Ceria modified titania supported Pd-Cu catalysts for nitrate reduction in water

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Introduction

The increasing nitrate levels in water have been an intensive attention because nitrate caused serious health risk [1]. To remove hazardous nitrate, Vorlop and Tacke suggested a catalytic reduction method which used metal-supported oxide as catalyst and hydrogen as reductant [2]. Many studies presented that bimetallic type of the catalyst including a noble metal (Pd or Pt) and a promoter such as Cu was suitable for the nitrate reduction because the nitrate could be converted nitrite on the promoter by hydrogen spilled over from noble metal and the nitrite was reduced to N_2 or ammonium on noble metal site [3]. Among the catalysts, Pd-Cu-based catalysts showed high nitrate conversion and N_2 selectivity [4].

In our previous work using Pd-Cu/TiO_2 catalysts, we observed that metallic Cu state was the active phase for the nitrate reduction and TiO_2 support could enhance the catalytic activity because the nitrate could be bound to oxygen vacancies formed on the reduced support surface [5]. The metallic states of active species and the oxygen vacancies were generated in the catalyst with the most reduced support (i.e., $Ti^{4+} \rightarrow Ti^{3+}$). Thus, it could be speculated that the reduced state of the support was important factor for the nitrate reduction activity.

Besides titania, ceria has widely known as the reducible support. Using these properties, Li et al. demonstrated that the titania containing ceria had more Ti^{3+} than single titania [6]. From this result, the TiO_2-CeO_2 support might be a promising material. In this study, we prepared Pd-Cu/TiO_2-CeO_2 catalysts with different ceria amount, and investigated the effect of the ceria addition on the catalytic performances and the catalytic properties.

Materials and Methods

The TiO_2-CeO_2 supports were synthesized by co-precipitation method, then palladium and copper were impregnated on the supports by deposition-precipitation method. The abbreviations, BET properties and chemical compositions of the catalysts are shown in **Table 1**. The nitrate reduction reactions were carried out in a semi-batch reactor and performed under 25°C and atmospheric pressure. 0.15 g of catalyst was located in the reactor and hydrogen was continuously fed to the reactor (90 ml/min). 2 mM of nitrate solution prepared from KNO_3 was subsequently added into the reactor.

Results and Discussion

Figure 1 displays the concentration profiles of nitrate over all catalysts. For comparison, the activity of Pd-Cu/TiO_2 catalyst (PCTC0) in our previous work [5] is also presented. During the first 20 min of reaction, the nitrate was more rapidly reduced in TiO_2-CeO_2 supported catalysts than in PCTC0. Among the catalysts, the fastest initial reaction rate (calculated as consumed nitrate concentration per amount of catalyst per the first 3 min) was shown in PCTC1 (3.20 mmol/min/gcat) and the value was about 8 times greater than that of PCTC0 (0.41 mmol/min/gcat).

Table 1. Chemical compositions and BET properties of Pd-Cu/TiO_2-CeO_2 catalysts.

Abbreviation	Chemical composition		BET properties	
	Ti:Ce content (mol ratio)	Pd [Cu] content (wt. %)	Surface area (m^2/g)	Pore volume (cm^3/g)
PCTC1	18:1	3.0 [1.0]	86.1	0.305
PCTC2	5:1	3.1 [1.1]	72.7	0.226
PCTC3	2:1	3.1 [1.1]	62.7	0.316

In Ti $2p_{3/2}$ spectrum, the value of lower binding energy of PCTC1 (456.9 eV) was very close to that of Ti^{3+} (456.8 eV). On the other hand, the peak shifted to the higher binding energy with increasing the amount of ceria. For Ce 3d, PCTC1 had the largest portion of Ce^{3+}. Similar to Ti 2p spectrum, the Ce^{3+} contents of PCTC2 and PCTC3 lowered as ceria content increased. The formation of Ti^{3+} and Ce^{3+} indicated that the surface of PCTC1 was rich in oxygen vacancies. In the cases of Pd and Cu, the chemical state of PCTC1 was closer to metallic Pd and Cu than other catalysts. These results suggested that the synergetic effect of oxygen vacancies and metallic Cu states in PCTC1 significantly enhanced the nitrate reduction activity.
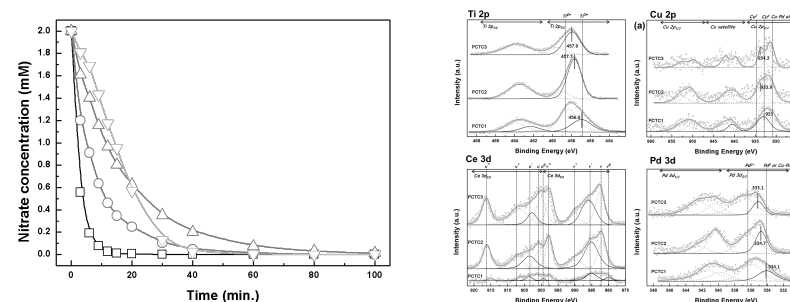

Fig. 1. (Left) Nitrate concentrations as a function of reaction time for catalytic nitrate reduction (▽: PCTC0, □: PCTC1, ○: PCTC2, △:PCTC3); (Right) XPS spectra of the prepared catalysts.

Significance

The addition of small amount of ceria to Pd-Cu/TiO_2 catalyst was beneficial to the nitrate reduction.

References

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