

Mesoporous silica supported catalysts in the partial oxidation of methane

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Introduction

Mesoporous materials can be used as supports to disperse vanadium oxides to prevalent monomeric species. Furthermore, on these supports, a higher concentration of isolated active sites can be obtained than on conventional silica supports. Additionally, high and thermally stable surface areas of mesoporous silicas (e.g. MCM-41) are favourable for achieving a high concentration of isolated vanadium oxide species generally considered as active sites during the partial oxidation of methane [1]. In the present study, the expansion potential of this concept was investigated using various transition metal oxides such as VO_x , MoO_x , FeO_x and their mixtures.

Experimental

As catalyst supports mesoporous silica MCM-41 was used. Catalyst preparation was performed according to a previous work [1]. Comprising, the support material was added to an aqueous solution of NH_4VO_3 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ or their mixtures. The resulting slurry was evacuated for a short time to remove air from the pores. Water was slowly evaporated afterwards. The solid product thus obtained was further dried and finally calcined at 873 K in air for 16 h. The loading of transition metal was fixed to 2.8 wt%. The catalytic properties of the samples were investigated in a plug flow reactor equipped with several gas flow lines with mass flow controllers to supply the educt stream containing CH_4 , air, and nitrogen for dilution. Products were characterised via GC analysis.

Results/Discussion

Catalytic performance of different functionalized mesoporous silicas for the oxidation of methane was evaluated in a plug flow reactor ($m_{\text{Kat}} = 200$ mg, flow rate in ml/min: $\text{CH}_4:\text{O}_2:\text{N}_2 = 0.75:13.5:60.7$). Figure 1 illustrates the dependence of the conversion of CH_4 and the yield of CO_2 at 923 K over various transition metal oxides. It is evident from the Figure that FeO_x displayed the highest conversion of methane while MoO_x showed the lowest. It is noteworthy that the mesoporous glass supported MoO_x nearly promotes the total oxidation to CO_2 , whereas the FeO_x catalyst exhibits a small gap between CH_4 conversion and CO_2 yield. On the other hand, VO_x catalysts show a significant difference in methane conversion and CO_2 yield. This catalyst appears to decrease the tendency to overoxidation. However, desired oxygenate products are in minority since considerable amount of CO is also found in the product distribution.

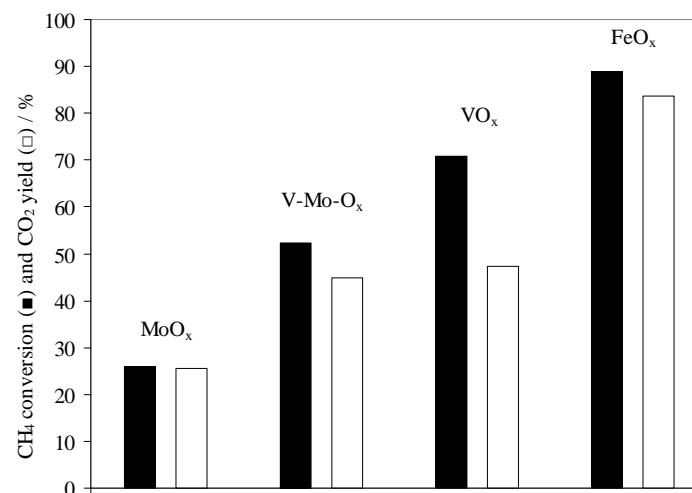


Figure 1. Comparison of catalytic performance of various transitional metal oxides in the oxidation of methane ($T = 923$ K).

The nature of the metal oxide has not only an effect on the conversion of CH_4 and yield of CO_2 but also on the composition of the products from partial oxidation, which are CO, H_2CO , H_3COH and HCOOH . From the carbon balances it can be seen that VO_x with the highest gap between CH_4 conversion and CO_2 yield does not necessarily lead to the highest oxygenate content. For instance at 923 K oxygenate content was found with only 2.2 %. Instead, the addition of equimolar amounts of molybdenum lead to a decrease in CO formation and an increase in oxygenate content. MCM-41 supported V-Mo- O_x catalysts improve the oxygenate yield to 4.0 %. Furthermore, FeO_x displayed the superior performance in terms of activity but also leads to a low CO formation beside a remarkable high oxygenate yield. Here, a significant higher oxygenate yield of 4.1 % was detected whereas CO formation was suppressed to 1%.

References

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