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Methane partial oxidation. Challenge and perspective

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Abstract

The perspectives of direct partial oxidation of methane is considered in the light of the stability of the products of its partial oxidation. New data on the partial oxidation of methane into syngas are presented. $x\,\mathrm{CoO}\cdot(1-x)\mathrm{MgO}\cdot\mathrm{Al_2O_3}$ catalysts exhibit excellent performance along with a high stability. Partial oxidation of methane to oxy-products – formaldehyde and methanol, which is relatively unstable, has been performed with the product's removal from the reaction stream. It allows, using a cold trap, reach remarkable conversion with a high selectivity in the case of oxidation into formaldehyde and produce high concentration of methanol solution with the use of a special reagent–adsorbent in the case of methane oxidation to methanol.

Keywords: Methane; Partial oxidation; Syngas; Oxy-products; Methanol; Formaldehyde

1. Introduction

Methane partial oxidation is an attractive route to involve methane into synthesis of liquid fuel and valuable chemicals [1]. The major constrains on this route arise from the large gap between chemical reactivity and thermal stability of methane and products of its transformation. Table 1 shows constant of equilibrium (K_f) for decomposition of the products of methane partial oxidation at the temperatures of the practical interest. One can see that both methanol and formaldehyde are unstable toward decomposition at these conditions. Indeed, the attempts to reach a high degree of methane conversion into oxy-products – methanol or formaldehyde lead to a sharp decrease in selectivity [1].

The partial oxidation of methane into carbon monoxide and hydrogen does not follow this pattern, as the product is relatively stable and can be produced with a high selectivity at high conversion of methane [2].

To overcome the problem of the large difference of reagent–product stability while producing oxy-products (methanol or formaldehyde) by partial oxidation of methane, the unstable product must be removed from the reaction cycle after short residence time. By this way a reasonable conversion of the methane can be achieved along with a high selectivity.

Below the results of partial oxidation of methane into syngas over new oxide catalysts as well as selective oxidation of methane into methanol and formaldehyde with the removal of products from the reaction cycle will be considered.

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Table 1
Relative stability of the products of partial oxidation of methane

Compound	Products of decomposition	lg K_f			
		400 K	600 K	800 K	1000 K
CH_3OH	$CO+2H_2$	−0.21	4.00	6.21	7.57
CH_2O	$CO+H_2$	5.08	5.46	5.72	5.88
CO	$C+1/2\ O_2$	−19.13	−14.34	−11.93	−10.48

2. Partial oxidation of methane into syngas

Partial oxidation of methane into syngas proceeds quite effectively on the many catalysts, mostly containing a high loading of noble metals, but only selected catalysts show more or less stable performance [3]. Here we report new selective and stable oxide catalyst, which does not contain a noble metal.

Catalysts of the composition xCoO·(1−x)MgO·Al_2O_3 were prepared by co-precipitation of nitrates of cobalt, magnesium and aluminum. Precipitate was dried overnight at 120°C and calcined at 800°C for 10 h. Catalysts were tested in fixed bed reactor. Before the reaction catalysts were reduced in the hydrogen flow at 500°C for 30 min. XRD study revealed that all active and selective catalysts contain metallic cobalt in the cubic form, which appears to be the active component of these catalysts [4].

The catalysts exhibit excellent activity and selectivity in both methane–air and methane–oxygen reaction mixtures (Table 2).

The above data show that in both mixtures xCoO·(1−x)MgO·Al_2O_3 catalysts provide high conversion with a good selectivity towards carbon monoxide and hydrogen (H_2/CO about 2).

Table 2
Relative xCoO·(1−x)MgO·Al_2O_3 catalysts performance (850°C, 0.1 g of catalyst, O_2: 90 ml/min, CH_4: 180 ml/min)

Catalyst composition	CH_4 conversion (%)	CO selectivity (%)	H_2/CO ratio
0.15CoO·0.85MgO·Al_2O_3[a]	88	97	2.1
0.25CoO·0.75MgO·Al_2O_3[a]	95	99	2.1
0.25CoO·0.75MgO·Al_2O_3[b]	87	98	2.1
0.5CoO·0.5MgO·Al_2O_3[b]	95	99	2.0
0.75CoO·0.25MgO·Al_2O_3[b]	92	98	2.0

[a] Methane–oxygen mixture.
[b] Methane–air mixture.

