Methane oxidation on bimetallic catalysts in the presence of NO

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Introduction

It is a large interest in using compressed natural gas (CNG) as a vehicle fuel [1]. CNG vehicles have several important benefits especially decreasing the emissions. The main component of CNG is methane, which can be oxidized on Pd-based catalysts promoted by Pt. During engine operation at high temperatures NO will be formed. In order to prepare a catalyst with optimal properties, the influence of NO on CH_4 oxidation should be considered. However, there are no studies available regarding the NO effect on methane oxidation over bimetallic catalysts. The purpose of this study is to investigate the behavior of Pt-Pd/Ce-Al₂O₃ catalysts with different Pt:Pd ratio in methane oxidation with and without NO in the gas mixture.

Materials and Methods

Two series of bimetallic Pt-Pd catalysts (Table 1) were prepared by sequential impregnation of the support (γ -Al₂O₃ or 20 wt.% Ce-Al₂O₃) with solutions of Pt(NO₃)₂ and Pd(NO₃)₂. Loading of Pd (3.8 wt.%) was constant in all catalyst formulations while atomic Pt:Pd ratio was adjusted (1:20; 1:10; 1:4). Monolith samples (l = 20 mm, d = 21 mm, 400 cpsi, mass of washcoat = 500 mg) prepared with dip-coating process were used for activity tests. The sample was placed in a quartz tube reactor (atm. pressure) using a gas feed of 500 ppm CH₄, 8 vol.% O₂, 300 ppm CO, 5 vol.% H₂O, balanced by Ar. For NO-containing experiments 500 ppm NO was added to the above mentioned gas mixture. The temperature was increased from 150°C to 700°C and was thereafter decreased down with a ramp rate of 5°C/min in the same gas mixture. All experiments were conducted with a flow rate of 3.5 L/min, which corresponds to GHSV = 30,000 h⁻¹.

Results and Discussion

Prepared catalysts (Table 1) were tested in methane oxidation. Figure 1 summarizes the data obtained from experiments with ordinary gas mixture (without NO) and with NO-containing mixture to evaluate the effect of NO addition on conversion of methane. Temperature of 50% conversion of CH_4 ($T_{50\%}$) was used as a measure of the catalytic activity. **Table 1.** Composition of the tested catalysts and temperatures of 50% conversion of CH_4 .

Number	Catalyst	Pt	Pd	Pt:Pd atomic	∆T=T _{50%} cool-T _{50%} heat, °C		E _{act} , kJ*mol ⁻¹		
		wt.%	wt.%		without NO	with NO	without NO	with NO	
1	Pt-Pd/Al ₂ O ₃	0,4	3,8	1:20	35	9	119	102	
2		0,8	3,8	1:10	34	3	118	106	
3		1,9	3,8	1:4	24	1	123	108	
4	Pt-Pd/Ce-Al ₂ O ₃	0,4	3,8	1:20	68	2	119	102	
5		0,8	3,8	1:10	61	8	118	104	
6		1,9	3,8	1:4	60	2	121	102	

For Al₂O₃-based catalysts (# 1-3) T_{50%} decreases with increasing Me loading (Fig. 1(A)). However the activity of these catalysts is lower during cooling, which is in agreement with necessary Pd reoxidation. Kinnunen et al. [2] suggested that there is an optimum ratio of metal to metal oxide for methane oxidation. Since the active phase for Pt is metallic form, the addition of Pt to Pd/PdO_x-based catalyst enhances the activity of catalysts at

low T (300-400°C) possibly due to the relation of Me/MeO_x. $T_{50\%}$ decreases also with increasing Pt loading for cooling mode. During NO-containing experiments the trend of CH₄ conversion is the same (Fig. 1(B)). However the light-off temperature in this case is significantly higher.

However, for Ce-Al₂O₃-based catalysts (# 4-6) $T_{50\%}$ are similar for catalysts with different Pt loading. These values are close to that obtained for Ce-free samples (heating mode). However NO addition still leads to the higher light-off temperatures during heating and cooling. In presence of NO, methane oxidation starts at 400 °C and does not depend on Pt loading. According to the literature, addition of ceria in loadings below 10-15 wt.% improves thermal stability of PdO and leads to high catalyst activity at low T. However, we did not observe an increase of catalyst activity for Ce-containing samples, which may be related to high CeO₂ loading in our samples and this might affect the reducibility of the catalyst.



Figure 1. Comparison of temperature of 50% conversion of CH_4 without NO (A) and in the presence of NO (B) during heating and cooling modes.

We calculated the temperature distinction (ΔT) between $T_{50\%}$ for heating and cooling modes (Table 1) for each sample: $\Delta T = T_{50\%, heating} - T_{50\%, cooling}$. ΔT decreases with increasing Me loading for both series of catalysts (Al₂O₃- and Ce-Al₂O₃-based) in NO-free experiments. During NO-containing experiments we observed that all samples have low ΔT , which means small difference between $T_{50\%}$ during heating and cooling. As can be seen in Table 1 activation energy of CH₄ oxidation (with NO in gas mixture) is slightly lower. However, the presence of NO results in higher light-off temperature for methane oxidation. **Significance**

Methane oxidation is crucial for aftertreatment for CNG engines. We observe that presence of NO results in significantly increase of light-off T (about 30° C). In addition, the hysteresis in the presence of NO was lower. For Ce-based catalysts no difference in CH₄ oxidation was observed when increasing Pt loading. We plan to further study the NO effect by means of DRIFT spectroscopy in order to detect possible surface species and increase the understanding of the mechanism.

Acknowledgments

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