Kinetic study of photo-oxidation of NH_3 over TiO_2

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Abstract

Kinetic study was carried out for photo-oxidation of NH_3 (photo-SCO: $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$) to elucidate the mechanisms of the photo-SCO over anatase and rutile TiO_2. The reaction orders of the reactant gases reveal that the photo-SCO activity depends only on the concentration of O_2 with either anatase or rutile TiO_2. Steady-state kinetics suggests that the rate-determining step is the formation of nitrosoamide species from surface NO species and NH_2 radical. The surface NO species may play an important role in the high activity of the photo-SCO. O_3 anion radical, which is a strong oxidant, was detected only over anatase TiO_2 and the concentration of surface NO species would be increased by O_3 anion radical. This may be the reason why anatase TiO_2 shows higher activity than rutile TiO_2. The photo-SCO activity is enhanced as the reaction temperature increased. 100% NH_3 conversion and 94% N_2 selectivity were achieved at GHSV = 50,000 h^{-1} at 435 K. This enhancement of the activity at higher reaction temperature is caused by (1) the increase in the surface NO species and (2) the improvement of reactivity between surface NO and NH_2 radical. The SCO activity is moderately high even at low temperature: the Arrhenius activation energy is only 24.4 kJ mol^{-1}.
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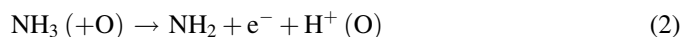
1. Introduction

It is desirable to remove ammonia from exhaust gas and/or waste water in industrial emission source in an environmental point of view. Ammonia can be eliminated by biological treatment, thermal combustion and catalytic oxidation. Recently, selective catalytic oxidation (SCO) of ammonia to nitrogen in the presence of excess oxygen has received much attention because this technique is promising for efficient removal of ammonia from exhaust gas [1–6]. The reaction stoichiometry in the typical SCO condition had been proposed as follows [7–12]:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (1)$$

The SCO process may be applied to remove unreacted ammonia in the selective catalytic reduction (SCR) of NO with ammonia process [13,14]. In the case of the SCO process located at the downstream of the SCR process, the low-temperature operation of the SCO is often required. Therefore, many efforts have been made in order to develop the low-

temperature SCO. Long and Yang reported that Cu- and Fe-exchanged ZSM-5 exhibited a good SCO activity at 623 K [1]. Gang et al. reported that Ag/Al_2O_3 showed high activity in the SCO in the range of >433 K [3]. A number of the other catalysts, such as CuO/Al_2O_3 [14,15], V_2O_5/TiO_2 [16], Pt-, Pd- and Rh-exchanged ZSM-5 [17], showed SCO activity. However, the aforementioned catalysts need high temperature (>433 K) in the SCO reaction.

Some kinetic studies of the SCO reaction over metal oxides have been reported in order to determine the rate-determining step and the activation energy [10,18–20]. Eqs. (2)–(5) are the most probable SCO reaction mechanism over metal oxide catalysts [10,14,19–22].

$$NH_3 (+O) \rightarrow NH_2 + e^- + H^+ (O) \qquad (2)$$

$$NH_2 + O_2 \rightarrow NO + H_2O \qquad (3)$$

$$NH_2 + NO \rightarrow NH_2NO \qquad (4)$$

$$NH_2NO \rightarrow N_2 + H_2O \qquad (5)$$

It has been proposed that the rate-determining step of the SCO over metal oxide catalysts is Eq. (2) (NH_3 activation process) [10,18–20]. Additionally, activation energy (E_a) of

Nomenclature

r	N_2 production rate (mol s^{-1})
k	rate constant
C_{NH_3}	concentration of NH_3 (mol L^{-1})
C_{O_2}	concentration of O_2 (mol L^{-1})
α	reaction order of NH_3
β	reaction order of O_2
$k_{\pm i}$	rate constant at Step i
K_i	equilibrium constant at Step i
S	Lewis acid site on TiO_2
S$^-$	reduced Lewis acid site
$O_{lattice}^{2-}$	lattice oxygen
[S]$_0$	total amount of Lewis acid site on TiO_2 (mol L^{-1})
[NH$_2^\bullet$–S]	concentration of NH$_2^\bullet$–S species (mol L^{-1})
[NO–S$^-$]	concentration of NO–S$^-$ species (mol L^{-1})
[O$_2$]	concentration of O_2 (= C_{O_2}) (mol L^{-1})
T	reaction temperature (K)

the SCO reaction is high (76–139 kJ mol^{-1}) [18–20]. These results indicate that the SCO of ammonia at low temperature is difficult due to the high E_a of NH_3 activation. Therefore, a development of new SCO system with low E_a of NH_3 activation is required.

