Selective deNO$_x$ catalysts using Pd-based intermetallic compounds supported on Al_2O_3

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Abstract: Catalytic reduction of NO by CO was studied over a series of Pd-M/Al_2O_3 catalysts (M = Cu, In, Zn, Sn, and Pb) prepared by co-impregnation with different metal precursors to develop selective deNO$_x$ catalysts at low temperature. PdIn/Al_2O_3 shows high N_2 selectivity (>99%) even at a low temperature region (<200°C), where the conventional monometallic Pd/Al_2O_3 catalyst shows very low N_2 selectivity (typically 30~40%). Addition of Cu to PdIn/Al_2O_3 significantly increased the catalytic activity without lowering of N_2 selectivity, affording a highly active and selective deNO$_x$ catalyst at low temperature region.

Keywords: Pd-M, deNO$_x$, synergistic effect.

1. Introduction

The exhaust gas purification catalyst is also known as a three-way catalyst (TWC) and is indispensable for removal of CO, hydrocarbons and NO$_x$ generated as exhaust gas of the internal combustion engine. Catalytic reduction of NO by CO, that is NO–CO reaction, is one of the important reactions proceeding over TWC. It is known that this reaction is catalyzed by Pd in the reaction mechanism shown in Figure 1. However, N_2O is also formed as a by-product by association of surface N atoms and NO. The by-production of N_2O is undesirable from the viewpoint of removal of NO$_x$, and it is important to design a catalyst to improve N_2 selectivity.

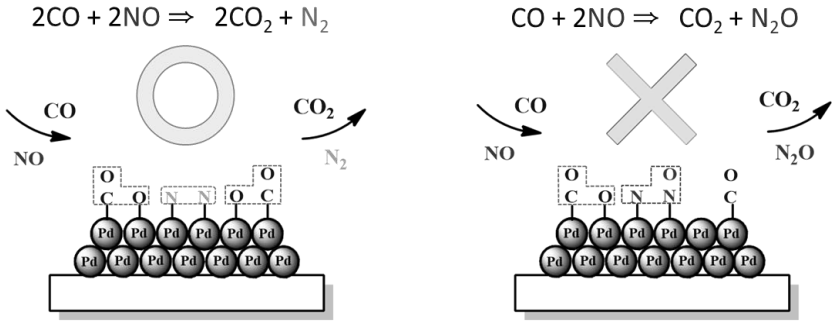

Figure 1. Mechanism of N_2 (left) and N_2O (right) formation in NO–CO reaction over Pd catalyst.

Intermetallic compounds have unique crystal structures, surface atomic arrangement, and specific electronic states, hence typically exhibit unique catalytic property compared with the conventional monometallic and solid-solution alloy catalysts. Therefore, in this study, we tested the catalytic performances of various Pd-based intermetallic compounds to investigate the effect of the second metal on N_2 selectivity.

2. Experimental

Al_2O_3 supported Pd and Pd–M (M = Cu, In, Zn, Sn, and Pb) catalysts were prepared by co-impregnation method using γ-Al_2O_3 and $Pd(NH_3)_2(NO_2)_2$, $Cu(NO_3)_2{\cdot}3H_2O$, $In(NO_3)_3{\cdot}xH_2O$, $Zn(NO_3)_2\cdot 6H_2O$, $(NH_4)4SnCl_6$ and $Pb(NO_3)_2$ as metal precursors. The catalyst (0.15g) diluted with sea sand (1.85g) was treated under flowing hydrogen (50 ml·min^{-1}) at 400°C for 30 min. The NO–CO reaction was carried out in a fixed-bed continuous flow system by feeding NO (0.5%), CO (0.5%), and He (balance) with the total flow rate of 96 ml·min^{-1}. The gas phase was analyzed by an on-line TCD gas chromatography (Shimazu GC-8A) equipped downstream.

3. Results and discussion

XRD patterns of the prepared catalysts revealed that the desired intermetallic phases were formed with high phase purities. The monometallic Pd catalyst showed a higher NO conversion than other Pd-based bimetallic catalyst (Figure 2a). However, its N_2 selectivity was very low (30~40%) in this temperature range (Figure 2b). When some intermetallic compounds were used, N_2 selectivity was improved. In particular, intermetallic PdIn showed very high N_2 selectivities at the wide range of NO conversion (20-100%, Figure 2c) and even at low temperatures (175-200ºC, Figure 2b). The PdIn/Al_2O_3 catalyst gave a high N_2 yield without N_2O emission with a smaller space velocity (87%, at 250°C).

