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High temperature stable magnesium oxide catalyst for catalytic combustion of methane: A comparison with manganese-substituted barium hexaaluminate

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Abstract

The activity of magnesium oxide for catalytic combustion of methane was examined and the results were compared with experimental results for manganese-substituted barium hexaaluminate. The catalysts were calcined at temperatures up to 1 500°C and the effects of temperature, space velocity and calcination temperature were examined. The catalysts were also characterized with BET and XRD. For magnesium oxide calcined at 1 100°C the ignition temperature ($T_{10\%}$) was decreased by 270°C compared to the non-catalyzed reaction. For the same catalyst $T_{50\%}$ was measured to be 795°C. The corresponding temperature for the hexaaluminate was 640°C. The difference between the two catalysts decreased after calcination at 1 500°C. For the magnesium oxide the influence of catalytically initiated homogeneous gas phase reactions was studied by varying the post catalytic volume of the reactor (and hence the residence time in the heated zone after the catalyst). It was shown that these catalytically initiated homogeneous gas phase reactions are significant for the methane conversion.

Keywords: Catalytic combustion; Magnesium oxide; Methane; Barium hexaaluminate

1. Introduction

During the past ten years there have been an increasing number of articles on high temperature catalytic combustion and these are summarized in some recent review articles [1–3]. The main goal for the high temperature catalytic combustion is to increase the efficiency and decrease the emissions of gas turbines. To increase the efficiency higher nominal turbine inlet temperatures are used, and in the near future 1400°C will be a reality. To be able to simultaneously decrease the NO_x emissions, it is important to control the combustion and to keep the actual combustion temperature low and even. This can be achieved with catalytic combustion [3].

Most of the work on catalytic combustion has been focused on using methane or natural gas as fuel. Methane is used both since it is the main component in natural gas and also because of the chemical stability that makes methane suitable as a model substance for other light hydrocarbons.

The oxidative coupling of methane has attracted increasing interest over the last decade. Many different catalysts have been studied for this reaction [4] and one of them is magnesium oxide, either pure or doped with lithium [5–7]. Pure magne-

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sium oxide is more active but less selective towards C_2-hydrocarbons compared with the doped form [5,7]. The reaction mechanism is not clear, but most authors agree that the adsorption of an oxygen species is responsible for the initial activation of methane. This is followed by the abstraction of one hydrogen atom from methane and the formation of a methyl radical. The methyl radicals can either start a chain reaction, directly combine to C_2-hydrocarbons or form CO and CO_2 [4–7]. Even though oxidative coupling is carried out under substoichiometric conditions and lower temperatures than catalytic combustion the results show a strong effect on methane activation. Therefore the experience from oxidative coupling can contribute to the development of combustion catalysts.

The influence on the kinetics of catalytically produced radicals that react in the gas phase is difficult to examine. Ito et al. [5] came to the conclusion that additional formation of methyl radicals through branching chain reactions cannot be excluded, and that the importance of the chain reactions probably increases with partial pressure of oxygen. This can be compared with results that show the influence from other catalytically formed radicals which influence the reaction as, e.g. discussed by Pfefferle and Pfefferle [2]. The importance of the catalytically initiated gas phase reactions increases with temperature until the reaction can be regarded as catalytically stabilized thermal combustion. These catalytically initiated homogenous gas phase reactions should be regarded separately from the homogenous gas phase reactions that take place in non-catalyzed combustion.

Magnesium oxide has a melting point of 2 850°C. As a result of this, magnesium oxide can maintain a large surface area at high temperature compared to most other oxides and can thus be used as a catalyst support for high temperature applications [8]. The surface area of magnesium oxide decreases from 100 to about 10 m^2/g, which can be compared with Al_2O_3 that decreases from 200 to less than 1.5 m^2/g, when the temperature is increased from 600 to 1 400°C [9].

