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RESEARCH NOTE

Nitric Oxide-Promoted Partial Oxidation of Methane under Strongly Oxidising Conditions

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Addition of catalytic amounts of NO to methane-containing mixtures under oxidising conditions selectively promotes partial oxidation reactions at expense of the total combustion, the effects being more pronounced in the ZrO_2 and Al_2O_3 catalysts compared to those in CeO_2-containing ones because of the high-combustion activity of CeO_2. © 2000 Academic Press

INTRODUCTION

Conversion of methane and other paraffins to more useful products is a research area of strong interest. For example, the catalytic partial oxidation of methane to syngas, which is expected to afford a ratio of H_2/CO of about 2, makes methanol synthesis an ideal follow-up process. Similarly, the dehydrogenation of paraffins in the presence of oxygen (oxydehydrogenation) may be a cheap source of olefins and provide valuable feedstock for many industrial processes (1). Generally speaking, in all the selective catalytic oxidation reactions, oxygen-deficient reaction mixtures must be employed to minimise the production of CO_2, which is a by-product of the undesirable nonselective oxidation. Typically in the CH_4 conversion to syngas, e.g., partial oxidation according to

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2,$$

the ratio $O_2/CH_4 \leq 0.5$ is employed. Under these conditions catalyst poisoning easily occurs due to carbon deposition (2). Schmidt and co-workers reported in a series of papers that high selectivity to CO (>90%) at O_2/CH_4 ratios close to 0.5, which are of practical interest, can be obtained over NM monoliths operating at very short contact times (3, 4). However, very high temperatures, typically above 1000°C, have to be maintained to avoid carbon formation since equilibrium dictates the presence of significant carbon fraction below that temperature (5). Fluorite-type metal oxide catalysts containing CeO_2 and ZrO_2 has recently received considerable interest as oxidation catalysts due to their high efficiency as total oxidation catalysts (6, 7).

In the present note the effects of NO addition on the selectivity of the combustion reactions catalysed by CeO_2- and ZrO_2-containing oxides is reported. It is observed that the addition of catalytic amounts of NO favours a high selectivity toward partial oxidation, even under strongly oxidising conditions. This adds interest to these findings since co-activation of hydrocarbons and NO at the support was indicated as the reaction pathway for the removal of NO_x under lean conditions (strongly oxidising) from simulated auto exhausts, using saturated hydrocarbons as the reductants (8).

EXPERIMENTAL

ZrO_2 and mixed CeO_2–ZrO_2 oxides were synthesised as previously reported (9). All the catalysts were characterised by powder XRD measurements (Rietveld refinement), Raman spectroscopy, and surface area (BET) measurements. Single-phase mixed oxides were obtained with the following phase attribution (10): CeO_2, $Ce_{0.8}Zr_{0.2}O_2$ cubic, and $Ce_{0.2}Zr_{0.8}O_2$ tetragonal (*t*). ZrO_2 consisted of a mixture of *m* (monoclinic, 24%) and *t* (76%) after calcination at 900°C. Catalytic experiments were carried out in a continuous flow reactor; 30–85 mg of catalysts were employed, using a gas mixture feeding rate of 40 ml min^{-1}. Typically, the following conditions were employed: time factor, W/F, 2.12×10^{-3} g min ml^{-1}; CH_4 concentration, 0.2%; $O_2/CH_4 = 5$–15; total pressure, 1 atm. Light-off curves were measured in run-up/run-down experiments using a heating/cooling rate of 1°C min^{-1}. Catalysts were tested in powdered form and were pretreated in a flow of O_2 in He at 600°C for 5 h. Analyses of feed and products were carried out by on-line gas chromatography and mass spectrometry. In the mass spectra, cracking patterns were accounted for.

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TABLE 1

Catalytic Activity and CO Selectivity in the Partial Oxidation of Methane for the Investigated Catalysts

Feeding mixture							
O_2/CH_4	NO (%)	Catalyst	Temperature range of CO formation (°C)	CO selectivity (maximum)[a] (%)	CH_4 conversion at CO maximum (%)	Temperature of CO maximum (°C)	$T_{50\%}$[b] (°C)
5	/	CeO_2		Traces			750
5	0.06	CeO_2	610–830	19	87	700	650
5	/	$Ce_{0.8}Zr_{0.2}O_2$		Traces			700
5	0.06	$Ce_{0.8}Zr_{0.2}O_2$	620–730	21	65	660	640
5	/	$Ce_{0.2}Zr_{0.8}O_2$	630–900	<3	81	900	840
5	0.06	$Ce_{0.2}Zr_{0.8}O_2$	630–850	22	97	780	720
5	/	ZrO_2	760–900	18	33	900	
5	0.06	ZrO_2	610–900	59	85	730	690
5	0.8	ZrO_2	650–900	27	86	790	750
15	—	ZrO_2	730–860	61	93	850	840
15	0.006	ZrO_2	610–760	51	84	675	650
15	0.06	ZrO_2	600–810	58	94	650	630
15	0.8	ZrO_2	620–900	64	85	730	700
5	/	Al_2O_3	650–880	23	40	825	832
5	0.06	Al_2O_3	580–830	50	85	665	635

Note. Time factor, W/F, 2.12×10^{-3} g min ml^{-1} (5.25×10^{-4} g min ml^{-1} for CeO_2 and Al_2O_3); CH_4 concentration, 0.2%; range of temperatures, 200–900°C.

