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The catalytic oxidation of heated lean homogeneously premixed gaseous-fuel air streams

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Abstract

Results are presented of an experimental laboratory investigation of the oxidation reactions of heated low velocity streams of homogeneous lean fuel–air mixtures within a packed bed tubular reactor at atmospheric pressure in the presence of non-noble metal oxides catalysts. The main fuel considered was methane, however, other common gaseous-fuels, i.e. propane, carbon monoxide, hydrogen and ethylene were also examined for comparative purposes. It was shown that binary cobalt oxide/chromium oxide catalysts can be effective in the oxidation of very lean fuel–air mixtures. Furthermore, there is an optimum value of their mass ratio that could produce a significant improvement to the low temperature oxidation of the lean mixtures examined and the corresponding resulting emissions.

Keywords: Catalytic oxidation; Lean mixtures; Gaseous-fuel air streams

1. Introduction

It has been well recognized over the years that it would be highly desirable both economically and environmentally to be able to lower the threshold temperature of the oxidation reactions of common gaseous-fuels in air and burn fuel–air mixtures that are leaner than their recognized corresponding lower flammability limits. It would then be possible to utilize the energy release from such exothermic reactions in conventional thermal power devices and heating furnaces. So far this remains not an easy task. The practical limitations arise from the fact that gas-phase reactions, especially those of the common low molecular weight gaseous-fuels, such as methane in air proceed far too slowly to be a worthwhile practical source of energy release. Only through the use of sufficiently high reaction temperatures and avoiding having mixtures that are too lean that gas-phase reactions involving these fuels can proceed at rates suitable for practical exploitation. This is also the case in relation to the gas-phase oxidation of the small concentrations of unreacted fuel and carbon monoxide in the exhaust gases of common combustion devices. These gases cannot be made to oxidize completely on their own within the exhaust systems of engines or other combustion devices. There is obviously a need to continue with the massive research effort to make these desirable features a practical reality.

It has been well known for many years that the rates of oxidation reactions within very lean mixtures of common gaseous-fuels in air can be increased very significantly through the presence of some catalytic materials. So far, most of the applications of catalysts in practical combustion systems, whether to enhance the rates of combustion processes or to complete the oxidation of undesirable pollutants in the exhaust gas have involved expensive and relatively rare metals such as platinum, combined with elaborate methods for process control. Obviously, it would be highly desirable to continue to investigate whether there are some more common and hence cheaper metals, their oxides and some of their mixtures that can serve as possible catalysts for enhancing the oxidation rates of lean homogeneous mixtures of common gaseous-fuels in air. Any material found capable of doing this to any significant degree would be economically most welcome even if the extent of improvement were significantly less than that obtained commonly with platinum or other noble metals.

The objective of the present work was to investigate the effectiveness of cobalt oxide (Co_3O_4), chromium oxide (Cr_2O_3), and their binary mixtures as inexpensive alternatives to the use of Pt catalyst for the oxidation of heated low velocity streams of lean homogeneous mixtures of methane and air, at atmospheric pressure. These catalysts were chosen as potentially active for oxidation of lean

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methane–air mixtures from [1–3]. They also exhibit high temperature stability over a range of temperatures typical for catalytic combustors [3]. Comparative tests were also made using these catalysts in combustion of other common gaseous-fuels that included propane, ethylene, hydrogen and carbon monoxide. The effects of changes in feed mixture flow rate, and hence residence time, initial temperature and equivalence ratio on the exhaust composition and the course of the reaction were established. Additionally, corresponding tests using platinum as catalyst were also made throughout for comparative purposes.

Table 1
Characteristics of the catalysts tested

Catalyst	Material	Co_3O_4/Cr_2O_3 ratio (by mass)	Catalyst loading (wt.%)
(1)	Co_3O_4	–	5.01
(2)	Co_3O_4/Cr_2O_3	4.00	5.66
(3)	Co_3O_4/Cr_2O_3	3.13	5.33
(4)	Co_3O_4/Cr_2O_3	2.00	4.50
(5)	Co_3O_4/Cr_2O_3	0.33	4.04
(6)	Co_3O_4/Cr_2O_3	0.25	4.75
(7)	Cr_2O_3	–	4.88
(8)	Pt	–	0.50