High thermal stability together with the reported activity for methane conversion in oxidative coupling makes magnesium oxide interesting as a catalyst for catalytic combustion. Despite these features the activity of magnesium oxide under oxidizing conditions has previously not been examined in depth. Aigler and Lunsford [7] mention the possibility of using the magnesium oxide catalyst under oxidizing conditions, and some initial work has also been done at TPS Termiska Processer [10]. Recently an article discussing the possibility of using magnesium oxide as a catalyst for the catalytic combustion of methane and evaluating the kinetics for this reaction was published by Berg and Järås [11]. The aim of the present study has been to continue that work and to compare the results achieved with magnesium oxide with experimental results for manganese-substituted barium hexaaluminate, with the composition (Ba/Mn/Al = 1:1:11).

2. Experimental

2.1. Catalyst preparation

The magnesium oxide catalyst was prepared following the procedure by Kimble and Kolts [6] and calcined at 900, 1 100, 1 300 or 1 500°C during 4 h. The preparation of barium hexaaluminates [12] and the activity for catalytic combustion of the substituted barium hexaaluminates was first shown by Machida et al. [13]. They showed that the highest activity and BET-area after high temperature calcination could be achieved using the alkoxide method. During 1993 Groppi et al. [14] presented a simple alternative preparation method based on precipitation in aqueous medium that, according to them, resulted in a hexaaluminate with a surface area and activity in the same range as the material prepared by the alkoxide method. The manganese-substituted barium hexaaluminates used in this study had the composition Ba/Mn/Al = 1:1:11 and were prepared following the method suggested by Groppi et al. [14]. The catalysts were calcined during 4 h at three different

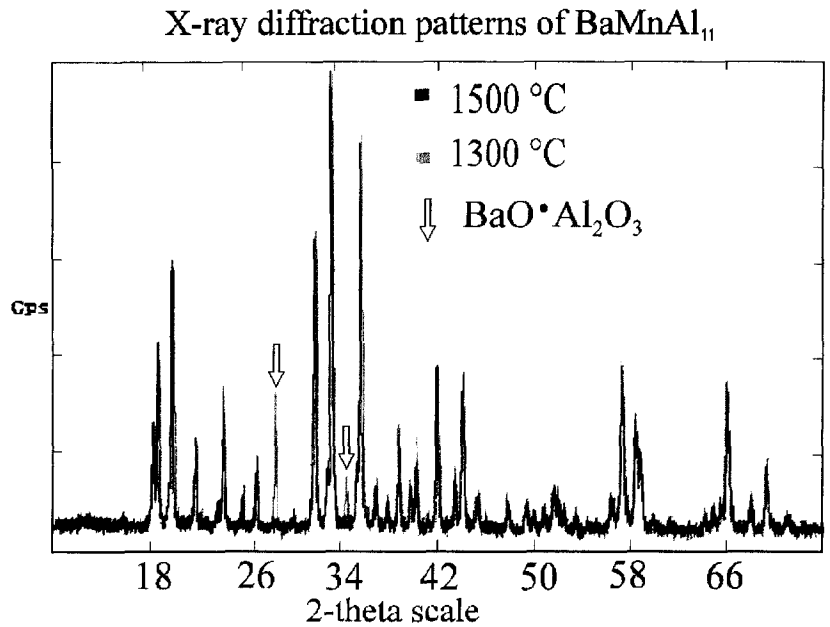

Fig. 1. XRD spectra for barium hexaaluminate Ba/Mn/Al = 1:1:11 calcined at 1 300 and 1 500°C.

temperatures, 1 100, 1 300 or 1 500°C. Both the magnesium oxide and the manganese-substituted barium hexaaluminate were crushed and a fraction between 0.36 and 0.50 mm was used for all the experiments.