[a] CO selectivity: mol CO $\cdot$ (mol CO + mol CO_2 + mol CH_4)$^{-1}$.

[b] Temperature of 50% CH_4 conversion.

RESULTS AND DISCUSSION

$T_{50\%}$ temperatures (defined as temperature of 50% CH_4 conversion) and selectivity in CO production in the oxidation of methane measured over the CeO_2–ZrO_2 mixed oxides, ZrO_2, and CeO_2 are reported in Table 1. Figure 1 reports typical results shown here for ZrO_2. Methane combustion is effectively catalysed by all the catalysts employed, except ZrO_2, which shows rather poor activity. The $T_{50\%}$ is higher than 900°C in the latter catalyst. Partial oxidation to yield CO is highest over pure ZrO_2, which is consistent with its scarce ability to act as a combustion catalyst. Noticeably, even relatively small amounts of CeO_2 inserted into the ZrO_2 lattice strongly promoted the total combustion of CH_4. This is in agreement with the high-combustion efficiency of this oxide. The effects of addition of catalytic amounts of nitric oxide to the feed are remarkable (Fig. 1). There is a strong enhancement of the catalytic activity and the $T_{50\%}$ decrease by 60–120°C (Table 1). The effect is particularly high in the case of ZrO_2, where the addition of 600 ppm of NO decreases the temperature for 30% CH_4 conversion by 250°C. Most importantly, the nonselective combustion appears partially inhibited in all the catalysts: for example, over ZrO_2 a yield calculated on a carbon basis of 59% of CO is observed at a CH_4 conversion as high as 85% (Table 1). Remarkable is the observation that

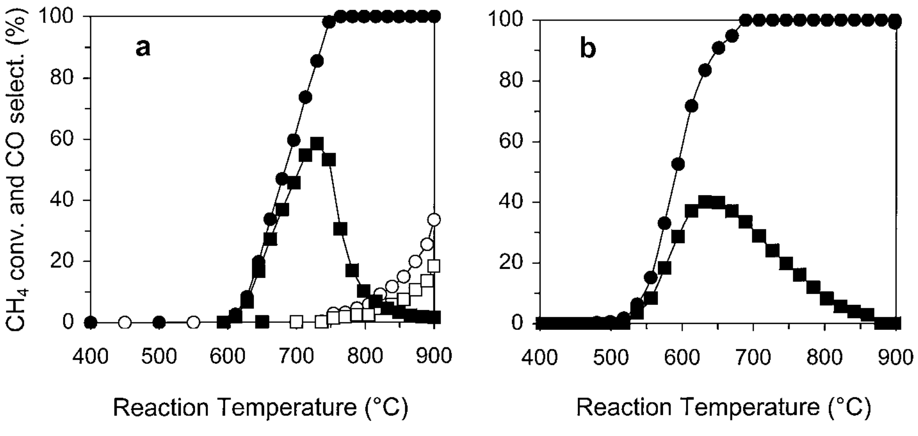

FIG. 1. CH_4 (○●) conversion and CO selectivity (□■) vs reaction temperature over ZrO_2 (open symbols): (a) effect of nitric oxide addition (filled symbols) (0.06%) to the $O_2/CH_4 = 5$ mixture; (b) effect of using NO_2 as the oxidant, $NO_2/CH_4 = 10$. Reaction conditions as reported in Table 1.

significant amounts of CO are produced under oxidising conditions, even on pure CeO_2 which is a total combustion catalyst (6). No deactivation of the catalysts was observed after 10 h under reaction conditions. Selectivity in CO formation up to 95% was observed at low conversions ($<5\%$). Changes of the O_2/CH_4 ratio and amount of NO added were also investigated. No significant decrease of CO production is observed by increasing the O_2/CH_4 up to 15. To our knowledge, this is the highest CO selectivity in the partial combustion of CH_4 under such strongly oxidising conditions. An increase of NO concentration from 600 ppm to 0.8% at $O_2/CH_4 = 5$ results in an increase of the light-off temperature and lower CO selectivity. This suggests that at high NO concentration there is some competition of NO on the active sites. Accordingly, ZrO_2 shows negligible activity at the temperatures investigated for the direct NO/CH_4 reaction.

To check the extension of the present observation, δ-Al_2O_3 (BET surface area, 90 $m^2\ g^{-1}$) has also been tested in the CH_4 combustion (Table 1). A poor oxidation activity is observed in the absence of NO. In contrast, the addition of ppm of NO strongly favours the activity of the catalyst.