2. Experimental apparatus and procedure

The experimental set-up designed to study the catalytic oxidation of preheated homogeneous fuel–air mixtures is shown schematically in Fig. 1. The circular cylindrical smooth test reactor of 29 mm inside diameter and 300 mm long was made of alumina. The reactor was heated uniformly with external electrical heating so as to produce a 100 mm long section that was kept at a uniform temperature to within ±5° where the catalytic bed is located. The packed bed was 50 mm long made up of 3.2 mm diameter catalytic pellets and was held in place by two honeycomb monoliths (ceramic cordierite—Ceclor made by Corning Glass). The air supplied to the reactor was controlled over a wide range of flow rates and temperatures. The gaseous-fuel was injected radially into the air stream some 500 mm upstream of the reactor section to ensure rapid and thorough mixing before arrival at the catalytic bed. The fuel and air streams were metered using precalibrated choked nozzles. The temperature within the center of the reactor was measured using Pt/Pt–Rh thermocouple ceramic shielded to avoid any catalytic action. Gaseous-fuels employed included methane, propane, ethylene, hydrogen and carbon monoxide. The concentrations of the major stable product species in the reacting flow (e.g. CH_4, C_3H_8, CO_2, CO and O_2) were sampled using a retractable probe along the axis of the reactor and established using mainly N.D.I.R. type analyzers.

The catalysts listed in Table 1 were prepared and deposited on γ-alumina support pellets. They were examined under a scanning electron microscope to ensure satisfactory dispersion of the metal oxides on the support. The activity

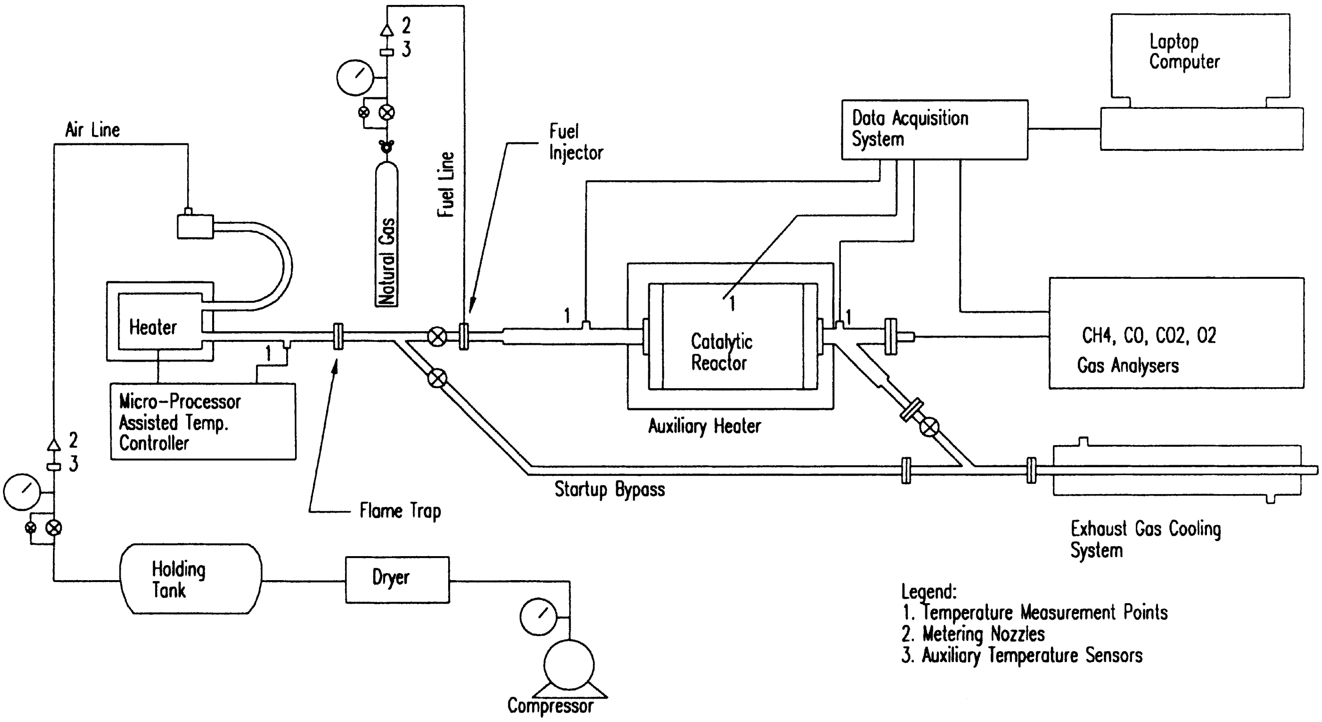

Fig. 1. Experimental set-up.

of the prepared catalysts was compared to that of a platinum catalyst supplied by Johnson Mathey Inc. having 0.50% Pt by weight on y-alumina. The equivalence ratio of the test fuel–air mixture was varied from 0.15 to 0.50. The corresponding range of equilibrium temperature rises (ΔT) was from 360 to 1100 K. The approach velocity at the inlet to the bed ranged from 1.0 to 3.0 m/s.

