Selective Oxidation of Methane Using Bimetallic Catalysts Prepared by a Novel Cross-Reduction Technique

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Abstract: A new synthesis method for highly dispersed bimetallic catalysts of wide-ranging composition is described, and the application of the catalysts in the partial oxidation of methane is detailed. The method utilizes the redox potential difference between different elements to promote the reduction of one element A and the oxidation of a second element B. The method is general and has been applied for the formation of a wide combination of noble metals (Pd, Ru, Ir, Rh, Pt, Au) and base metals (Fe, Co, Ni, Cu) supported on silica. The catalytic oxidation of methane at atmospheric pressure and 200-400 ^{o}C was investigated. A reactive couple was used as a shuttle to transfer single oxygen atoms from O_2 to the catalytic site. The results showed that the addition of the couple strongly enhanced the conversion of methane. Although many of the initially tested catalysts formed CO_2, several were active in the formation of oxygenates. Kinetic studies allow the determination of the reaction steps and in situ spectroscopic measurements allow identification of active intermediates. The results suggest that catalytic oxidation of methane by single atomic oxygen using the oxygen shuttle could efficiently convert methane to oxygen-containing chemicals.

Keywords: Methane oxidation; bimetallic alloy synthesis; kinetics; mechanism; in situ FTIR and EXAFS.

1. Introduction

Selective oxidation is a promising process to effectively utilize abundant methane resources for producing value-added chemicals. Despite many efforts [1,2,3] using a variety of oxidants, no completely satisfactory solution has been obtained so far. A key problem is that it is difficult to avoid overoxidation of the oxygenated products, because oxygen-containing hydrocarbons such as CH_3OH and CHOH have more reactive C-H bonds than methane. Therefore, it is important to develop a method to control the supply oxygen species and to find proper catalysts. In this study, we present a general method of synthesis of supported bimetallic catalysts that ensures controlled alloy formation. It is important for the active site not to have too much of the component used to activate oxygen, so the control of metal ratio was important. This is the principle of site-isolation, which allows limited adsorption of oxygen atoms while permitting activation of methane.

2. Experimental

The catalysts were prepared by a cross-redox method between noble metals (A) and base metals (B). The base metal was reduced first in solution, with the addition of $NaBH_4$ to a suspension containing the support. The support was silica from the Cabot corporation (either L90 of 90 m^2g^{-1} or EH5 with 200 m^2g^{-1}). The catalyst composition, structure, and active surface area were obtained using various techniques.

A quantity of 500 mg catalyst was packed in a stainless reactor to form a catalyst bed layer in each test. All activity evaluation tests were conducted at atmospheric pressure and various temperatures. The products of CO, CO_2, CH_4, CH_3OH, HCHO, DME and HCOOH were analyzed by flame and plasma ionization detectors.

3. Results and discussion

The synthesis method is shown in Fig. 1. It is a solution method, which starts with reduction of a base metal, and then addition of a noble metal. An example is given for A=Ni and B=Pt but the method is general.

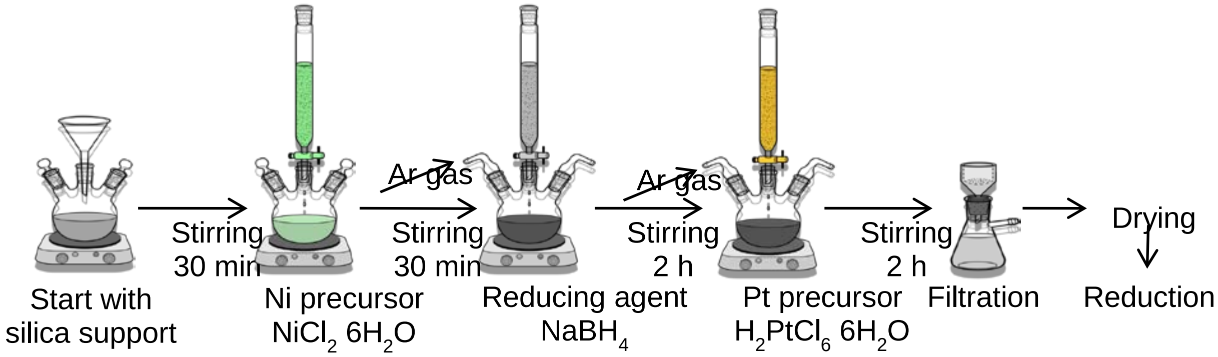

Fig. 1. Cross-redox process for synthesis of bimetallic alloys.

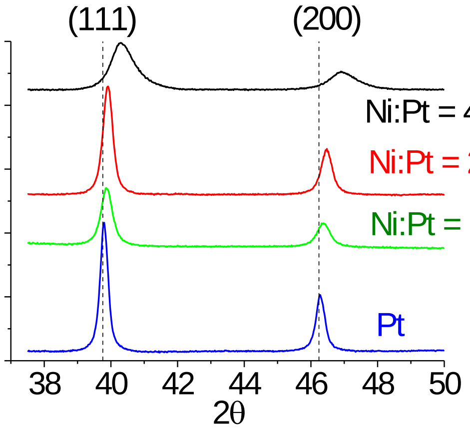

Fig. 2. X-ray diffraction patterns of NiPt/SiO_2 catalysts

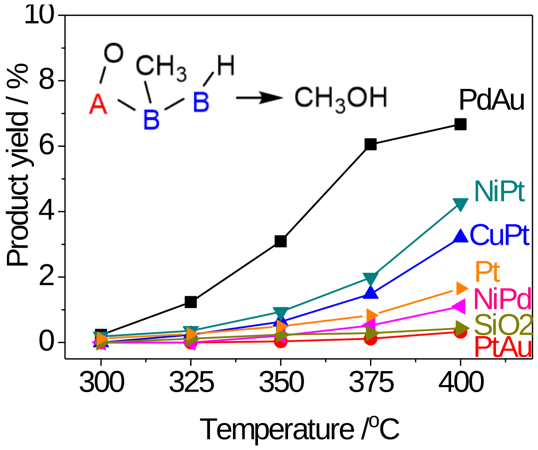

Fig. 3. Combustion on various alloys

The results of X-ray diffraction analysis of various NiPt alloys are shown in Fig. 2. Their patterns show shifts of the Pt lines in the direction of greater angle with increasing Ni, consistent with Vegard's law, and demonstrate the formation of alloys. A large number of combinations of noble metals (Ru, Pd, Ag, Ir, Pt, Au) and base metals (V, Cr, Mn, Fe, Co, Ni, Cu Zn, Mo, W) and main elements (Ga, In Sn, Bi) were successfully prepared and tested. The activity of various alloys in methane oxidation are shown in Fig. 3. The partial pressure dependencies of the best catalysts were studied and the kinetics gave rise to a co-adsorption mechanism. In situ FTIR and EXAFS were used to give evidence for the mechanism.

4. Conclusions

Activity evaluations of the oxidation of methane over single metal and alloy catalysts were conducted under atmospheric pressure and various temperatures with new catalysts. The highest formation rate of oxygenates could be obtained over alloys of noble metals and base metals with a feed containing a redox agent. It can be concluded that oxidation of methane over bimetallic alloy catalysts by using an oxygen shuttle to transfer single atoms of oxygen is an efficient method to obtain value-add chemicals. In situ structural analysis gives insight on the structure of the catalysts and the adsorbed species.

References

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