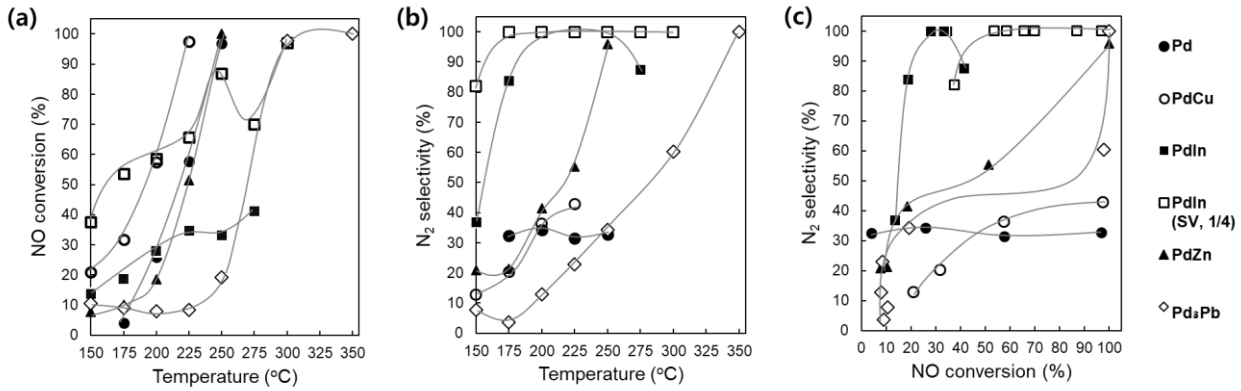

Figure 2. (a) NO conversion and (b) N_2 selectivity in NO–CO reaction over various Pd-based catalysts. (c) Relationship between NO conversion and N_2 selectivity.

We also prepared a Pd-In-Cu/Al_2O_3 catalyst, which showed higher NO conversions than PdIn/Al_2O_3 without lowering the high N_2 selectivity. Optimization of the metal composition ratio revealed that Pd : In : Cu atomic ratio of 3: 1: 2 gave the highest catalytic activity and selectivity (92% NO conversion and 100% N_2 selectivity at 250°C, Figure 3).

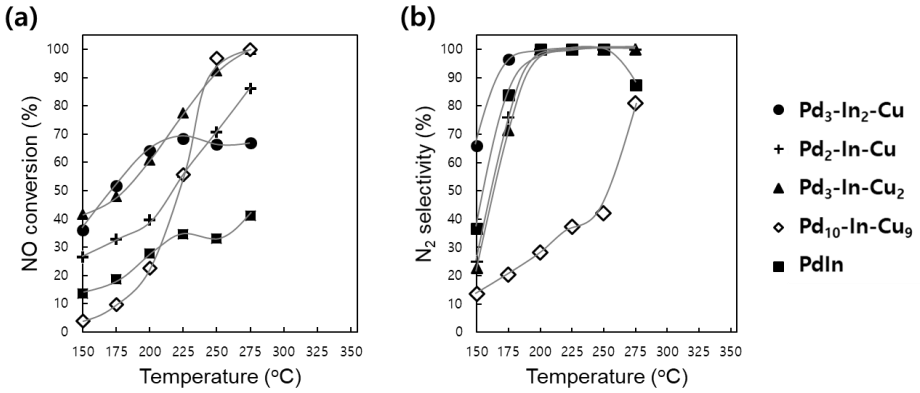

Figure 3. (a) NO conversion and (b) N_2 selectivity in NO–CO reaction over various Pd-In-Cu catalysts.

4. Conclusions

Intermetallic PdIn supported on Al_2O_3 showed high N_2 selectivities in NO–CO reaction at low reaction temperatures (<200°C). Addition of Cu to Pd-In/Al_2O_3 showed drastic increase in catalytic activity without lowering N_2 selectivity, which provides a highly active and selective deNO_x catalyst.

References

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