3. Results and discussion

The results of methane oxidation within the reactor as a function of the temperature of the methane–air mixture in the presence of different prepared single and binary chromium oxide/cobalt oxide catalysts are shown in Fig. 2, for equivalence ratio of 0.35 and approach velocity of 1 m/s. Methane conversion was calculated on the basis of the measured concentrations of methane at the inlet and the exit of the reactor. It can be seen that the composition of the catalyst affected significantly the methane conversion at the same temperature (Fig. 3). Pure chromium oxide Cr_2O_3 (catalyst (7)) was more effective than pure Co_3O_4 which was unexpected on the basis of the literature (e.g. [3]). The binary catalysts performed significantly better than the single catalysts. Similar trends have previously been reported in [4]. The activity of the binary catalysts increased with decreasing Co_3O_4 content. The catalysts with Co_3O_4/Cr_2O_3 mass ratio of 0.33 (catalyst (5)) and 0.25 (catalyst (6)) were more active than others with the higher mass ratio of 4.00, 3.13 and 2.00. However, all these catalysts remain significantly less effective than platinum, especially at lower and intermediate temperatures.

Table 2
"Light-off" temperature ($T_{\text{light-off}}$) and temperature of 90% CH_4 conversion for catalytic oxidation of methane at $N = 0.35$ and $V = 1$ m/s over the tested catalysts

Catalyst	$T_{\text{light-off}}$ (K)	$T_{90\%}$ (K)
(1)	820	1030
(2)	780	995
(3)	780	975
(4)	760	1115
(5)	730	960
(6)	700	1030
(7)	780	970
Pt	670	845

The methane conversion versus temperature curves for all the catalysts tested have the characteristic S-shape of catalytic combustion of hydrocarbons [3,5]. Typically fuel conversion of up to 20% constitutes the regime of kinetically-controlled surface reactions. With a further increase in the inlet temperature and subsequent enhancement of the reaction rate, the concentration of the fuel at the surface depletes rapidly. At these conditions, the overall oxidation rate in the bed would be determined by the transport of reactants to the surface. Fuel conversions of 30–70% are observed typically under such conditions [6].

The temperature at which transition from the kinetically-controlled regime to the mass transfer controlled regime takes place is called the "light-off" temperature. In nearly

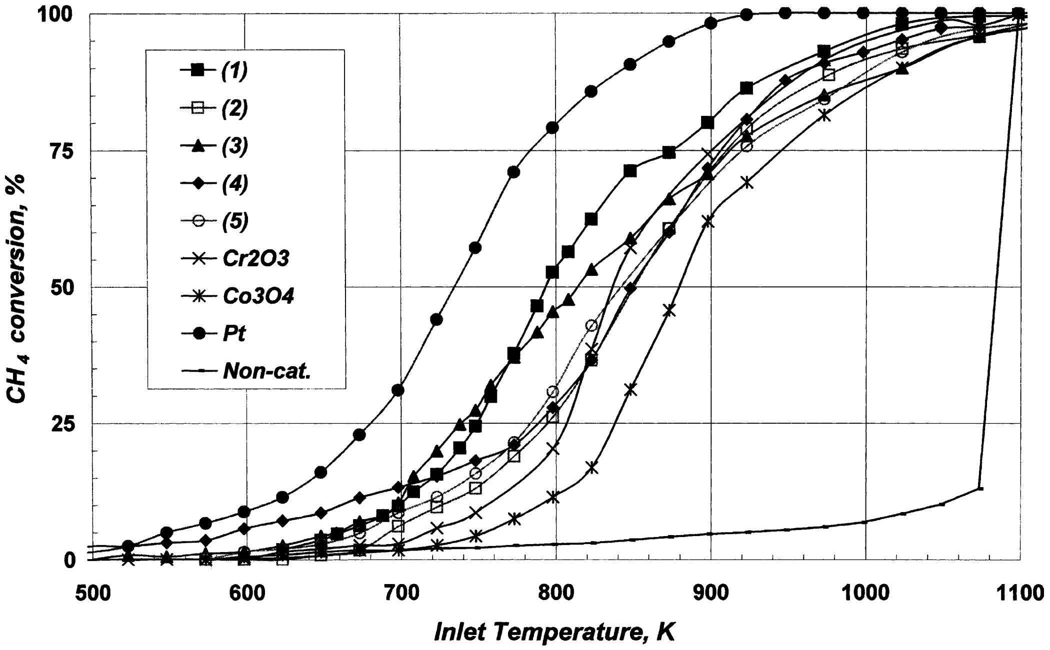

Fig. 2. Methane conversion as a function of temperature for different catalysts at $\phi = 0.35$, approach velocity $V = 1.0$ m/s, space velocity $= 1.71 \times 10^5$ $m^3/(m^3$ h).