2.2. Catalyst characterization

The BET surface area and the pore size distribution was measured using nitrogen adsorption in a Micromeretics ASAP 2000. For the manganese-substituted barium hexaaluminate XRD was used for the characterization of the different crystal phases formed during calcination. These studies showed that more hexaaluminate was formed at higher calcination temperature and that the amount of the mixed oxide $BaO \cdot Al_2O_3$ decreased with temperature. At the lowest calcination temperature, 1 100°C, some hexaaluminate was present but it was only at the highest calcination temperature, 1 500°C, that the pure hexaaluminate phase without any traces of $BaO \cdot Al_2O_3$ could be achieved. This is shown in Fig. 1 where the hexaaluminates calcinated at 1 300 and 1 500°C, respectively, are compared and the peaks that originate from the remaining $BaO \cdot Al_2O_3$ are marked with arrows.

The disappearance of the $BaO \cdot Al_2O_3$ phases with increasing calcination T is in accordance with Groppi et al. [14] but, using the same composition (Ba/Mn/Al = 1:1:11), they achieved the pure hexaaluminate at a lower temperature, 1 100°C. In the original work done by Machida et al. [12] using a powder mixture of $BaCO_3$ and γ-Al_2O_3 (Ba/Al = 1:12) the hexaaluminate phase was not present below 1 200°C and the pure hexaaluminate phase was achieved at 1 450°C.

2.3. Experimental equipment and procedure

The experiments were performed in a vertical quartz glass reactor using down flow through a packed bed. The temperature was measured in the catalyst bed but to ensure that the thermocouple was not in direct contact with the gas a quartz glass pocket was used. For further details on the experimental reactor and the procedure refers to Ref. [11] where this is previously described. For the gas analysis a Hewlett Packard gas chromatograph, model 5880 A, with a thermal conductivity detector was used. The produced gas mixture was first dried using a $CaCl_2$ and then analyzed for the following components: H_2, O_2, N_2, CO, CH_4, CO_2, C_2H_4 and C_2H_6. The columns used

were molecular sieve 5A for the first four components and Porapak Q for the last four. For the molecular sieve another Porapak column was used as a precolumn. In the previous study [11] argon was used as carrier gas but to increase the sensitivity for the carbon containing species the carrier gas was switched to helium. This resulted in a detection limit of down to ppm levels for the C_2-hydrocarbons.

The space velocity for the catalyst was varied between 50 000 and 200 000 h^{-1} but the value 100 000 h^{-1} was used when comparing the different catalysts. For the comparison the inlet methane concentrations were kept at 0.5 vol.-% and the O_2 concentration at 4 vol.-%. Before each experiment the catalyst was pretreated at 900°C in the reaction mixture to decompose any compounds formed on exposure to the atmosphere.

3. Results and discussion

3.1. Effect of temperature and space velocity

The effect of temperature on the conversion for both the magnesium oxide and the manganese-substituted barium hexaaluminate was measured, see Fig. 2. It is clear that the magnesium oxide has a significant catalytic effect on the combustion of methane although not as strong as the hexaaluminate. For magnesium oxide calcined at 1 100°C, a space velocity of 100 000 h^{-1} and a partial pressure of methane and oxygen of 0.5 and 4 kPa, respectively, the $T_{10\%}$ decreases with 270°C in comparison with an empty reactor. For the same conditions $T_{50\%}$ was found to be 795°C.

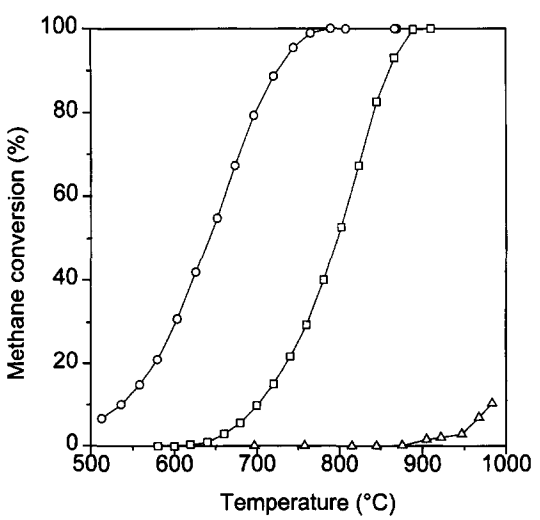

Fig. 2. Activity of magnesium oxide and Ba/Mn/Al = 1:1:11 calcined at 1 100°C. SV 100 000 h^{-1}, CH_4 0.5 vol.-%. (○) (Ba/Mn/Al = 1/1/11), (□) MgO and (△) empty reactor.

