulite were put together and rolled to form a monolith with a height of 2.6 cm and a cross section of 4.10 cm^2. The monoliths obtained had 40 triangular channels per 1 cm^2 of the cross section. The content of Carulite in each monolith was 0.06—0.07 g.

An air mixture containing 2.52 vol.% CH_4 was used for methane oxidation. Experiments were carried out at an atmo-

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spheric pressure in a flow-type reactor at 360—500 °C. In experiments with the granulated catalyst, a quartz reactor with a cross section of 0.82 cm^2 was used. The height of the catalyst bed in two experiments was 4 and 6 mm, and the weighed samples were 0.40 and 0.60 g, respectively. The reaction on monolith catalysts was performed in a quartz reactor with a cross section of 4.15 cm^2. The deep oxidation of CH_4 on granulated Carulite was studied in the 360—400 °C temperature interval. The methane conversion was varied in experiments from 20 to 99 vol.%. The oxidation of CH_4 on the metallic monoliths with the supported catalyst was studied at 400—500 °C, and the methane conversion was varied from 10 to 99%. The reaction products were analyzed by GLC on a column packed with Polysorb-1 (thermal-conductivity detector, helium served as a carrier gas, and the temperature was 25 °C). Chromatograms were detected and processed in the on-line mode on PC. Only CO_2 and H_2O were found as reaction products, indicating a high selectivity of the process. The methane conversion measured in experiments was determined from the amount of CO_2 formed. Activities of the catalysts were compared by monitoring the feed gas flow rate (v_0) corresponding to equal conversions of methane to CO_2. The flow rate of the initial mixture at a specified conversion is proportional to the reaction rate constant[6,10] and, unlike T_α and α_T, can be related to the catalyst weight. Since the volume of monoliths is determined by their construction and is not directly related to the volume of the active component, it is difficult to determine the real volume of the active component, therefore, instead of the contact time (s)

$$\tau' = V_c/v_0,$$

where V_c is the catalyst volume, for the monolith catalysts we used the proportional value of the effective contact time (s g cm^{-3})

$$\tau' = m/v_0$$

where m is the weight of the active component (Carulite). The obtained values of activities were independent of the sizes of reactors in which the reaction was performed.

Results and Discussion

To study the influence of mass exchange on the reaction kinetics, we studied the catalyst activity by changing the height of the catalyst bed and the gas flow rate at a constant space velocity. A good coincidence of the plots of the conversion of CH_4 *vs.* contact time τ (Fig. 1) was obtained for two different catalyst beds, suggesting the absence of diffusion limitations.[11] The kinetic data obtained are well described by the first-order rate law. The reaction rate constants were determined from the plot

$$\ln(1 - x) = -k\tau,$$

where x is the conversion, k is the reaction rate constant, and τ is the contact time. The calculated reaction rate constants are presented in Table 1.

The feed gas flow rates corresponding to conversions of 20, 30, and 40% were determined from the kinetic data on methane conversion obtained at 365—409 °C. In the flow-type reactor, the feed gas flow rates corresponding to the same conversion are proportional to the reaction rate constants

$$(v_{T1}/v_{T2})_\alpha = k_{T1}/k_{T2},$$

and the following equation is valid:

$$E = RT^2(\partial \ln v/\partial T)_\alpha.$$

Based on the Arrhenius plots of V_α *vs.* T^{-1} (Fig. 2), we determined the activation energy of methane oxidation. It was 25.8±1.9 kcal mol^{-1} for the granulated catalyst.

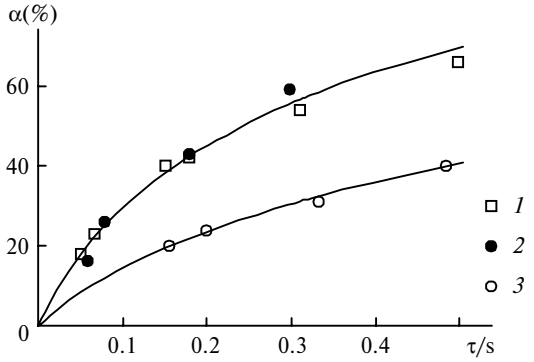

Fig. 1. Conversion of CH_4 into CO_2 by the oxidation with air on the granulated catalyst at 400 °C and different weighed samples: *1*, 0.4 g, bed height 4 mm; *2*, 0.6 g, bed height 6 mm; and *3*, 0.6 g, after preliminary heating to 450 °C.