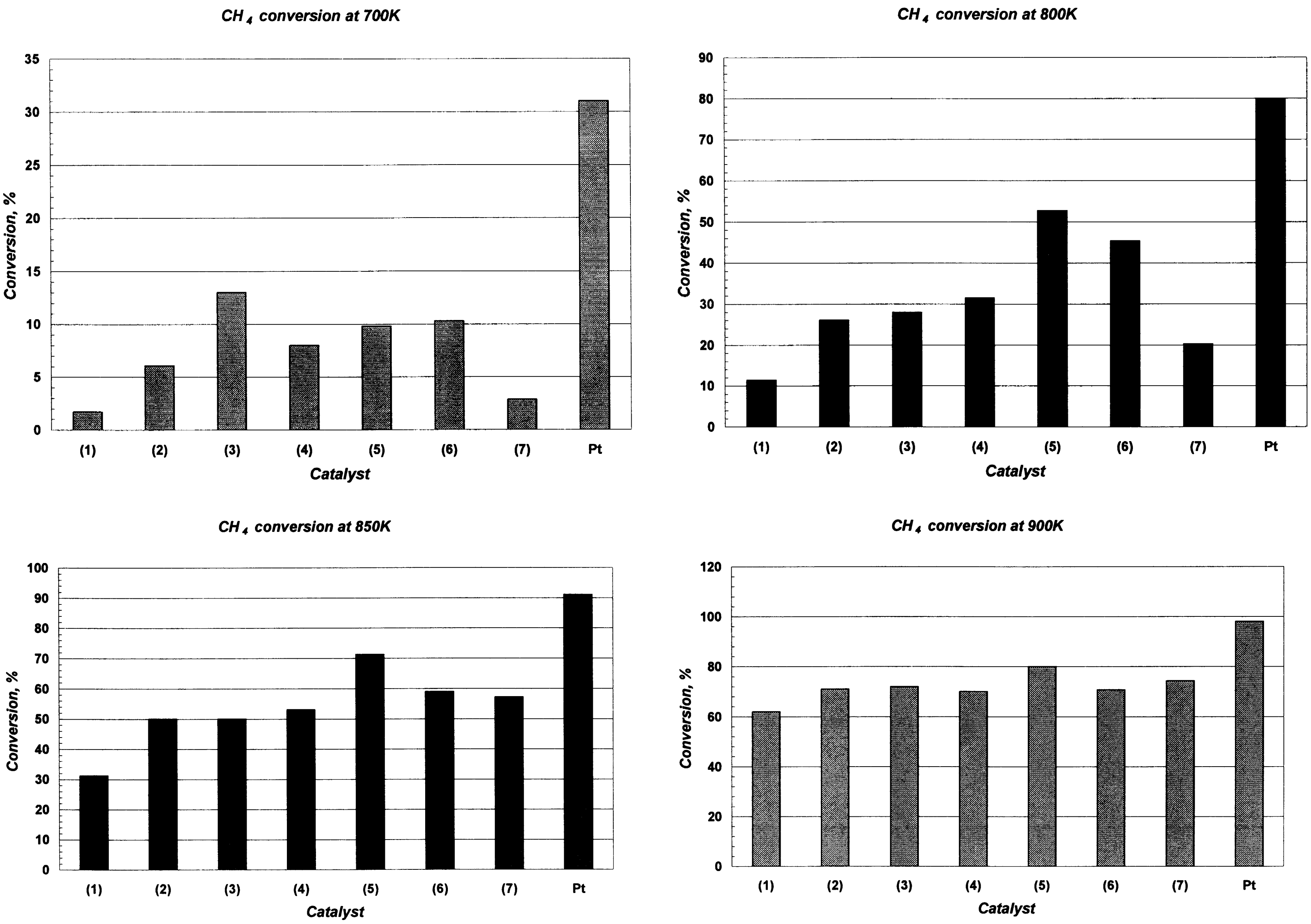

Fig. 3. Methane conversion over different catalysts at different temperatures, $N = 0.35$, $V = 1.0\,\mathrm{m/s}$.

