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ENHANCED DECOMPOSITION OF NO ON THE ALKALIZED PdO/Al₂O₃ CATALYST

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Abstract

Experimentally, decomposition of NO on the alkalized Pd/Al₂O₃ catalyst is remarkably enhanced at 825-1000 K. The enhancement in N₂ yield may be due to the additional basic sites on the alkalized catalyst that can trap NO molecules. However, at T > 1000 K, due to the fact that the absorbed oxygen in subsurface or bulk of Pd was involved in the formation and desorption of oxygen molecules, yield of oxygen was enhanced. © 1999 Elsevier Science Ltd. All rights reserved

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1. Introduction

Nitrogen oxides (NO_x) cause many environmental problems including formation of acid rain and the resultant acidification of aquatic systems, ground-level ozone (smog), and general atmospheric visibility degradation. Many methods for reduction of NO_x emissions such as reduction-absorption, chelation absorption, catalytic decomposition and catalytic reduction have been widely investigated and practically used [1].

Thermodynamically, NO molecules are unstable towards decomposition into N₂ and O₂ ($\Delta G^{\circ} = -173 \text{ kJ mol}^{-1}$) [2]. However, due to a high activation energy of $E_a > 254 \text{ kJ mol}^{-1}$ for decomposition of NO [2], the reaction is not to proceed appreciably at < 1273 K. Therefore, many catalysts have been investigated in enhanced decomposition of NO at moderate reaction conditions [3-9]. Platinum and palladium have been

widely used in exhaust emission controls [3,4]. Palladium has a similar catalytic activity for decomposition of NO as that of platinum but with a better thermal stability [10]. Alumina supported Pd catalysts have been recognized very active in catalytic decomposition of NO in an oxidized environment at 1100 K with 80% conversion, for instance [4]. Desorption of oxygen molecules from Pd surfaces in the NO reduction process is also a highly endothermic reaction ($\Delta H \approx 200 \text{ kJ mol}^{-1}$) [10]. In a separated experiment, an increase in $-\Delta H$ for NO adsorption on NaOH-modified Al_2O_3 supported Pd catalyst was observed [11]. However, decomposition of NO on the alkalinized Pd/ Al_2O_3 catalyst has not been well studied. Thus, the main objective of this work was to study the enhancement of adsorption and decomposition of NO on the alkalinized Pd/ Al_2O_3 . In addition, the alkalinized Al_2O_3 was also studied by ^{27}Al NMR spectroscopy.

2. Experimental

γ -Alumina support (Merck, surface area = $108 \text{ m}^2\text{g}^{-1}$) was alkalinized with a NaOH solution (13 wt%) at 298 K and calcined at 950 K for four hours. The alkalinized Pd/ Al_2O_3 catalyst was prepared by impregnation of an aqueous solution of $\text{Pd}(\text{NO}_3)_2$ onto the pre-alkalinized $\gamma\text{-Al}_2\text{O}_3$. Detailed preparation procedures were described previously [11]. Catalytic decomposition of NO was carried out in a fixed-bed flow reactor at a W/F of 1.6 g/mL. The flow-rate of the 4% NO/He gas was regulated at 30 mL/min by a mass flow controller (Tylan, FC-280). The composition of gas was analyzed by gas chromatography (GC) using a column of molecular sieve 5A. The catalytic activity was estimated from the N_2 yield in the reaction product according to $\text{N}_2 \text{ yield} = 2 [\text{N}_2]_0 / [\text{NO}]_i$, where $[\text{NO}]_i$ and $[\text{N}_2]_0$ denote concentrations of reactant NO and product N_2 , respectively.

In the temperature programmed reduction (TPR) experiments, the alkalinized catalyst was reduced in 10% H_2/He gas with a heating rate of 10 K/min at 300-773 K. A thermogravimetry analyzer (TGA) (SDT 2960 simultaneous TGA-DTA) was used to monitor the weight change of samples in the reduction process. Temperature programmed desorption (TPD) of NO on the catalyst were also determined in the TGA system with a heating rate of 10 K/min up to 873 K. The composition of gas was analyzed by on-line FTIR spectroscopy. Infrared spectra were recorded on a Bio-rad FT-IR spectrometer (FTS-40) with fully

computerized data storage and data handling capability. For all spectra reported, a 64-scan data accumulation was carried out at a resolution of 4 cm^{-1} . NMR spectra were recorded at 9.4 T on a Bruker Avance DSX 400 spectrometer. Zirconia rotors (4 mm outside diameter) are spun up to 5 kHz by dried compressed air. The ^{27}Al NMR spectra were recorded at 104 MHz.

