

ARTICLE

Effect of H₂O on NO Reduction over NSR Catalyst 12CaO·7Al₂O₃/10%K

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A novel NO_x storage/reduction catalyst 12CaO·7Al₂O₃/10%K, defined as C12A7/K, was prepared, which possesses good NO_x storage/reduction ability with a high sulfur-tolerance. The effect of H₂O on the NO reduction features over the C12A7/K catalyst was investigated. The NO conversion and the N₂ selectivity were measured as a function of temperature and H₂O concentration. In the presence of 1.2% H₂O, both the NO conversion and the N₂ selectivity significantly decrease at lower temperature region (<500 °C). At temperatures over 500 °C, however, the NO reduction is only slightly influenced by H₂O. The species of NO₃⁻/NO₂⁻ are confirmed as main storage components in the C12A7/K catalyst, which are further reduced into N₂ by H₂ under the reduction conditions.

Key words: NO reduction, Water, N₂ selectivity

I. INTRODUCTION

Reduction of nitrogen oxides emissions, the most serious pollutants contributing to the decrease of tropospheric ozone, acidification of environment and general damage to human health, has become one of the greatest challenges in environmental protection [1]. An alternative approach is the so-called NO_x storage/reduction (NSR) concept [2-7]. In the NSR approach, NO_x is trapped in a catalyst during the relatively long lean period, and then NO_x stored as nitrites or nitrates is decomposed in the rich period, and subsequently reduces to nitrogen. In previous work, the compounds Pt/BaAl₂O₄-Al₂O₃, BaFeO₃, BaCeO₃ and BaZrO₃ were investigated as NO_x storage-reduction catalysts [8-13].

It is well known that the active anion species O⁻ is a key intermediate in anion chemistry [14-19]. The microporous material 12CaO·7Al₂O₃ (C12A7) is characterized by a positive charged lattice framework [Ca₂₄Al₂₈O₆₄]⁴⁺ including 12 subnanometer sized cages. The two remaining O²⁻ ions are clathrated in the cages, which is able to substituted by other mono-charge anion X⁻ (X⁻ = O⁻, H⁻, OH⁻, etc.) to form the derivatives [Ca₂₄Al₂₈O₆₄]⁴⁺·4(X⁻) (C12A7-X⁻). For microporous crystal 12CaO·7Al₂O₃ (defined as C12A7), the O⁻ anions can be stored in the cages of C12A7 and also be emitted into the gas-phase by applying an extraction field under suitable temperature [20-22]. In this work, a novel NO_x storage-reduction catalyst C12A7/K was prepared, which possesses good NO_x storage-reduction ability with a good sulfur-tolerance. The effect of H₂O on the NO reduction features over the 12CaO·7Al₂O₃/10%K catalyst was focused on.

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II. EXPERIMENTS

A. Catalyst preparation

The C12A7 sample was prepared by a solid-state reaction at 1350 °C for 16 h. The more detailed preparation procedures have been described elsewhere [21,22]. The C12A7/K was prepared by adding KHCO₃ to C12A7 (KHCO₃:C12A7=3:10, weight ratio) and calcining at 900 °C for 4 h. The final potassium content in total is 10wt%.

B. Flow-reaction experiments

As shown in Fig.1, the catalytic activity was measured using a fixed-bed flow micro reactor by passing a feed gas mixture containing 4.33% NO, 8.13% H₂, and 0-7.2% H₂O diluted in Ar at a rate of 30 mL/min over 1.0 mL of a catalyst. Product analysis was performed by an on-line set of gas chromatographs (GC) with a thermal conductivity detector (TCD). The NO conversion and the N₂ selectivity was defined as $C_{NO} = ([NO]_{in} - [NO]_{out}) / [NO]_{in}$ and $S_{N_2} = 2[N_2 \text{ in effluent}] / ([NO]_{in} \times C_{NO})$ respectively.

C. Fourier transform infrared spectroscopy

Fourier transform infrared absorption (FT-IR) spectra were measured at 298 K by a Bruker EQUINOX55 FT-IR spectrometer using the KBr pellet method. The resolving power is 1 or 0.5 cm⁻¹ (choosing), and the signal-to-noise is better than 30000:1 (peak/peak). The samples for FT-IR measurements were mixed with KBr at a weight ratio of sample: 100:3.