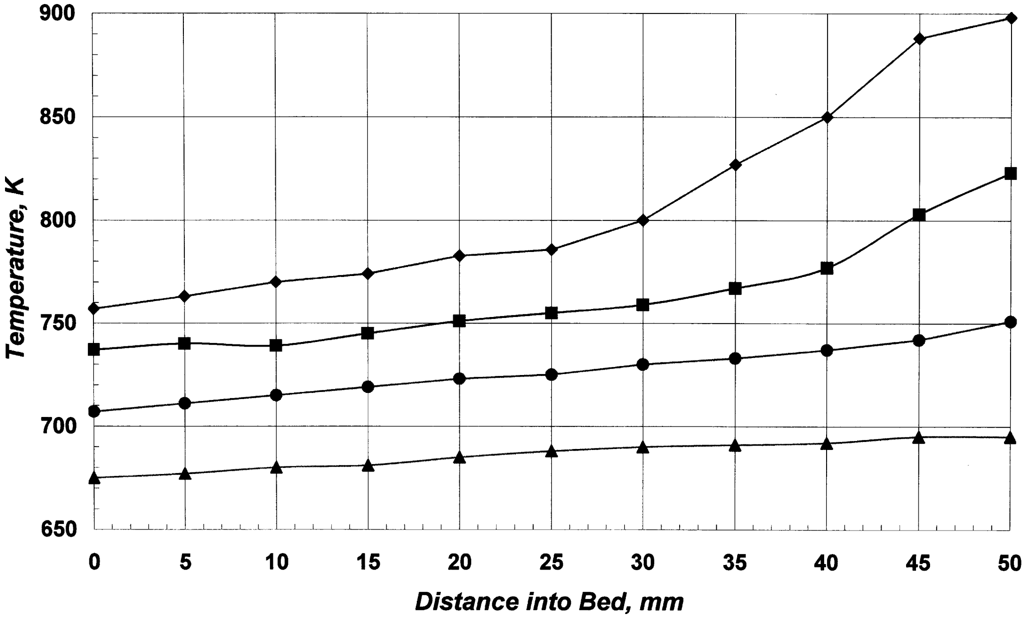

Fig. 4. Temperature profiles within the catalytic bed with catalyst (5) at $N = 0.35$, $V = 1.0$ m/s.

all experiments, fuel conversion leveled at around 90%, which is probably due to diffusion limitations. At higher temperatures, the rate of gas-phase reactions can become significant in comparison to the surface reactions and the fuel conversion would then proceed to completion with energy release rates comparable to those of conventional flames. It is commonly accepted to describe catalysts in terms of their "light-off" temperature and the temperature at which 90% of fuel is converted. The corresponding values of these temperatures for all the catalysts tested are shown in Table 2. The lower these temperatures are, the more effective is the catalyst.

Temperature and methane concentration profiles within the catalytic bed were measured for the mixture equivalence ratio of 0.35 and approach velocity of 1.0 m/s. The catalyst (5) the most effective among the metal oxides catalysts tested was employed and the results are shown in Figs. 4 and 5. It can be seen that at temperatures lower than the "light-off"