3. Results and Discussion

Decomposition of NO on the Pd/Al₂O₃, alkalinized Pd/Al₂O₃, PdO and alkalinized Al₂O₃ catalysts at elevated temperatures was investigated in the fixed-bed reactor. Generally, desorption of oxygen may be the rate determining step for decomposition of NO on the Pd/Al₂O₃ catalyst [10]. In Figure 1, the catalytic activity

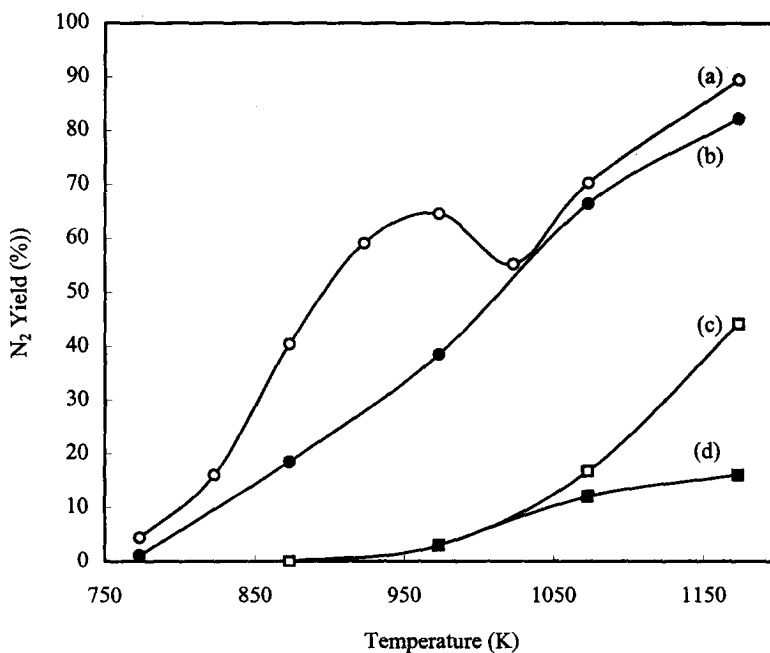


Figure 1 Catalytic activity on N₂ yield for decomposition of NO on (a) alkalinized Pd/Al₂O₃, (b) PdO/Al₂O₃, (c) PdO, (d) alkalinized Al₂O₃.

on N₂ yield for the Pd/Al₂O₃ catalyst increases as the reaction temperature increases and subsequently reaches 80% at 1170 K. Most interestingly, the catalytic activity was remarkably enhanced on the

alkalized Pd/Al₂O₃ catalyst at 825-1000 K. Note that the catalytic activity of the PdO powder and the alkalinized Al₂O₃ support seems ineffectively at this reaction temperature region (825-1000 K). The activity enhancement for decomposition of NO on the alkalinized Pd/Al₂O₃ catalyst may be due to at least two possibilities: (1) Additional sites on the alkalinized catalyst that can adsorb NO molecules. (2) An adsorption intermediate species (NaOH(NO)Pd) is postulated.

In order to examine the interaction between NaOH and Al₂O₃, magic angle solid state NMR spectra of the alkalinized catalysts was measured using a 4-mm rotor at 300 K. The ²⁷Al NMR spectra of the alkalinized γ-Al₂O₃ in Figure 2 show two features at 70.53 and 10.02 ppm that may be attributed to tetrahedral Al (Al_{Td}) and octahedral Al (Al_{Oh}), respectively [12]. It is clear that Al_{Td} feature for Al₂O₃ decreases in intensity by approximately 20% in the alkalinization process. Aluminum ions may be extracted from the Al_{Td} sites in the NaOH solution. However, in the process of impregnation of Pd on to the alkalinized Al₂O₃ support, Pd-NaOH species may be formed favorably and the octahedral Al is consequently transferred into its tetrahedral form. The Pd-NaOH species was eventually supported on the Al₂O₃.

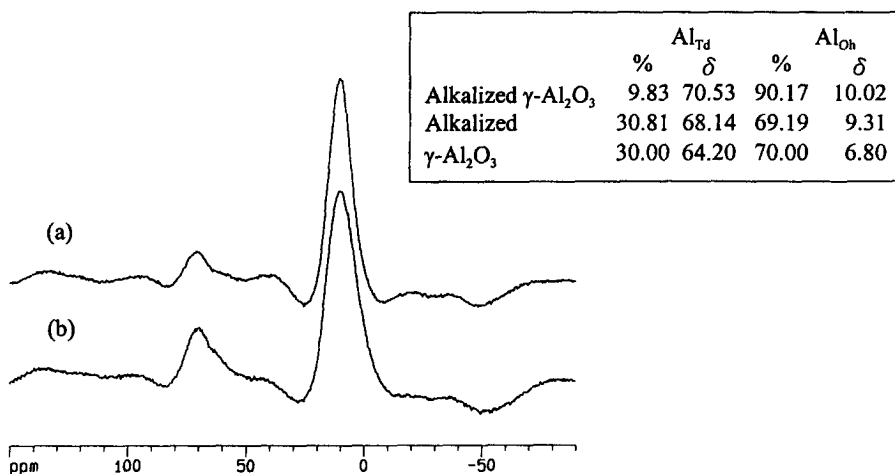


Figure 2 ²⁷Al NMR spectra of (a) alkalinized γ-Al₂O₃, (b) alkalinized Pd/Al₂O₃.