The stability test was performed with two different catalyst compositions using methane–oxygen and air–oxygen reaction mixtures. The results are presented in Table 3. One can see from this table data that catalysts practically did not change activity and selectivity after hundreds of hours on stream. The presented results evidence that cobalt–magnesia–alumina catalysts are prominent for partial selective oxidation of methane into syngas.

3. Partial oxidation of methane into formaldehyde and methanol

As has been pointed out above the remarkable conversion of methane at high selectivity can be achieved by removal of product from the reaction cycle at low methane conversion (and a low contact time). This can be done by two ways: (i) cooling of the reaction mixture below temperature of the product condensation; (ii) extraction of the reaction product from the reaction mixture by special adsorbent, from which the product can be recovered easily. Both of these ways have been applied in the study.

3.1. *Partial oxidation of methane into formaldehyde with the product condensation*

Partial oxidation of methane into formaldehyde was performed in continuous plug-flow and the batch reaction system on 5% V_2O_5/SiO_2 catalyst, possessing by the excellent activity in oxidation of methane to formaldehyde [5]. At a short contact time the catalyst exhibits quite a high selectivity, but it quickly dropped while conversion increases (Fig. 1). One can suppose that the observed sharp drop of selectivity is a result of formaldehyde decomposition under the reaction conditions. Indeed, when total selectivity towards formaldehyde+CO was plotted (Fig. 1), it only slightly declines and remains very high over the range of the investigated contact time.

In order to overcome the difficulty with fast formaldehyde decomposition during the reaction the batch reaction system with circulation of the reaction mixture via the trap, cooled to −15°C was applied. This procedure allows remove quickly formaldehyde

Table 3
The stability test in methane oxidation on xCoO·(1−x)MgO·Al_2O_3 catalysts

Catalyst	T (°C)	CH_4 conversion (%)	CO selectivity (%)	H_2/CO ratio
0.5CoO·0.5MgO·Al_2O_3	837	94.4	98.4	2.0
after 255 h on stream in air–methane mixture	837	94.0	99.0	1.9
0.25CoO·0.75MgO·Al_2O_3	850	95.0	99.0	2.1
after 313 h on stream in oxygen–methane mixture	850	95.2	99.0	2.1

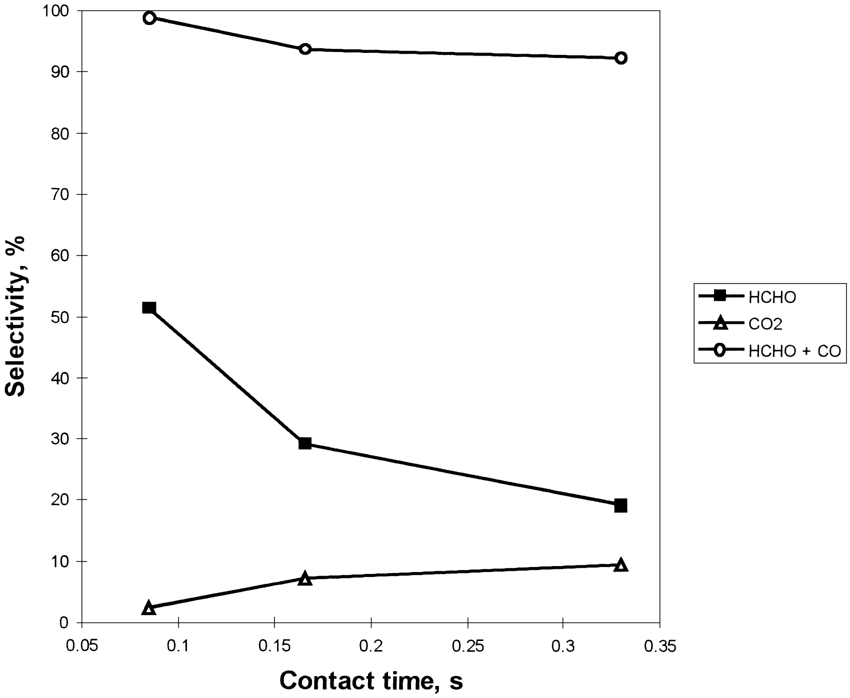

Fig. 1. Dependence of the product selectivity on the contact time in the process of methane partial oxidation to formaldehyde over 5% V_2O_5/SiO_2 catalyst (T=600°C).

from the reaction mixture preventing its decomposition. During a typical reaction run on at 520°C conversion linearly increased with the reaction time while the selectivity did not change being of the value of about 50%. Thus, after 3 h on stream conversion of methane was 12% at 53% selectivity towards formaldehyde. As no decrease of selectivity with the reaction time was observed, in principle, theoretical yield equal to selectivity (~50%) can be achieved at complete methane conversion.