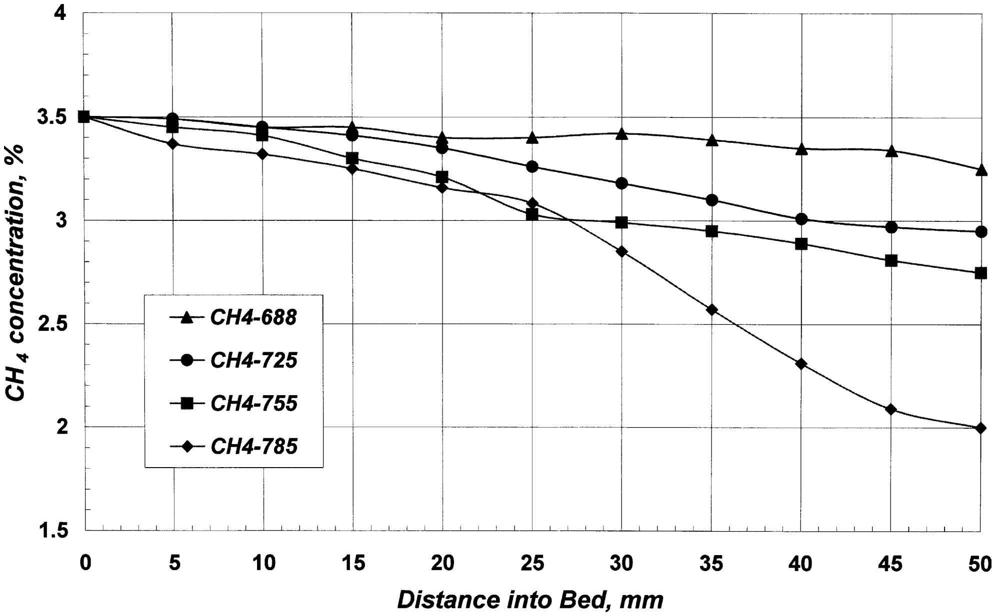

Fig. 5. Methane concentration profiles within the catalytic bed with catalyst (5) at $N = 0.35$, $V = 1.0$ m/s.

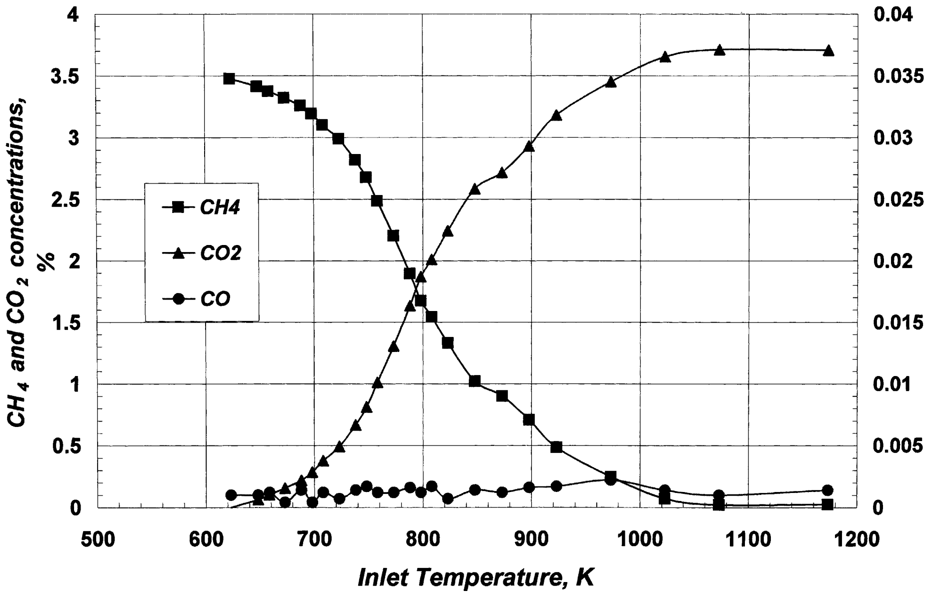

Fig. 6. Exhaust concentrations of CH_4, CO and CO_2 as a function of temperature for the catalytst (5) at $N = 0.35$, $V = 1.0\,m/s$.

temperature (e.g. 688 K), the methane oxidation rate is low and the corresponding increase in the gas temperature is also small. With an increase in the initial temperature of the gas mixture, higher methane oxidation rates were accompanied by higher increases in the temperature, especially in the second half of the reactor.

The exhaust concentrations of CH_4, CO and CO_2 measured at the earlier mentioned conditions are shown in Fig. 6. The concentration of CO in the exhaust was below 0.01% (within the uncertainty of measurement of the CO analyzer). Although the concentration of NO_x was not measured, it is expected to be very low at the temperature levels encountered.

The effects of the equivalence ratio and approach velocity on methane conversion over catalyst (5) were also investigated and can be seen in Figs. 7 and 8. The methane conversion decreased with increasing equivalence ratio. This effect was especially pronounced within the temperature range from 750 to 850 K corresponding to the mass controlled regime. Under such conditions the conversion rate could be improved by, for example, increasing the residence time (Fig. 8), or by using higher

