

Rational Design of Ni-Co/Hydrotalcite Catalyst for Methane Total Combustion

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Highlights

- In-situ technique to correlate catalyst state with activity
- Bimetallic Ni-Co enhances the activity compared to pure Ni and Co
- Investigating the relationship between the reduction and oxidation rates in-situ

1. Introduction

A complete oxidation of methane has been a significant topic in the field of heterogeneous catalysis for decades since methane is the most abundant hydrocarbon source on earth. It can be used to substitute the petroleum based fuel for transportation or unburned methane can be transformed in power plants[1]. High activity and thermal stability of a catalyst (for removal of CH₄ or other hydrocarbons) at a temperature of 1,300°C for applications to power plants or at least 800°C for engines using gasoline or diesel is requested. Catalytic combustion of methane (CCM) has used metal or transition metal oxides as catalyst. Noble metal (Pd and Pt) catalysts demonstrate an excellent catalytic performance in CCM at low temperature, but they are limited in commercial application due to high prices and rarity. Transition metal (Mn, Fe, Co, Ni etc) oxide catalysts have been receiving considerable attention to substitute for noble metal catalysts. Therefore, attempts have recently been made to use transition metal oxide catalysts for the CCM on the enhancement of catalytic performance to reach the level of noble metal based catalysts. Among them, Co oxide, Co/Ce-, Co/Mn-, Co/Cr- and Mn/Ni mixed oxide are known to be very active for methane oxidation. However, very recently, Ni/Co mixed oxide is explored to study the catalytic performance on CCM knowing the synergism between Co₃O₄ and NiO [2]. The active sites in the oxidation process are dynamic, and the oxidation state of the transition metals might changes with operation conditions. The oxidation state of the metal could be a crucial parameter for the catalyst design, which could govern the surface O concentration and barriers for methane activation. [1,2]. Therefore, an attempt would be made similar to our previous study of ethylene oxychlorination [3,4] to explore the CCM catalyst activity and oxidation state of catalyst quantitatively and subsequently establish a method. Our operando setup combined with a novel, *in situ* UV-Vis-NIR spectroscopy approach allows for detailed kinetic studies of the individual reduction and oxidation steps as well as for the overall reaction. The kinetic analysis of the catalytic cycle [3,4] combined with microkinetic analysis is applied to rational design of catalysts for methane oxidation. In this way, Ni-Co bimetallic catalysts were developed to have a high activity. We believe that our method developed pave the way for rational design of heterogeneous catalysts which undergoes oxidation state changes.

2. Methods

A series of well-controlled Ni-Co catalysts supported on a hydrotalcite-like structure have been synthesized using co-precipitation. The catalysts contain a total metal loading of 5wt% with various ratios of Ni and Co content. The metal nomenclature is given as 5Ni_{1-x}Co_x, where x is the Co fraction of the total metal (Ni + Co) weight loading. The catalysts were calcined at 600 °C for 6h and then characterized using X-ray fluorescence, X-ray diffraction, hydrogen chemisorption and nitrogen adsorption. Reduction at 670 °C in a H₂/N₂ (1:1) flow for 16 h was performed prior to any activity measurements. The catalysts activities were analyzed in a fixed-bed quartz reactor with a fiber optic probe. The probe is pointing directly towards the catalyst bed and connected to a UV-vis spectrometer giving valuable information on the in-situ state of the catalyst. The compositional gas changes were analyzed using a gas chromatograph and a mass spectrometer. Micro kinetic

analysis using UEB-QEP method modified with DFT adsorption energies is used for rapid screening high activity metal catalysts of CCM, with C-, H- and O-metal binding energy as three sole descriptors.

