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High-Temperature Oxidation of Methane by Supported Lead Oxide

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Abstract—The kinetics of the reduction of PbO supported on Al_2O_3 by methane is studied in the temperature range 760–927°C. The reaction order with respect to methane is equal to unity and the apparent activation energy is ~40 kcal/mol. When the extent of PbO reduction is 0.5–0.6, the selectivity of methane conversion changes drastically: only CO_2 is formed at lower extents of reduction, whereas CO is the main product at higher extents.

INTRODUCTION

The reaction of methane oxidation by metal oxide

$$CH_4 + 4MO \longrightarrow CO_2 + 2H_2O + 4M \qquad \text{(I)}$$

is an interesting alternative pathway for natural gas conversion. The metal oxide is an oxygen-transfer agent in this reaction. Reaction (I), metal oxidation by air

$$2M + (N_2 + O_2) \longrightarrow 2MO + N_2, \qquad \text{(II)}$$

and carbon dioxide–steam reforming

$$3CH_4 + CO_2 + 2H_2O \longrightarrow 4CO + 8H_2 \qquad \text{(III)}$$

enable syngas production without oxygen.

This idea is not new (see, e.g. [1]). Iron and nickel oxides have been considered as a promising system [2]. Recently, interest in this problem has risen and new solutions to it have appeared. Specifically, metal (e.g., lead) [3] oxide melts are proposed. Whereas the reactions of iron oxides with methane are well studied (see, e.g. [4]), the reduction of lead oxide by methane is not. This is largely due to the corrosiveness of lead oxide melt with respect to conventional materials for building reactors and difficulties in kinetic experiments associated with it.

We studied the reduction of PbO by methane on Al_2O_3 over a wide temperature range, which involves the temperature above the PbO melting point (888°C). This system shows the catalytic activity in the oxidative coupling of methane [5, 6]. To avoid the effect of this reaction on the kinetics of methane oxidation, the latter was studied in methane mixtures diluted with helium.

EXPERIMENTAL

Figure 1 shows the schematic of the setup for the study of methane oxidation by supported PbO. The setup consists of a block for dosing gaseous reactants (gas cylinders *1* and *2*, gas pressure regulators *3* and *4*, and fine-control valve *5*), a reactor (*13*) and an analytical block (dosing valve *6*, rheometer *7*, and chromatograph *12*).

The schematic of reactor *13* is shown in Fig. 2. It consists of quartz tube *1* with an inner diameter of 10 mm and a length of 180 mm and with quartz capillary *2* along the axis of the tube. The capillary had an outer diameter of 1.5 mm and a length of 300 mm. It was used as a thermocouple *7* well. To fix a bed of PbO/Al_2O_3 inside tube *1* (at a distance of 70 mm from the bottom), quartz support *3* was soldered into the tube.

The initial samples of the oxidant were prepared by the impregnation of alumina (γ or α-Al_2O_3; fraction 0.1–0.3 mm) by an aqueous solution of $Pb(NO_3)_2$ with further careful heating of the resulting suspension to evaporate water.

To decompose lead nitrate, the sample was calcined at 400°C for 3 h and then at 800°C for 6 h.

Analyses of the lead concentration in the initial oxidant samples and in samples after the runs were carried out by UV spectroscopy (271 nm). The spectra were recorded after dissolving the sample in 6 mol/l HCl. The amount of lead in the sample was accurate to ±10%. The analytical concentration of lead in freshly prepared samples coincided with the calculated concentration. The loss of lead after runs was at most 25% with respect to its initial amount.

Initial gaseous mixtures (methane–helium and oxygen–helium) were prepared by the sequential filling of steel cylinders preevacuated to a pressure of 1 Pa with individual gases. The concentration of methane in the mixtures was 0.4–5 vol % and the concentration of oxygen was 5 vol %.

Gaseous mixtures were analyzed by GLC using a Chrom-5 chromatograph with a thermal-conductivity detector, helium as a carrier gas, and stainless steel columns packed with Porapak-Q 80/100.

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† Deceased.