Figure 3 shows the temperature programmed desorption (TPD) profile of NO on the alkalinized Pd/Al₂O₃.

catalyst. Two main desorption bands at about 450 and 700 K are observed. Desorbed species was monitored by on-line FTIR spectroscopy. Relative nitrogen oxides concentration ratios are also show in

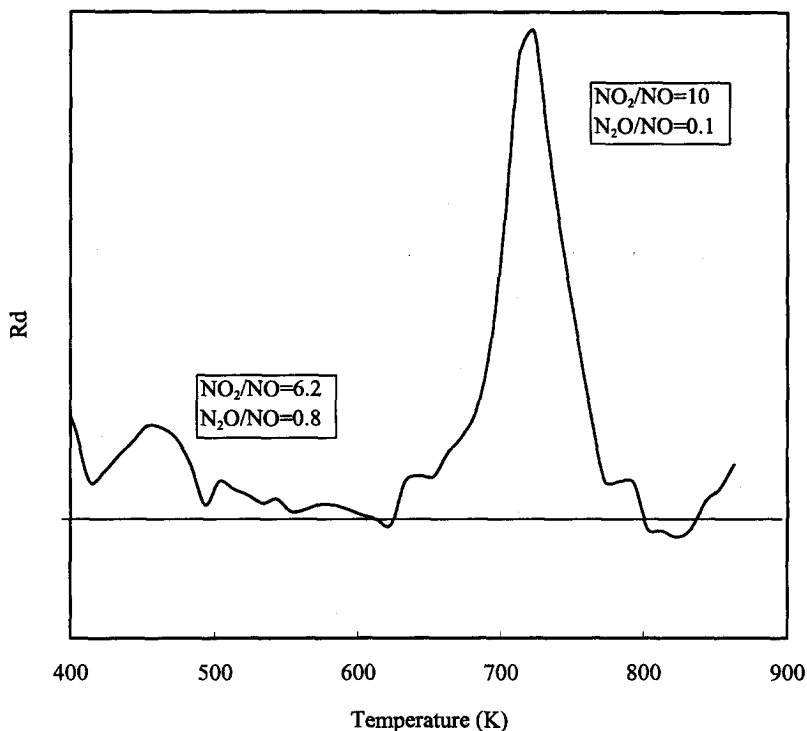


Figure 3 Temperature programmed desorption (TPD) of NO on the alkalized Pd/Al₂O₃ catalyst.

Figure 3. It is clear that NO₂ molecules are the main desorbed species from the alkalized catalyst surfaces at 450 and 700 K. A dissociate adsorption of NO on palladium surfaces into oxygen and nitrogen atoms generally occurs at ~ 400 K [11]. The adsorbed nitrogen atoms may be subsequently desorbed into N₂O at 450 K via a combination with the adsorbed NO. Since the reactivity of oxygen or NO with the incorporated oxygen in the subsurface or bulk of Pd is very low at < 1050 K, the observed NO₂ desorbed at 450 and 700 K in Figure 3 may be formed through a surface reaction between the surface oxygen atoms that formed via the dissociate adsorption of NO and the trapped NO in NaOH. The reactions involved in the

adsorption and decomposition of NO on the alkaliPd/Al₂O₃ may be described as follows:

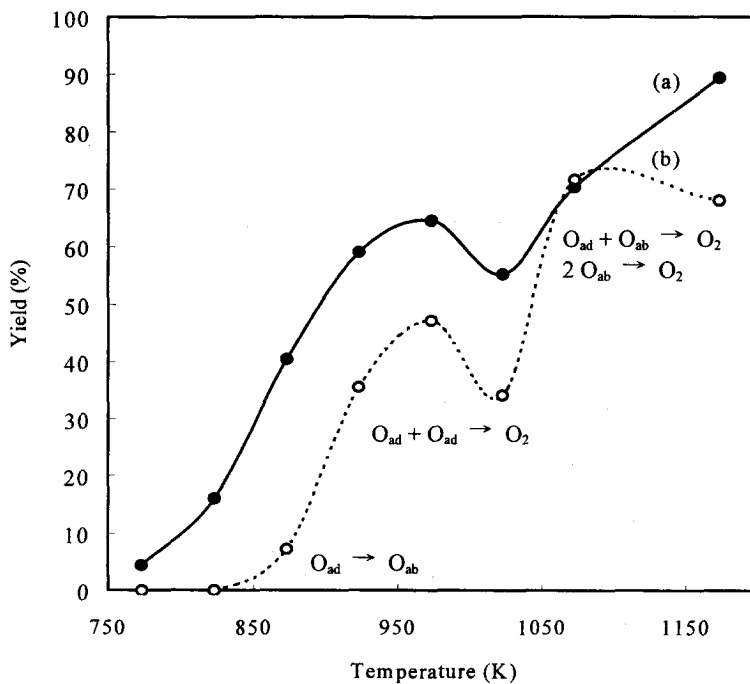
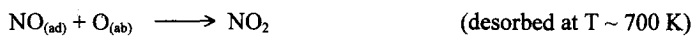
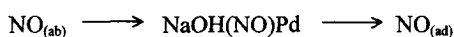
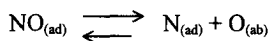
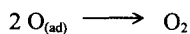
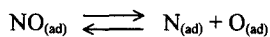
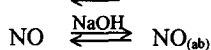
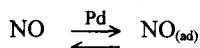


Figure 4 (a) N₂ and (b) O₂ yield for decomposition of NO over alkaliPd/Al₂O₃.

In Figure 4, at $T < 825$ K, because of the high energy barrier for desorption of oxygen molecules from Pd surfaces, most oxygen formed from the dissociative adsorption of NO on Pd was incorporated into the subsurface or bulk of Pd. Thus, yield of oxygen molecules from the alkalinized Pd catalyst was not very effective till saturated absorption of oxygen in Pd occurred. At $T > 1023$ K, due to the absorbed oxygen involved in the formation of oxygen molecules, yield of oxygen has been enhanced.

The alkalinized Pd/Al₂O₃ catalyst was also studied by temperature programmed reduction (TPR). Figure 5 shows that the TPR profile of the catalyst has two features at 380 and 410 K. The feature at 380 K may be attributed to hydrogen consumption in the reduction of PdO. The high temperature reduction feature (410 K) may be assigned to adsorption of hydrogen on Pd surface. As expected, adsorption of NO on the alkalinized catalyst may cause additional incorporated oxygen into subsurface or bulk of Pd. Therefore, the feature at 460 K may be due to reduction of the incorporated oxygen (O_{ab}).

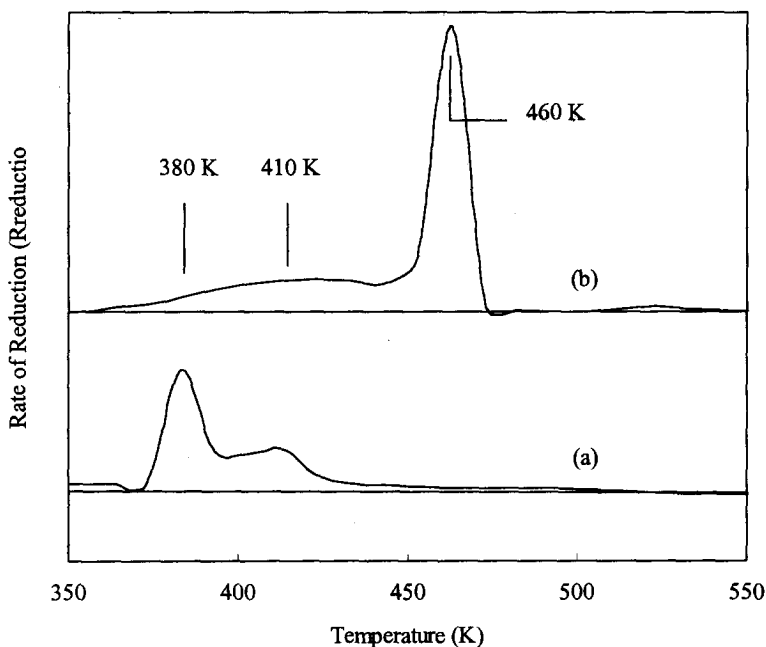


Figure 5 Temperature programmed reduction (TPR) of (a) alkalinized Pd/Al₂O₃ and (b) NO preadsorbed on alkalinized PdO/Al₂O₃.

4. Conclusions

The alkalized Pd/Al₂O₃ significantly enhances the decomposition of NO at 825-1000 K. The enhancement in N₂ yield may be due to the additional basic sites on the alkalized catalyst that can trap NO molecules. However, at T > 1000 K, due to the fact that the absorbed oxygen in subsurface or bulk of Pd was involved in the formation of oxygen molecules, yield of oxygen was enhanced.

Acknowledgements

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