3.2. *Partial oxidation of methane into methanol with the product adsorption*

Methane partial oxidation into methanol was investigated with as well as without catalysts. The only system which has shown catalytic effect in comparison with the gas phase non-catalytic oxidation under normal pressure was 30% H_3BO_3/Al_2O_3. Under the elevated pressure (3 and 50 bar) the best results were obtained by gas phase oxidation without catalyst, that

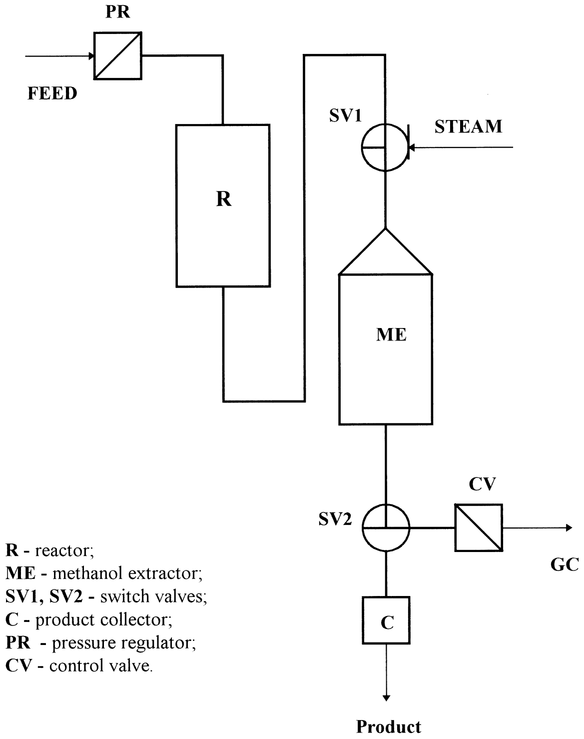

Fig. 2. Scheme of installation for methane partial oxidation to methanol.

is in agreement with the literature data [6]. The maximal yield per pass at $P=3$ bar, $T=475°C$ was 1.7%, which is very low to make practical separation of the product.

In order to increase the total yield of the product and its concentration methanol was extracted from the reaction cycle by passing the reaction mixture via the trap, filled with silica treated by boric acid. The trap was held at 120°C and effectively removed methanol from the reaction stream. After passing of a certain amount of the reaction mixture via the trap, it was switched off the reaction stream and connected to a steam generator (Fig. 2).

Adsorbed into the trap methanol was released by the steam treatment and collected under the trap. The results of these experiments are presented in Table 4. These results show that the extraction efficiency is quite high and a concentrated methanol solution can be produced by this way.

4. Conclusion

As mentioned above, the direct selective oxidation of methane is largely restricted by product stability. The only relatively stable product of the methane partial oxidation is carbon monoxide, which can be produced with high selectivity along with a high degree of conversion. New effective catalytic system $x\mathrm{CoO}\cdot(1-x)\mathrm{MgO}\cdot\mathrm{Al_2O_3}$ has been found in this study. The system has demonstrated high selectivity at almost complete conversion of methane showing also exceptionally high stability under reaction conditions. Many attempts have been done to reach considerable yield of oxy-products: methanol and formaldehyde by direct conversion of methane. They were not successful due to low product stability under conditions of methane partial oxidation. The approach used in the study was to remove product from the reaction mixture at low conversion, when high selectivity can be maintained. For partial oxidation of methane into formaldehyde it was condensation of formaldehyde in the cooled trap with re-circulation of the reaction mixture. In the case of oxidation of methane to methanol the product was extracted from the reaction mixture by special adsorbent – reagent, from which methanol was recovered by substitution with water. The latter procedure allows also to recover methanol with high efficiency as a concentrated solution.

Table 4
Methane partial oxidation with methanol extraction

Run	CH_4 conversion (%)	MeOH selectivity (%)	MeOH concentration (%)	Extraction efficiency (%)
1[a]	12.2	13.8	47	81
2[b]	2.6	50.3	52	78.5

[a] Reaction: 475°C, CH_4:O_2:N_2=80:17:3; $P=3$ bar.

[b] Reaction: 455°C, CH_4:O_2=95.8:4.2; $P=50$ bar.

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