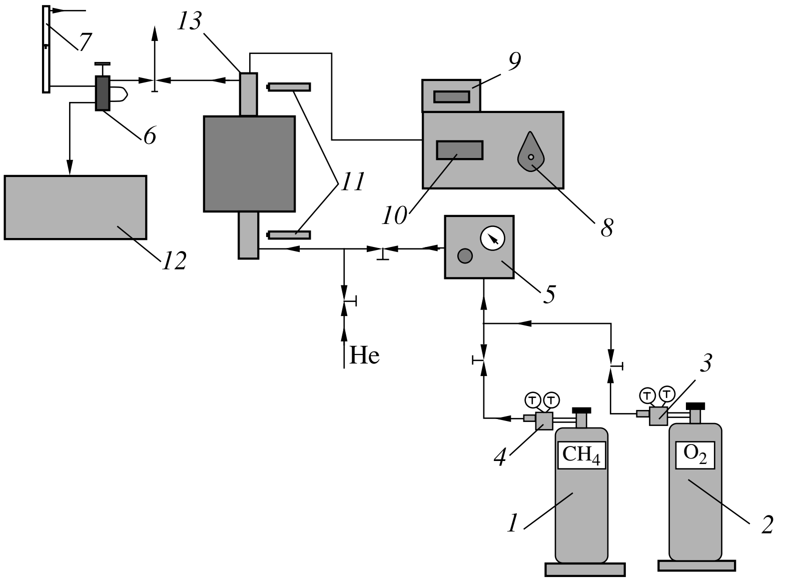

Fig. 1. Schematic of the setup: (*1*, *2*) gas cylinders; (*3*, *4*) pressure regulators; (*5*) fine-control valve; (*6*) dosing valve; (*7*) rheometer; (*8*) autotransformer; (*9*, *10*) digital voltmeters; (*11*) fitting for cooling air; (*12*) chromatograph; and (*13*) reactor.

The error in analyses of all components was ±2.5%. The sensitivity of GLC analyses was 0.03–0.05 vol %. The error in the determination of water was ±5% and the minimal detectable concentration of water was 1 vol %.

The experiments on methane oxidation using PbO/Al_2O_3 as an oxidant were carried out in a cyclic mode (incomplete reduction–complete oxidation by the O_2–He mixture).

The PbO/Al_2O_3 loading usually was 0.50–0.55 g. Methane was supplied in separate pulses for oxidation (the time for settling the stationary flow after changing the gas flow was as short as 2 s). The duration of pulses ranged from 45 to 90 s. At the end of a pulse, the product gas was analyzed. Then, the sample was oxidized. The extent of lead oxide reduction in the reaction of a separate pulse was not higher than 5–10%.

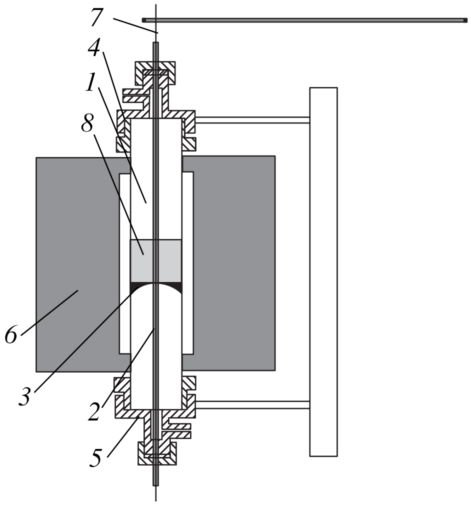

Fig. 2. Schematic of the reactor: (*1*) quartz tube; (*2*) quartz capillary; (*3*) quartz support; (*4*, *5*) metallic flanges; (*6*) electric furnace; (*7*) thermocouple; and (*8*) sample.

In the study of methane interaction with partially reduced PbO/Al_2O_3, the initial sample was preliminarily reduced by the known amount of the methane–helium mixture.

RESULTS AND DISCUSSION

Our experiments showed that, at low methane concentrations and in the studied temperature range, gaseous products of the reaction between methane and PbO contain CO, CO_2, and H_2O (H_2), whereas C_2 hydrocarbons are absent. At low extents of PbO reduction, only CO_2 and H_2O are formed.

Figure 3 shows a temperature dependence of methane conversion into carbon dioxide in the reaction with supported lead oxide for different concentrations of methane in the initial mixture. The concentration of lead oxide on alumina was 20 wt % in this experimental series. The conversion of PbO is at most 10%.

As can be seen from this figure, with a change in the initial concentration of methane by a factor of 4, the conversion of CH_4 into CO_2 remains virtually the same over the whole range of concentrations studied. Since the conversion is independent of the reactant concentration only in the case of a first-order reaction, the data suggest that the reaction order of CH_4 oxidation to CO_2 is equal to unity.