For the manganese-substituted barium hexaaluminate and the same experimental conditions the $T_{50\%}$ was 640°C and 700°C at calcination temperatures of 1 100°C and 1 300°C, respectively. These results can be compared with results achieved by Groppi et al. [14] ($T_{50\%}$ 660°C, calcination temperature 1 300°C) using the same preparation technique and also results obtained by Machida et al. [13] ($T_{50\%}$ 660°C, calcination temperature 1 300°C) using the preparation technique based on hydrolysis of metal alkoxides. In these studies higher methane and oxygen concentrations (1% methane in air compared with 0.5% methane and 4% oxygen) and lower space velocity (48 000 h^{-1} compared with 100 000 h^{-1}) were used. The difference between our results and these two studies can be explained by these differences in the testing methods used even if the difference in surface area also could be of importance.

3.2. Effect of high temperature calcination

The magnesium oxide and the manganese-substituted barium hexaaluminate were both treated for four hours at different temperatures up to 1 500°C. The effect of calcination temperature on the BET-surface area is shown in Table 1 together with the corresponding values for $T_{50\%}$. The activities for methane combustion are also shown in Fig. 3 and Fig. 4. From Table 1 it can clearly be seen that the barium hexaaluminate maintains a higher surface area but at the same time it can be seen in Fig. 3 and Fig. 4 that the relative loss of catalytic activity is more rapid with increasing calcination temperature for the hexaaluminate compared with the results obtained for magnesium oxide.

Table 1
Surface area, pore size and $T_{50\%}$ of the catalysts at different calcination temperature (°C)

	MgO				Hexaaluminate (Ba/Mn/Al = 1:1:11)		
	900	1 100	1 300	1 500	1 100	1 300	1 500
BET surface area (m^2/g)	43.4	24.2	9.2	0.9	35.0	10.1	3.1
Average pore diameter (nm)	19.8	17.5	13.9	11.9	17.2	10.1	9.7
Pore volume (cm^3/g)	0.24	0.14	0.04	0.003	0.17	0.04	0.009
$T_{50\%}$ (°C)	795	795	820	880	640	700	790

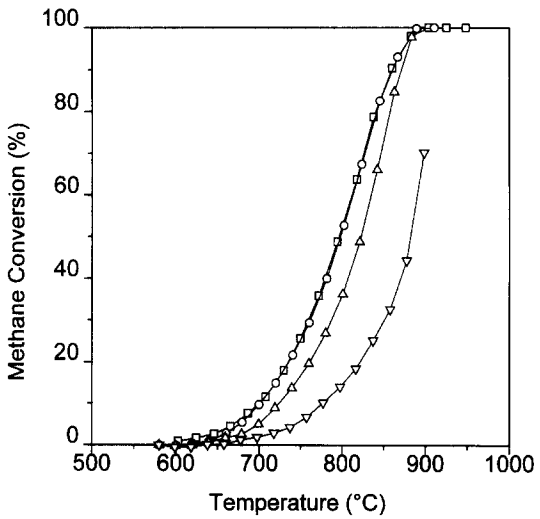

Fig. 3. Activity of magnesium oxide at different calcination temperatures. SV 100 000 h^{-1}, CH_4 0.5 vol.-%, O_2 4 vol.-%. (□) 900°C, (○) 1 100°C, (△) 1 300°C, (▽) 1 500°C.