Table 1. Calculated rate constants of CH_4 oxidation to CO_2

Catalyst	T/°C	h/mm (monolith)*	k/s^{-1}	k /cm^3 (s g^{-1})
Granules	400	4	2.80	2.13
	400	6	2.53	1.93
Granules**	400	6	1.15	0.88
Monolith	400	(2)	—	1.88
	500	(1)	—	16.66
	500	(2)	—	16.77

* Bed height.
** Granules after calcination at 450 °C.

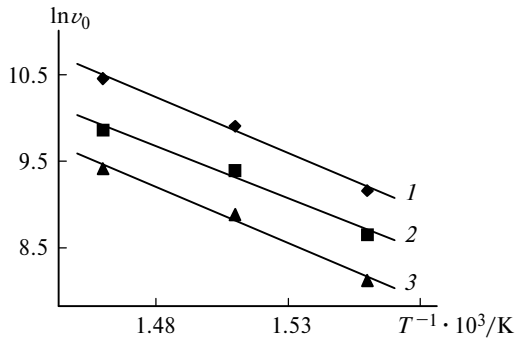

Fig. 2. Temperature dependence of the activity of the granulated catalyst in CH_4 oxidation to CO_2 at conversion (%): 20 (*1*), 30 (*2*), and 40 (3).

It was found that heating of the catalyst in the reaction mixture for 1 h at 500 °C decreases its activity (see Fig. 1), and the activation energy increases to 30.1±2.2 kcal mol^{-1}.

As in the case of the granulated catalysts, the catalyst activity of monoliths was studied at different flow rates and the same space velocity. With this purpose, the reaction was first performed on one monolith and then on two similar monoliths placed one above another in the reactor. The plots of the methane conversion into CO_2 *vs.* effective contact time obtained in these two experiments virtually coincide (Fig. 3). This indicates the absence of external diffusional limitations. The activation energy calculated from the feed gas flow rates corresponding to conversions of 20, 30, and 40% is 25.9±1.1 kcal mol^{-1} (Fig. 4) and coincides with the activation energy for the starting granulated catalyst. This indicates that the same mechanism is operative in the reaction on the granulated and monolith catalysts. The data obtained for both the monolith and granulated catalysts are well approximated by the first-order rate law. The calculated constants are presented in Table 1, and the curves are shown in Fig. 3. The obtained rate constants for CH_4 oxidation at 400 °C related to the unit weight of the active component are virtually identical for the monolith and granulated catalysts.

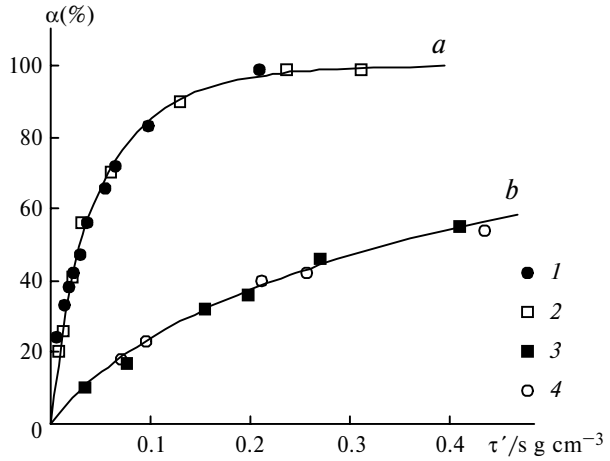

Fig. 3. Oxidation of CH_4 to CO_2 with air on the monolith catalyst at different temperatures: *a*, 500 °C and *b*, 400 °C: *1*, one monolith (height 26 mm, volume 10.8 cm^3, content of Carulite 0.067 g); *2* and *3*, 2 monoliths (height 52 mm, volume 20.7 cm^3, content of Carulite 0.127 g); *4*, granulated catalyst.