Figure 4 shows the dependence of CH_4 conversion into CO_2 (in the reaction with supported lead oxide) on the contact time, which was varied by changing the space velocity of the flow, at different temperatures and low PbO conversions. Because the reaction has the first order with respect to methane, the points are plotted that correspond to different concentrations of methane in the initial gaseous mixture. The curve is convex over the whole range of studied temperatures and concentrations.

These data were used to determine the apparent activation energy of methane oxidation into carbon dioxide. For better reliability, we used the temperature dependence of the contact time needed to achieve the same conversion of methane. This method is applicable to reactions with any kinetics. Indeed, the rate law of any reaction can be described as follows:

$$k = (1/\tau) f(x), \tag{1}$$

The form of the $f(x)$ function is determined by the rate law. At a constant conversion x $f(x)$ = const and the temperature dependence of k quantitatively corresponds to the temperature dependence of $1/\tau$, where τ is the contact time. In the experiments within this series, we used samples with a concentration of lead oxide of 20 wt %. The initial concentration of methane in helium is 0.91 vol %.

Figure 5 shows the Arrhenius plots. As can be seen from this figure, at moderate conversions, the above dependence gives close values of the apparent activation energy (~40 kcal/mol). It is worth mentioning that the points corresponding to $T = 927$°C (above the melting point of PbO) fall onto the same general straight lines. Therefore, we may assume that the strength of PbO binding to the support (Al_2O_3) is higher than the strength of binding in the PbO phase. At high conversions of methane (~70%), the apparent activation energy is ~60 kcal/mol, which can be due to a change in the process behavior at substantial conversions in methane oxidation. Another possible explanation is inaccuracy in the determination of τ at high conversions.

To study the dependence of the selectivity in methane oxidation on the extent of lead oxide reduction, we carried out a series of successive reductions of supported PbO without intermediate oxidations. Thus, the extent of reduction increased from one reduction run to another.

Figure 6 shows changes in the methane conversion and the selectivity of methane oxidation as PbO is reduced. As can be seen, the selectivity radically changes as the extent of reduction increases: for the sample with a stoichiometric composition close to PbO, the only oxidation product is CO_2; for the sample where lead is reduced for the most part, the main product is CO. A change in the selectivity of methane oxidation depending on the extent of PbO reduction is rather sharp, if not to say jumpwise. The amount of supported lead oxide, which in one experiment is twice as high as in the other (Fig. 6), does not affect observations: selectivity changes at close extents of reduction.

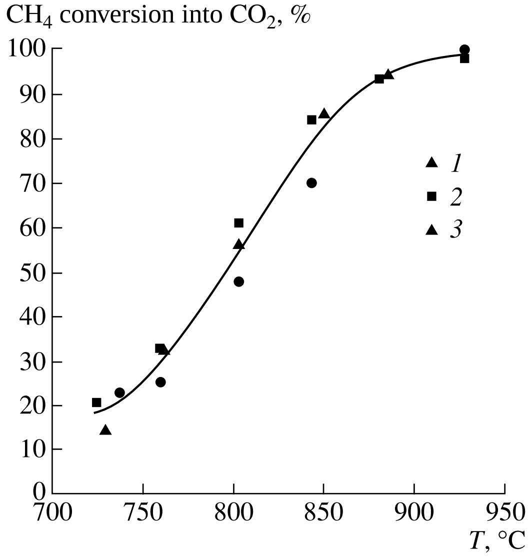

Fig. 3. Dependence of CH_4 conversion into CO_2 on temperature at different initial concentrations of methane: (*1*) 0.48 vol % CH_4 in He, (*2*) 0.91 vol % CH_4 in He, and (*3*) 1.61 vol % CH_4 in He.