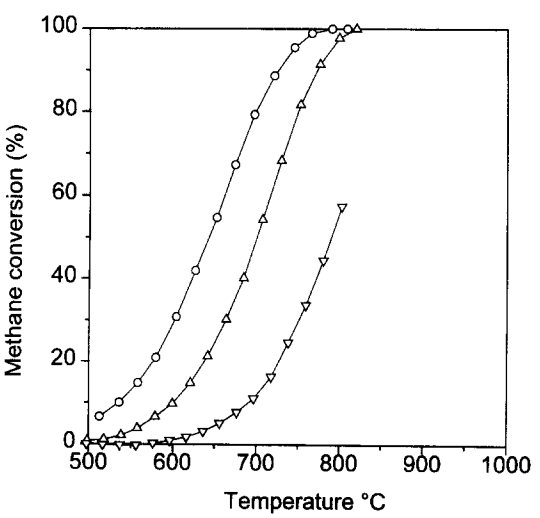

Fig. 4. Activity of Ba/Mn/Al = 1:1:11 at different calcination temperatures. SV 100 000 h^{-1}, CH_4 0.5 vol.-%, O_2 4 vol.-%. (○) 1 100°C, (△) 1 300°C and (▽) 1 500°C.

The surface area achieved for the magnesium oxide at 1 300°C is the same as reported by Arai and Machida [9], but the decrease in surface area with increasing calcination temperature was stronger in the present study. It is likely that the difference can be explained by the variations in the preparation techniques that were used. The strong effect of the preparation technique on the surface area and the surface basicity of magnesium oxide catalysts have previous been shown by Choudhary and Pandit [15]. Another example of the effect of preparation technique on the properties of magnesium oxide was shown by Hashimoto et al. [16]. After calcination at 1 500°C they achieved a surface area of 72 m^2/g with ultra fine single crystals of magnesium oxide but magnesium oxide prepared from precipitation of magnesium nitrate with aqueous ammonia resulted in a surface area of 0.4 m^2/g. In the study the magnesium oxide was used as support for noble metal combustion catalysts and the activity for methane combustion of the different catalysts as well as the support was measured. For the support (ultra fine single crystals of magnesium oxide calcined at 1 250°C) a $T_{90\%}$ of 690°C was achieved (1% methane and 20% oxygen at a space velocity of 50 000 h^{-1}).

3.3. Selectivity of the catalyst

Among the analyzed compounds, the products detected in significant concentrations were carbon dioxide, carbon monoxide, ethane and ethylene. For magnesium oxide the main product at temperatures above 750°C was carbon dioxide and the

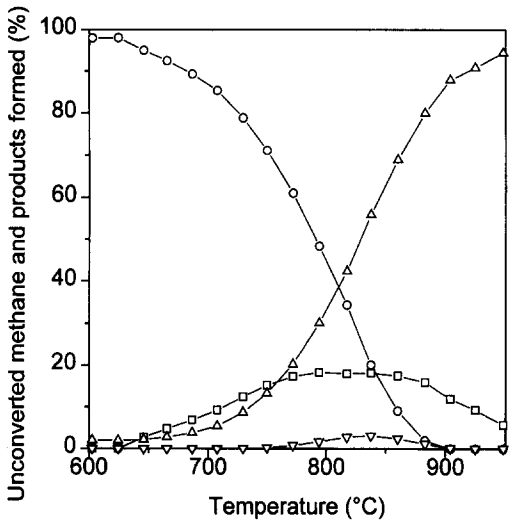

Fig. 5. Carbon distribution of the different products and unconverted methane. Magnesium oxide calcined at 900°C, SV 100 000 h^{-1}, CH_4 0.5 vol.-%, O_2 4 vol.-%. (○) Methane, (△) CO_2, (□) CO and (▽) C_2-hydrocarbons.