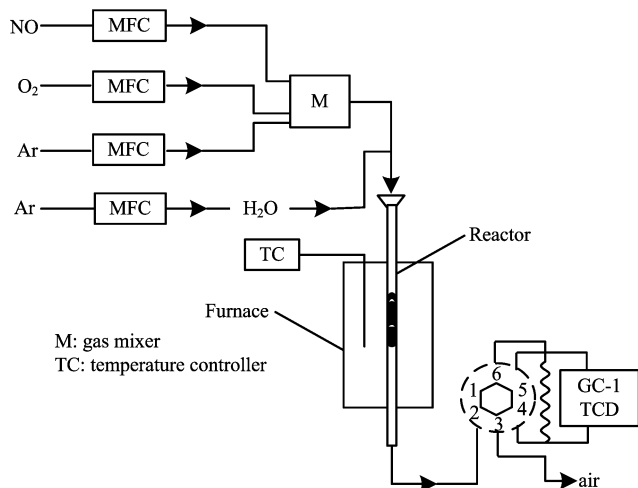


FIG. 1 Schematic diagram of the experimental apparatus.

III. RESULTS AND DISCUSSION

A. Effect of temperature on the NSR capacity of C12A7/K

Figure 2 shows the temperature effect of the NO reduction under dry and wet conditions over C12A7/K. When NO is reduced by H₂ in a dry environment, the NO conversion increases with increasing temperature in the temperature range of 300–700 °C and reaches about 70% at 700 °C. An optimum operating temperature window for the NO conversion about or over 50% with C12A7/K catalyst ranges from 500 to 700 °C. It is noted that in the reduction of NO, the selectivity of N₂ rather than N₂O is important because N₂O itself is a pollutant. Figure 2(b) shows the dependence of the N₂ selectivity on the sample temperature over C12A7/K. The N₂ selectivity increases with increasing temperature in the range of 200–600 °C, and reaches a maximum value of about 95% at about 600 °C. Over 600 °C, the N₂ selectivity appears to decrease slightly. Over 50% of NO can be reduced to N₂ by H₂ at 550–700 °C, which is quite close to the performance of Pt/Al₂O₃ catalyst [23].

Because most exhaust gases containing NO_x also contain 2%–18% water vapor [24], the response of catalysts in wet feed should be taken into account. An important aspect of catalyst performance is its ability to maintain high levels of NO_x conversion with the typical concentrations of water present in real exhaust. As shown in Fig. 2, both the NO conversion and the N₂ selectivity are significantly influenced in the lower temperature region (<500 °C) under wet conditions (1.2% H₂O). At temperatures over 500 °C, however, the influence of water on the NO reduction becomes unimportant. The NO reduction to N₂ is only slightly affected by the presence of H₂O over 500 °C. The above behavior would be due to the larger adsorption of water at lower temperature

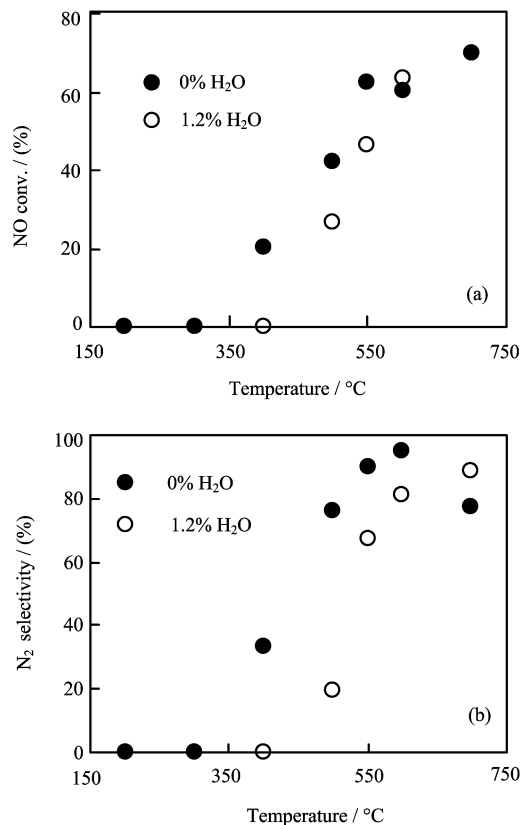


FIG. 2 The temperature effect of the NO reduction under dry and wet conditions over C12A7/K (NO: 4.33%, H₂: 8.13%, H₂O: 0 or 1.2%, Ar: the balance gas, total flow rate: 30 mL/min).

region, leading to serious coverage of the active sites and the decrease of the NO reduction ability. Lawson has also observed that the water strongly inhibited NO decomposition over copper chromite under 550 °C [25]. The larger impact of H₂O at low temperature may be due to competitive adsorption with both NO and H₂ [26]. Also H₂O may affect various reactions by directly influencing the formation of the intermediate species.

B. Effect of the H₂O concentration on the NO_x storage reduction capacity of C12A7/K

Figure 3 shows the effect of H₂O concentration on the reduction of NO over C12A7/K. As the H₂O concentration increases from 0 to 1.9%, the NO reduction to N₂ is severely decreased and the N₂ selectivity falls from 90% to 44.8%. When the H₂O concentration is higher than 1.9%, the NO reduction is only slightly impacted by further increase of the H₂O concentration, which may indicate some saturation effect [26].