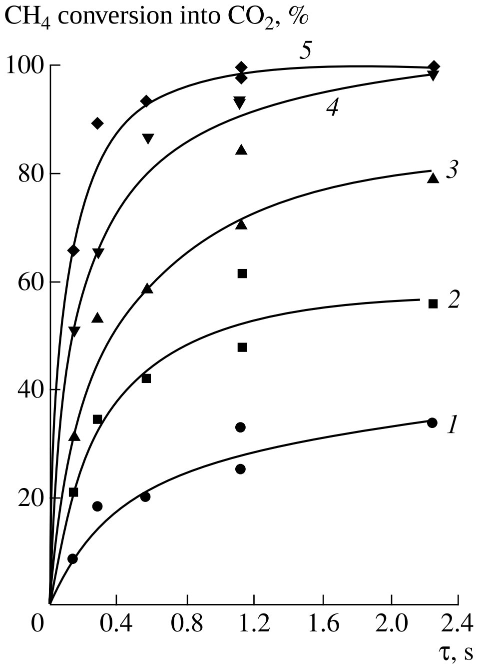

Fig. 4. Dependence of CH_4 conversion into CO_2 on the contact time at different temperatures for the 20 wt % PbO/Al_2O_3 sample: (*1*) 760, (*2*) 804, (*3*) 843, (*4*) 880, and (*5*) 927°C.

Thus, in dilute CH_4–He mixtures, the only products of methane oxidation by supported lead oxide are carbon oxides, and the process selectivity to CO or CO_2 is

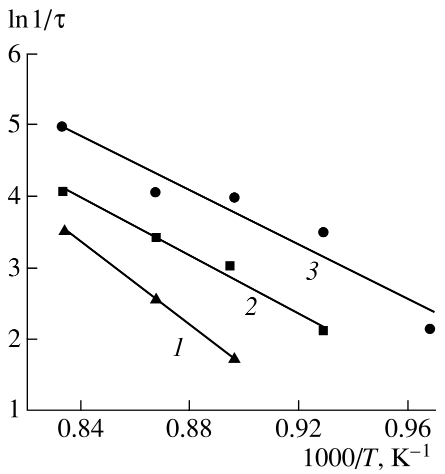

Fig. 5. Arrhenius plot for methane oxidation to CO_2 by supported PbO for the following conversions (τ is the contact time): (*1*) 70, (*2*) 40, and (*3*) 20%.

determined by the extent of lead oxide reduction. The selectivity changes drastically at an extent of PbO reduction equal to 0.5–0.6. To obtain the mixtures where CO dominates, the extent of reduction should be higher than this value.

Let us consider the kinetic features of lead oxide reduction. Metal oxide reduction reactions are usually topochemical. That is, the nuclei of the solid phase are formed and grow. This is reflected in peculiar kinetics: initially, the induction period is observed, which is replaced by a period when the reaction rate grows. Then, the reaction rate passes through a maximum and decreases. For the reduction of supported lead oxide, we did not observe these peculiar features that are characteristic of the reaction between a gas and a solid.

Figure 4 shows that the kinetic curves of PbO reduction by methane in the oxidation of the latter to CO_2 are convex over the whole time interval. Therefore, supported lead oxide mimics a homogenous system in the reduction reaction. This can be stipulated by a strong $PbO–Al_2O_3$ interaction and by the high mobility of ions in the system. The high mobility can lead to the relaxation of disturbance due to the reaction between pulses.

The apparent activation energy of PbO reduction characterizes energy required for the removal of oxygen from PbO to oxidize methane. It is interesting to compare this result with data for the complete oxidation of methane. The comparison shows that this value is within the interval found for the complete oxidation of methane (130–170 kJ/mol) [6] and does not contradict the opinion of Arutyunov and Krylov [6] that the mechanism of complete oxidation is associated with the activation of lattice oxygen.

Methane conversion into CO and CO_2 in the reaction with metal oxides was observed many times earlier (see, e.g. [4, 7]), but a drastic, almost jumpwise change in the selectivity of methane oxidation at ~50% extent of PbO reduction is unexpected. To the best of our knowledge, such a phenomenon has never been observed in the reactions of solids with gases. It might be assumed that the steps of adsorbed intermediate oxidation do not occur if oxygen is deficient on the surface, but then the selectivity should change gradually as oxygen becomes deficient on the surface in this case. Therefore, in the system under study, a more probable reason for a drastic change in the selectivity is a change in the structure of the dominant surface intermediate when oxygen is deficient. Because such a change is associated with the collective properties of the surface, a change in the selectivity may be rather drastic. That is, it may occur during a small change in the composition of the surface.

Note that a drastic change in the selectivity in a narrow range of the extents of PbO reduction shows that water-gas shift reaction and the reduction of CO_2 to CO do not occur to a noticeable degree, otherwise this change cannot be possible.