Cant and Cole reported that the SCO reaction was carried out in a closed system over TiO_2 photocatalyst under irradiation (photo-SCO) at room temperature although the activity was low [23]. Recently, we have reported that the photo-SCO proceeds with high activity (NH_3 conversion: 100%, N_2 selectivity: 84% at gas hourly space velocity (GHSV) = 25,000 h^{-1}) at room temperature over TiO_2 in a fixed bed flow system [24]. The photo-SCO reaction stoichiometry is same as that in the conventional SCO (Eq. (1)). The reaction mechanism of the photo-SCO over TiO_2 was elucidated by UV–vis, electron spin resonance (ESR) and Fourier transform infrared (FT-IR) spectroscopies and determined as shown in Scheme 1 [24,25]. Our proposed reaction mechanism is almost similar to the conventional SCO reaction mechanism. NH_3 is adsorbed to Lewis acid site of TiO_2 in the dark (Step 1). Adsorbed NH_3 is activated to NH_2 radical by trapping a photo-formed hole and a photo-formed electron reduces Ti^{4+} site to Ti^{3+}. O_2 reacts with an electron or a hole, which are formed under UV irradiation, to form oxygen anion radical species ($O_2^{\bullet-}$ or $O_3^{\bullet-}$) (Step 3). NH_2 radical reacts with oxygen anion radical species to form NO without light (Step 4). The NO reacts with NH_2 radical and NH_2NO species is generated as an intermediate (Step 5). The NH_2NO species is decomposed to N_2 and H_2O (Step 6). Finally, the reduced Ti^{3+} is re-oxidized by the reaction with O_2 (Step 7). Additionally, we found that the crystal phase of TiO_2 affects the types of oxygen anion radical [24]. Rutile TiO_2 generates only O_2 anion radical whereas anatase TiO_2 forms not only O_2 anion radical but also O_3 anion radical. The catalytic activities of various TiO_2 in the photo-SCO reaction indicate that O_3

anion radical plays a key role in the higher activity than O_2 anion radical.

The photo-SCO proceeds even at room temperature, since the activation of NH_3 proceeds at room temperature by photo-excitation (Step 2). Thus, the rate-determining step of the photo-SCO is different from the conventional SCO reaction and the activation energy of the photo-SCO is expected to be lower than that of the conventional SCO. In this study, we carried out the kinetic study of the photo-SCO over TiO_2 using steady-state approximation not only to determine the rate-determining step of the photo-SCO reaction but also to clarify the reaction mechanism as shown in Scheme 1. The thermal effect for the photo-SCO was also investigated. Furthermore, we discussed the reactivity of O_3 and O_2 anion radical species in terms of kinetics.

2. Experimental

2.1. Preparation and characterization of catalysts

Two kinds of TiO_2 (JRC-TIO-3 and JRC-TIO-8 supplied from the Japan Catalysis Society) were hydrated in distilled water for 2 h at 353 K, followed by filtration with suction pump. The sample was dried at 383 K overnight, followed by calcination in dry air at 673 K for 3 h. After the hydration and calcinaton described above, JRC-TIO-3 and JRC-TIO-8 were used in this study.

The specific surface area of the prepared JRC-TIO-3 and JRC-TIO-8 were evaluated to be 46 and 93 m^2 g^{-1} by the BET method using N_2 adsorption isotherm at 77 K. We confirmed that the prepared JRC-TIO-3 and JRC-TIO-8 consist of rutile and anatase phases respectively by the XRD patterns. Amount of acid sites on TiO_2 was determined by the adsorption equilibrium method of NH_3 according to the previous work [24,26]. Before the adsorption equilibrium method, TiO_2 was evacuated at 673 K as a pretreatment.
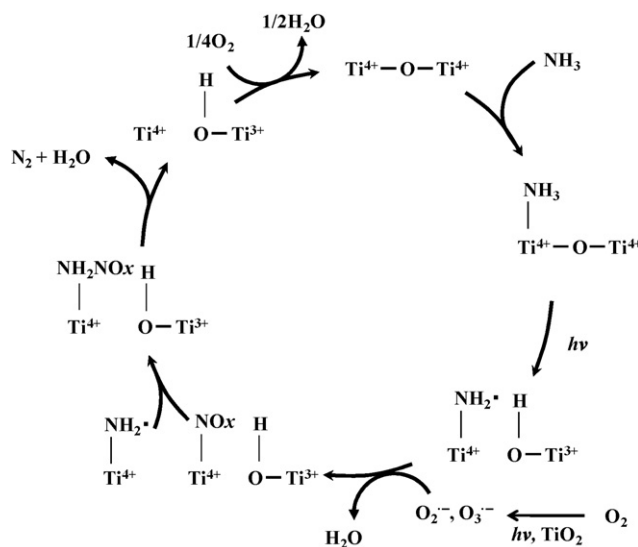
Scheme 1. Proposed reaction mechanism of photo-SCO.