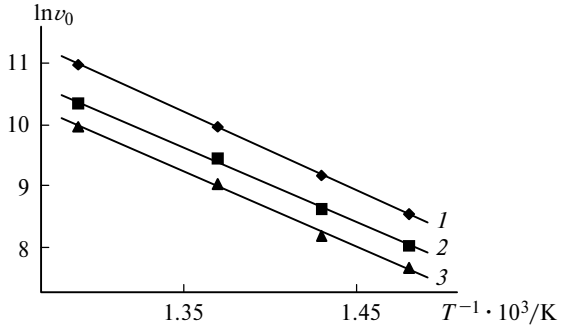

Fig. 4. Temperature dependence of the activity of the monolith catalyst in CH_4 oxidation to CO_2 at conversion (%): 20 (*1*), 30 (*2*), and 40 (*3*).

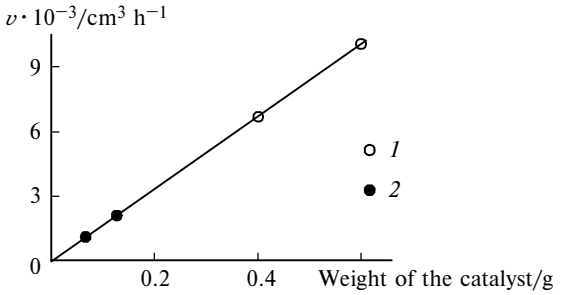

Fig. 5. Plot of the activity of the granulated (*1*) and monolith catalysts (*2*) in CH_4 oxidation to CO_2 *vs.* amount of the component; temperature 400 °C, conversion 40%.

Since the kinetics of methane oxidation on the monolith and granulated catalysts is described by the same rate law, their activities can be compared using the feed gas flow rate corresponding to the same conversion level. Comparison of the activities of the granulated and monolith catalysts at 400 °C by the feed gas space velocity corresponding to 40% conversion shows that the activity increases linearly with the amount of the active component (Fig. 5). This linear dependence indicates the absence of limitations due to bulk and internal diffusion.[10,12]

Thus, it follows from the data obtained that CH_4 oxidation at 400 °C on granulated Carulite and on the metallic monolith with the Carulite coating is controlled by kinetics. The reaction on both catalysts is characterized by the same activation energy and the rate constant, and the activities measured by the feed gas flow rate corresponding to the same conversion and related to the catalyst unit weight virtually coincide (Table 2). The deposition of the initial copper—manganese oxide catalyst by the electrophoretic method on a metallic support using Al_2O_3 as a binder has no effect on the catalytic activity of Carulite. At the same time, the distribution of the active component as a thin layer over the metallic monolith surface favors an increase in the

Table 2. Comparison of activities in CH_4 oxidation to CO_2 at 400 °C and conversion 40%

Catalyst	M^a /g	$v_\alpha{}^b$		v^c /h^{-1}
		cm^3 h^{-1}	cm^3(h g)$^{-1}$	
Granulated	0.6	10000	16670	20400
	0.4	6670	16670	20400
Monolith	0.067	1100	16420	100
	0.127	2100	16540	100

[a] Weight of active component.
[b] Feed gas flow rate.
[c] Space velocity.

thermal stability of the catalytic system. The performance of the monolith catalyst after thermal treatment in air at 500 °C was stable under the reaction conditions for 15 h at 500 °C (see Figs. 3 and 4).

The comparison of the activities of the granulated Cu—Mn-mixed oxide and metallic monolith catalysts shows that the feed gas flow rate corresponding to the achievement of a specified conversion and related to the unit weight of the active component can be used as a measure of activity of the monolith catalyst. The use of this value allows comparison of the activities of granulated and monolith catalysts to be conducted in a quantitative way.

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