Earlier, it was considered that methane can be converted into syngas by oxidation in metal–metal oxide systems with further oxidation of the reduced oxide [7]. Group VIII metals (primarily, nickel) were examples. Considering possible coking, Lebedev and Nikanorova [7] concluded that the extent of metal oxide reduction cannot be higher than 50%. This conclusion is right the opposite to the experimental findings for our system.

A substantial difference of the system studied in [7] (nickel oxide) from the Pb–PbO system is that the former system shows a high catalytic activity toward water-gas shift reaction. Therefore, when Group VIII metal oxides are used, the selectivity of primary methane conversions at relatively high temperatures does not affect the product composition: the CO/CO_2 ratio in the oxidation products is determined by water-gas shift equilibrium. In the case of systems based on lead, water-gas shift reaction is insignificant. Therefore, the ratio between carbon oxides in the products of methane oxidation is almost completely defined by the selectivity of the oxidation process. As we showed in this work, this ratio drastically change depending on the extent of reduction, which should be higher than 50–60% for the mixtures enriched in CO.

Because the interaction of methane with PbO is not complicated by water-gas shift reaction, the Pb–PbO system is a very convenient model for the characterization of the ratio between the rates of separate steps: the oxidation of methane and the oxidation of the reduced oxidant. This fact can be important for methane conversion within the framework of the above concept [7]. For this purpose, we carried out experiments on the oxidation of partially reduced PbO under conditions (the temperature, the concentration of the gaseous reactant, and the contact time) close to those for methane oxidation. The measured rates of PbO reduction were compared to the rates of the reduced Pb oxidation.

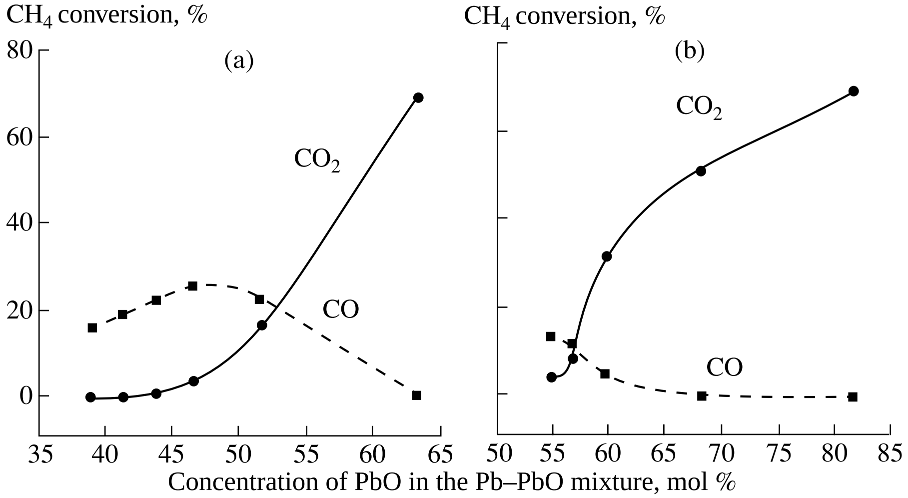

Fig. 6. Methane oxidation by the Pb–PbO mixtures with different compositions at 931°C: (a) 20 wt % PbO on Al_2O_3, (b) 40 wt % PbO on Al_2O_3. The initial mixture is 5 vol % CH_4 in He. The flow rate is 40 ml/min (normal conditions). The duration of a reductive pulse is 45 s.

The experiments showed that the oxidation rate of preliminarily reduced PbO is at least an order of magnitude higher than the rate of PbO reduction by methane. In the case of the 5% O_2 + He mixture, all of the oxygen is consumed up to the process completion. Lead is not very active in the reaction with oxygen. Therefore, we may consider that, in the catalysis via a stepwise mechanism, the reduction of oxide by methane is in most cases a slower process than reoxidation, which is a fast step.

Note that this conclusion that stems from our experimental observations does not agree with the conclusion of Arutyunov and Krylov [6, p. 281] that, in the complete catalytic oxidation of methane, the rate-determining step of the redox process is the catalyst oxidation. It is possible that this disagreement is also due to the effect of water-gas shift reaction on the composition of mixtures obtained in by methane conversion in the studies on which conclusion in Ref. 6 is based.

ACKNOWLEDGMENTS

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