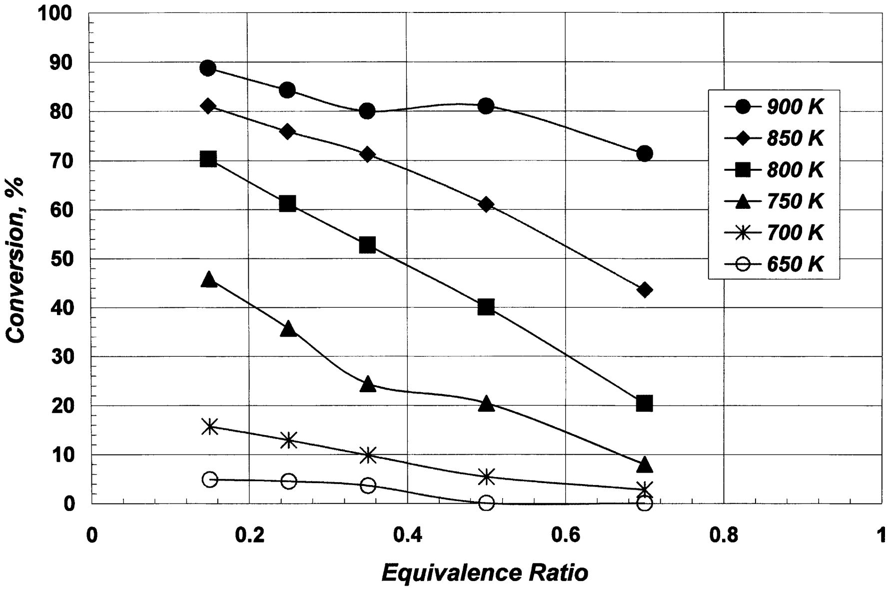

Fig. 7. Methane conversion as a function of equivalence ratio at different temperatures for the catalyst (5), $V = 1.0\,m/s$.

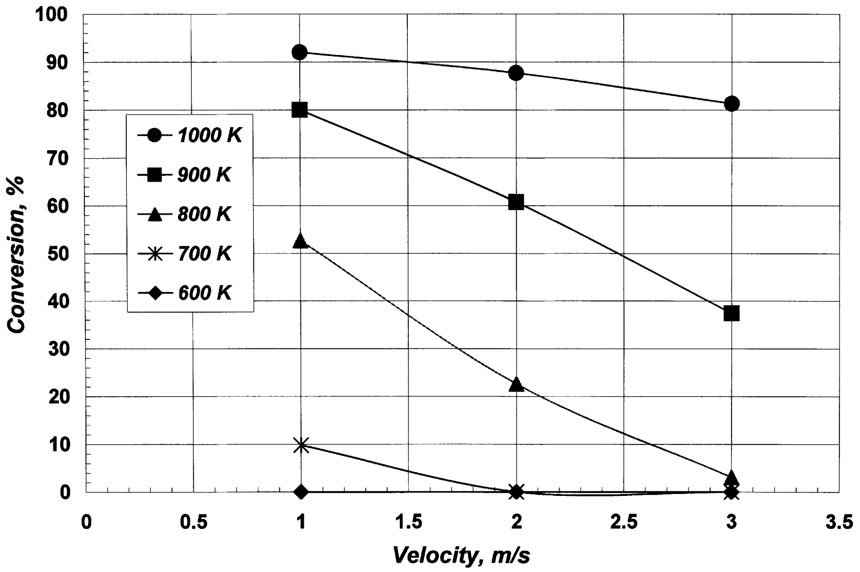

Fig. 8. Methane conversion as a function of the approach velocity at different temperatures for the catalyst (5), $N = 0.35$.

concentrations of the catalyst. An increase in the gas mixture velocity resulted in the decreased amount of the methane converted due to a reduction of the residence time.

Comparative tests were conducted on the oxidation of some other common gaseous-fuels also employing catalyst (5), as well as Pt catalyst for comparison. The results for carbon monoxide, propane, ethylene and hydrogen obtained for the equivalence ratio of 0.35 and an approach velocity of 1.0 m/s are shown in Figs. 9 and 10. The complete conversion of hydrogen was achieved at 400 K, while the complete conversion of ethylene, carbon monoxide and propane were achieved at 665, 800 and 975 K, respectively. The corresponding temperatures for 90% conversion were 375, 590, 675 and 885 K. In the case of ethylene, small amounts of CO were measured in exhaust gases with the maximum concentration of 0.04% at the temperature of ≈580 K corresponding to ≈80% of the fuel conversion. For propane concentrations of CO at the exhaust were significantly higher with the maximum value of 0.2% at the temperature of 760 K also corresponding to ≈80% of the fuel conversion. The presence of carbon monoxide in the exhaust is consistent with the onset of gas-phase reactions.