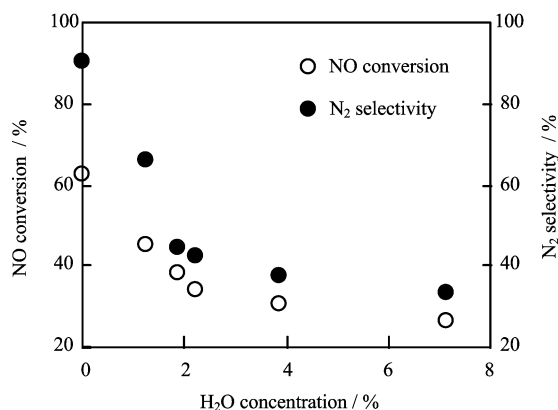


FIG. 3 Effect of H_2O concentration on the reduction of NO over C12A7/K at $550\text{ }^\circ\text{C}$ (NO : 4.33%, H_2 : 8.13%, H_2O : 0-7.2%, Ar: the balance gas, total flow rate: 30 mL/min).

C. FT-IR

To investigate the intermediate species on the C12A7/K surface formed in the NO_x storage processes, the FT-IR spectra were recorded for the following different samples: and the fresh C12A7/K, and the NO_x -stored C12A7/K, and the NO_x -stored C12A7/K in wet feed gas. Figure 4(a) displays the FT-IR spectra of the C12A7/K sample. The absorption envelopes in the $450\text{--}850\text{ cm}^{-1}$ region are attributed to the C12A7 characteristic absorption structures, corresponding to the Al-O stretching and bending modes in AlO_4 tetrahedra [27]. For NO_x -stored C12A7/K catalyst in dry gas for 3 h (shown in Fig.4(b)), there is a sharp peak (near 1384.2 cm^{-1}) and a small peak (near 1271.4 cm^{-1}), which is assigned to NO_3^- and NO_2^- respectively based on previous work [28]. This confirms the species of $\text{NO}_3^-/\text{NO}_2^-$ as main storage components in the

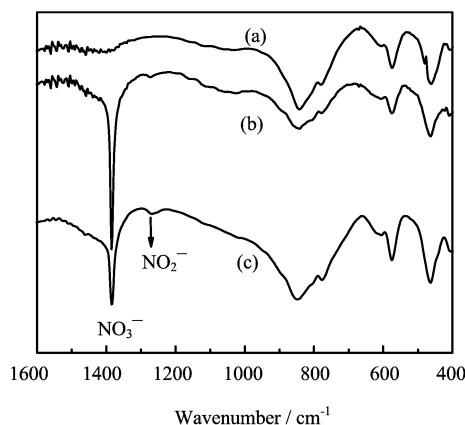


FIG. 4 FT-IR patterns for (a) the initial C12A7/K; (b) the NO_x -stored C12A7/K (stored condition: NO_x : 4.33%, O_2 : 5%, Ar: the balance gas, $550\text{ }^\circ\text{C}$ for 3 h) and (c) the NO_x -stored C12A7/K (stored condition: NO_x : 4.33%, O_2 : 5%, H_2O : 1.2%, Ar: the balance gas, $550\text{ }^\circ\text{C}$ for 3 h).

C12A7/K catalyst, which are further reduced into N_2 by the reducing agent. The NO_3^- peak is greatly decreased for the C12A7/K catalyst adsorbed NO_x in wet feed gas for 3 h (shown in Fig.4(c)), which means that the presence of water inhibits the formation of NO_3^- over the surface of C12A7/K.

IV. CONCLUSION

This work shows that over 50% of NO can be reduced to N_2 by the reducing agent H_2 over a novel NSR catalyst of C12A7/K at $550\text{--}700\text{ }^\circ\text{C}$. The NO reduction reaches a maximum value of about 95% at about $600\text{ }^\circ\text{C}$ under dry mixture gas. Both the NO conversion and the N_2 selectivity significantly decrease in lower temperature regions ($<500\text{ }^\circ\text{C}$) in the wet gas (1.2% H_2O). At temperatures over $500\text{ }^\circ\text{C}$, however, the NO reduction is only slightly influenced by H_2O . With an increase of the H_2O concentration, the NO conversion and the N_2 selectivity decrease. The species of $\text{NO}_3^-/\text{NO}_2^-$ are confirmed as the main storage components on the C12A7/K catalyst, which are further reduced into N_2 by H_2 . The presence of water inhibits the formation of $\text{NO}_3^-/\text{NO}_2^-$.

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