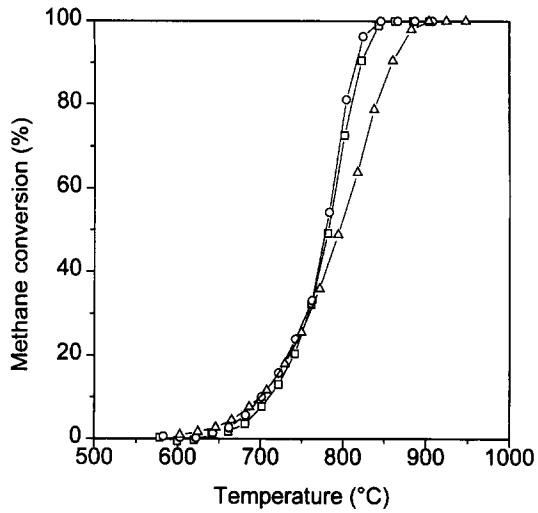

Fig. 6. The effect of an increase of the residence time in the heated zone after the catalyst. Magnesium oxide calcined at 900°C, SV 100 000 h^{-1}, CH_4 0.5 vol.-%, O_2 4 vol.-%. (○) Bed lifted 20 mm, (□) bed lifted 10 mm and (△) normal reactor.

selectivity towards carbon dioxide increased with temperature. The carbon distribution of the different products and unreacted methane is shown in Fig. 5.

For the manganese-substituted barium hexaaluminate carbon dioxide was the only product detected.

3.4. Influence of homogeneous and catalytically initiated homogeneous gas phase reactions

Experiments were carried out 1: in absence of catalyst, 2: with quartz wool and 3: with quartz powder. No significant differences were noticed between these three configurations and the data obtained in absence of a catalyst are shown in Fig. 2. The result implies that the homogeneous methane oxidation can be neglected below 880°C compared with the catalytic and catalytically initiated homogeneous reactions.

For magnesium oxide the influence of catalytically initiated homogeneous gas phase reactions was studied in two similar reactors where the quartz disk with the catalyst bed was placed either 10 or 20 mm higher than in the normal reactor. This resulted in an increase in the volume of the heated zone after the catalyst from less than one third to twice respectively four times the catalyst volume. The corresponding residence time in the post catalytic volume at the actual temperature is in the range from 3 to 40 ms. These configurations gave the possibility for homogeneous reactions after the heterogeneous reactions. From the results it is clear that a small increase in the residence time of the gas in the heated zone after the catalyst (bed lifted 10 mm) leads to a higher conversion at high temperatures (above 760°C), see Fig. 6. It can also be seen that the effect of increasing the residence time in the heated zone after the catalyst even more (bed lifted 20 mm) is almost negligible. This shows that the effect does not depend on homogeneous reactions. One likely explanation is the formation of methyl radicals formed on the catalyst surface that start chain reactions in the gas phase [5].

4. Conclusions

From these experiments it has been shown that magnesium oxide has a catalytic effect on the combustion of methane. The temperature needed for 10% conversion was decreased by up to 270°C compared to using a reactor without a catalyst. It was shown that under the experimental conditions

the heterogeneous catalytic reactions are dominant but with catalytically initiated homogeneous gas phase reactions contributing to the overall reaction rate, especially at high temperatures. In this region the kinetics are very complex with both the heterogeneous reactions and catalytically initiated homogeneous reactions contributing to the overall reaction rate. It was also shown that for magnesium oxide the most important factor for increasing the selectivity towards carbon dioxide was high temperature.

Manganese-substituted barium hexaaluminate showed a higher catalytic activity for methane combustion than magnesium oxide. After calcination at 1 300°C the $T_{50\%}$ was 700°C. This can be compared with 660°C as reported in the literature for both preparation methods discussed. Compared with literature data on the preparation method used a higher calcination temperature than reported was needed to achieve the pure hexaaluminate phase.

At high calcination temperatures the relative loss in activity was smaller for the magnesium oxide but the surface area decreased more compared with the manganese-substituted barium hexaaluminate.

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