To investigate the nature of this promotional effect, run-up experiments were carried out, monitoring the reaction products via mass spectrometry using $Ce_{0.2}Zr_{0.8}O_2$ as the catalyst (Figure 2). Negligible variations of the intensity of the NO signal are observed over the whole range of temperature, while O_2 is being consumed in correspondence of CH_4 consumption, indicating that the latter species acts as an oxidant. In agreement, a $T_{50\%} > 900°C$ was measured in a separate experiment using the NO/CH_4 mixture over the same catalyst. Remarkably, as the CO production starts, both H_2 and traces of NO_2 are formed. It is known that hydrocarbon oxidation is accelerated by the presence of NO_2 (11).

However, no NO_2 has been detected by carrying out a corresponding experiment with no CH_4 present. Consistently, at 650°C, where NO_2 formation starts, a maximum concentration of 0.4 ppm of NO_2 is calculated at equilibrium for a mixture containing 600 ppm of NO and 1% of O_2, which further decreases with temperature. This suggests that NO_2 is formed from a NO, O_2, and CH_4 mixture by co-reacting at the catalytic centre. NO_2, whose formation in catalytic amounts is assisted by the hydrocarbon (12), could therefore either act as a selective oxidant or assist the selective oxidation of CH_4 to CO, as previously suggested for the NO/O_2/propane reaction (8). The effectiveness of NO_2 to promote the selective oxidation of methane was tested under equivalent conditions, e.g., at the same excess of oxygen (Fig. 1b). The catalytic activity of ZrO_2 is by far higher when NO_2 is used as an oxidant instead of O_2 and good selectivity in CO is obtained, confirming that NO_2 may play a role as a selective oxidant. Notice, however, that under our reaction conditions NO_2 is catalytically formed/consumed since a ratio of $CO/NO_2 \approx 300$ can be estimated from data reported in Fig. 2. It should also be noted that the system NO (ppm level)/O_2 is more effective in producing CO. As shown in Table 1, the promoting effects are indeed observed at a NO concentration as low as 60 ppm. The specificity of NO to react at the catalytic centre seems remarkable since a ratio of $O_2/NO = 500$ was employed in this experiment.

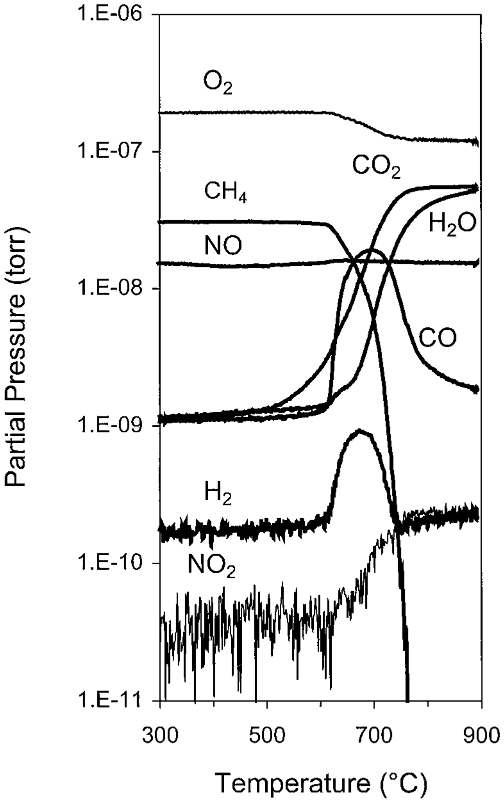

FIG. 2. Selected ion monitoring of CO, CO_2, NO_2, H_2, and H_2O formation and CH_4, O_2, and NO consumption as a function of reaction temperature. Catalyst, $Ce_{0.2}Zr_{0.8}O_2$; reaction conditions as reported in Table 1; heating rate, 10°C min^{-1}. Reactant mixture: 0.2% CH_4, 1% O_2, and 0.06% NO in He.

Formation of CO via steam or CO_2 reforming is unlikely in view of the very low CO production on CeO_2–ZrO_2, in the absence of NO. In addition, as the water production increases, CO formation drops. At this point a contribution to the formation of CO via a reverse water–gas shift reaction (r-WGSR) cannot be excluded. In fact, a separate experiment showed that this reaction is catalysed by ZrO_2 above 500°C. It should be noted, however, that even if some CO was formed via r-WGSR, the source of hydrogen, which is necessary for this reaction, would be a partial oxidation reaction.

The effect of NO addition in the oxidation of propane was preliminarily examined over ZrO_2. Also in this case the activity was improved and low conversion to CO_2 was observed, CO, CH_4, and other low molecular weight hydrocarbons being the main products of the reaction.

In conclusion, the present work disclosed that the selectivity of methane combustion over ZrO_2-, Al_2O_3-, and CeO_2-based oxide catalysts can be strongly modified by the addition of catalytic amounts of nitric oxide to the feed, remarkably increasing the CO formation, even under a large excess of oxygen.

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