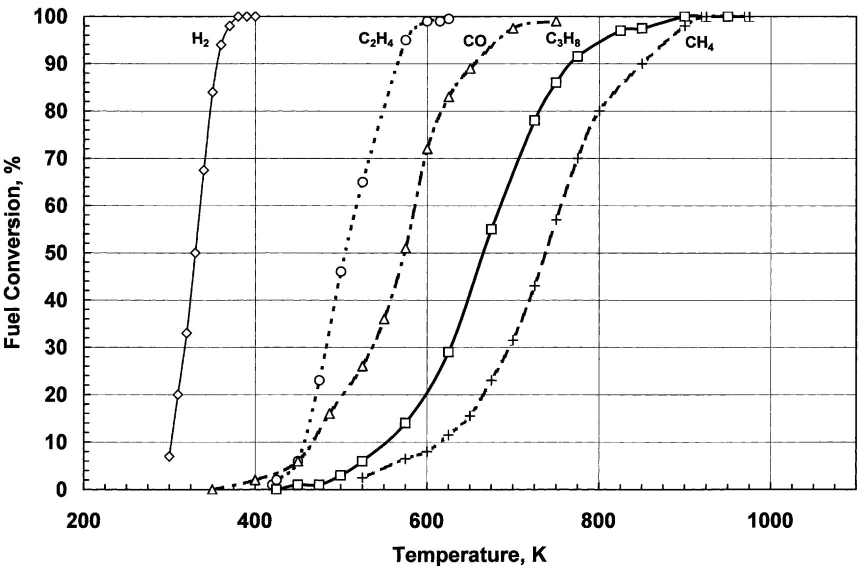

Fig. 9. Conversion of different fuels as a function of temperature for the catalyst (5) at $N = 0.35$, $V = 1.0$ m/s.

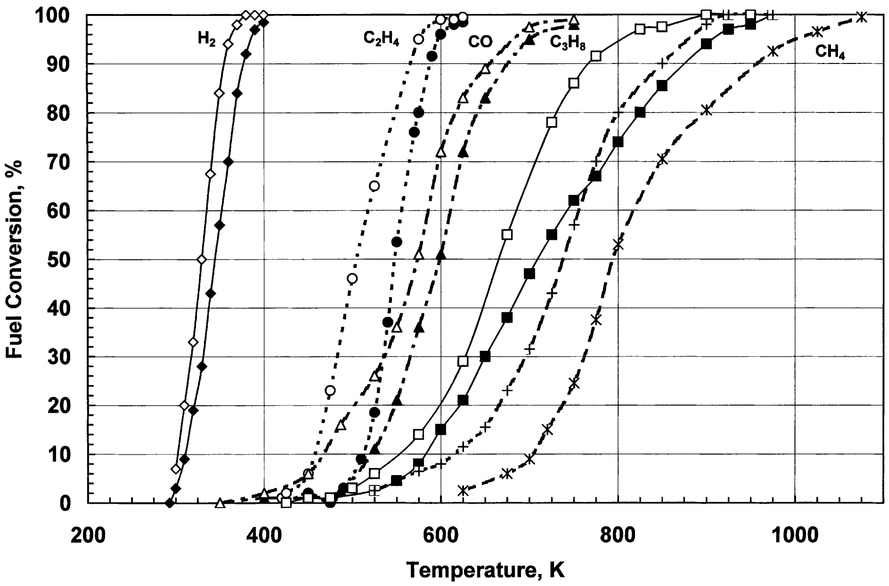

Fig. 10. Conversion of different fuels as a function of temperature for the catalysts (5) and Pt at $N = 0.35$, $V = 1.0$ m/s.

4. Conclusions

- Binary cobalt oxide/chromium oxide catalysts can be effective in the oxidation of very lean fuel–air mixtures.
- The most active among the different binary catalysts tested was a catalyst with a cobalt oxide to chromium oxide mass ratio of 0.33.
- The 90% conversion of methane, propane, carbon monoxide, ethylene and hydrogen in lean homogeneous mixtures with air in the presence of this catalyst was achieved at 960, 885, 675, 590 and 375 K, respectively at the mixture equivalence ratio of 0.35 and an approach velocity of 1.0 m/s. No carbon monoxide was recorded at these conditions in the case of methane oxidation. However, in the case of ethylene and propane noticeable amounts of carbon monoxide were present in exhaust.
- The conversion of all the fuels tested decreased with an increase in the mixture approach velocity. Methane conversion also decreased with an increase in the equivalence ratio generally at all different temperatures. The effect of the equivalence ratio on the conversion of the other fuels employed was influenced by the type of the fuel and the level of the temperature.

Acknowledgements

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