3. Results and discussion

Fig.1 a) shows the light-off curves of the methane combustion on the samples of Ni, Co and Ni-Co with different Co/Ni ratios. The figure shows the bimetallic Ni-Co catalyst possess higher activity (in the order of Ni/Co > Co > Ni) at low temperature (below 500 °C) compared to the pure transition metal catalyst. Whereas at higher temperatures (above 650 °C), Ni/Co and Co catalyst possess similar activities. The result from microkinetic modeling with modified UEB-QEP method confirms the trend. However, from Fig.1 a) it is believed that all the catalyst undergo reduction on the surface at around 600-700 °C, due to the change in activity around this temperature range. It is thought that the surface reduction rate becomes faster than the oxidation rate, causing a drop in the activity since the oxide phases are more active than the metal phase. The UV-vis confirms that the bulk structure keep oxidizing as the temperature increases. From Fig.1 b), it is found that Ni²⁺ is reducing to Ni⁰ during reduction and it oxidizes back to Ni²⁺ during CCM (Fig.1 c) as suggested by the UV-Vis features at around 380 nm. Transient experiments for sequential reduction and oxidation steps are currently running in order to develop a kinetic rate diagram connecting activity and oxidation state of the catalyst similar to our earlier study, which will predict catalytic activity of CCM. Adding Co into the catalysts increased the oxidation state of the catalysts due to the oxophilicity of Co, which increase the O surface concentration and reduce the barrier of methane activation.

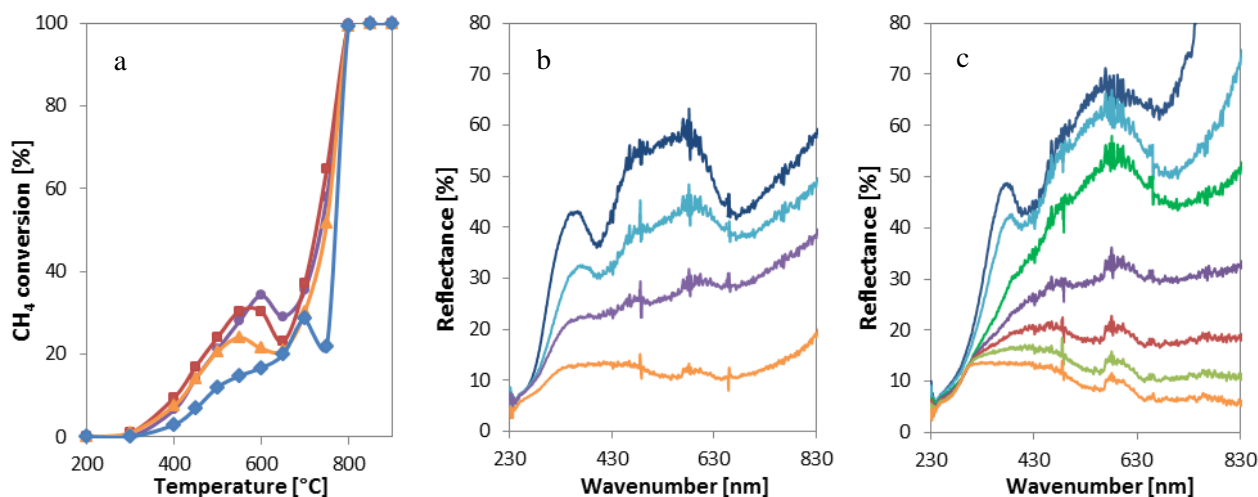


Figure 1. a) Light-off curves of methane combustion (● 5Co₁ ■ 5Ni_{0.3}Co_{0.7} ▲ 5Ni_{0.3}Co_{0.7} ◆ 5Ni₁), b) UV-Vis spectra during reduction of Ni catalyst (— 200 °C, — 550 °C, — 600 °C, — 670 °C), c) UV-Vis spectra during methane combustion using Ni catalyst (— 200 °C, — 300 °C, — 400 °C, — 500 °C, — 600 °C, — 700 °C, — 800 °C); Reaction conditions: 150 mg catalyst diluted 20 times with α -Al₂O₃, total flow 300mL/min, 3.5% CH₄, O₂/CH₄=2.5

4. Conclusions

We expect our approach to rational catalyst design to be general in nature, applicable to any catalysts partaking in redox reactions. It is a cheap and time efficient screening tool and vital for understanding promoter influence on the individual redox steps as well as overall.

References

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Keywords

In-situ, combustion, kinetics, bimetallic