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Influence of Moderate Temperature Treatment under Oxidation Atmosphere on Acidic Site Distribution of γ-Alumina

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Abstract. In order to elucidate the role of acidity in reaction of selective NO reduction by hydrocarbons in oxygen-rich circumstances, a commercial γ-alumina was treated under atmosphere at moderate temperature range and the acidic sites of treated alumina were determined by differential NH_3 adsorption heat at 473 K. The alumina has little impurity of Na, Fe, Si. The BET surface area and average pore width are 350 m^2/g and 4 nm respectively. Air treatment at moderate temperature has no serious effect on the total amount of acidic sites above 70 kJ/mol, but influences the acidic site distribution at the initial and the tail energy sides. Treatment at higher temperature gives rise to a higher initial adsorption heat due to activation of alumina surface. Disappearance of carbon-contained species and appearance of distinct surface hydroxyl groups under air treatment above 673 K are plausibly observed by FT-IR. Degree of dehydration has a tremendous effect on development of Brönsted acidic sites. The relationship of changes in acidic site distribution at moderate temperature and De-NOx activity at the same temperature was discussed.

Keywords:

Introduction

γ-alumina as well as a group of γ-alumina supported metal oxide catalysts were found to have selective reduction activity towards NO in oxygen-rich (lean-burn) circumstances (Hamada, 1994). The selective activity of NO reduction occurs usually in lower or moderate temperature range (573–773 K), depending on the supported metal species. Although surface acidity of the catalysts was realized by many researchers to have possibility to be responsible for selective NO reduction, there is not yet quantitative investigation on relationship of acidic site change and the De-NOx efficiency at temperatures at which the selective De-NOx activity appears. In order to elucidate the role of catalyst acidity in selective NO reduction, it is of first importance to obtain a quantitative and an as feasible as possible profile of catalyst acid sites distribution.

As a kind of transition aluminas, γ-alumina is of porous and usually possesses high surface area, which enables its wide application as a porous adsorbent, a support of catalyst, as well as an as-is catalyst. Surface acidity which dominates the catalytic property of γ-alumina is owing to its nature of defective spinels structure as well as surface hydroxyl species inside it. There are extensive researches on the acidic property of γ-alumina by approach of temperature-programmed-desorption (TPD) (Take et al., 1981), FT-IR (Tsyganenko et al., 1975) and direct calorimetry (Cardona-Martinez and Dumesic, 1992). Direct calorimetry is a more reliable approach for quantitative determination of acidic sites of catalysts in comparison with TPD and FT-IR. Measurement of acidity of γ-alumina from high-temperature calorimetry becomes quite active in the recent years (Auroux, 1997). Among several recent researches, for example, Auroux et al. examined energy distribution of surface acid sites of metal oxides including γ-alumina at different series of temperatures and correlated the experimental data very well with a mathematical model (Carniti et al., 1994). They also studied the influence of high temperature pretreatment on the change of acid sites and found a rather complex activity in changes of acid sites from 523 to 1023 K (Auroux, 1997). Dumesic et al. studied the relationship of results from high temperature calorimetry and those from thermogravimetric method. A nice consistence between these methods was shown (Spiewak et al., 1994). The update researches for determination of acid sites of γ-alumina were underwent at rather purified surface. Since the acid sites of γ-alumina are greatly influenced by the surface chemical environment, a real surface at which catalytic reactions usually occur should be quite different from an ideal surface. Thus, the information of acid sites in the real reaction condition are necessary for determination of the role of acidic sites in a reaction. Although it is difficult to reproduce a real surface on a catalyst for a base to probe its acidic sites, the information of a real surface can be approached and assumed by applying appropriate treatment on the catalysts. At aim of this consideration, here a commercial γ-alumina was treated under condition of atmosphere at moderate temperature range. The acidic site distributions of treated alumina were determined by differential NH_3 adsorption heat at 473 K with a special treatment procedure. The change in acidic site distribution of the alumina with active temperature and treatment procedure will be investigated. The adsorbed species of NH_3 at the same treatment procedure from FT-IR and the relationship of changes in acidic sites with a De-NOx reaction will be discussed.

Experimental

A commercial alumina from Nishiokougyo Co. with slight impurity of Na, Fe, and Si was used. X-ray Diffraction (XRD) measurement indicates that its crystal structure is of γ mixining with some χ structure. The N_2 adsorption isotherm was determined by an automatic volumetric method for investigating the pore structure. The dehydration properties of the alumina were determined by measurement of thermogravimetry (TG, Shimadzu TGA-50) and differential scanning calorimetry (DSC, Shimadzu DSA-50). Before measurement of TG and DSC, the sample was dried in a thermostat at 393 K for one night. The measurement of TG and DSC was carried out at a ramp rate of 10 K/min. A commercial α-Al_2O_3 was used as a reference material for measurement of DSC.

The NH_3 differential adsorption heats were determined by a twin-type calorimetry (HAC-450G, Tokyo Richo Co.) at 473 K. Before measurement of NH_3 adsorption heat, sample was treated in the following procedure (procedure A): dried overnight in a thermostat at 393 K, activated in air at 673, 723, 773, and 823 K respectively for 3–4 h, then vacuum-pumped with temperature holden constant for 5–10 min until 1.3 Pa, and at last further evacuated at 473 K below 1 mPa for 2–3 h. A sufficient dehydration condition was made by the following procedure (procedure B): dried overnight in thermostat at 393 K, and then evacuated below 1 mPa at 723 and 823 K respectively for about 4–5 h. A commercial ammonia gas of high purity was used after further purification with freeze-pump-thaw method.

FT-IR measurements of the sample after a same pretreatment using procedure A were carried out with a Shimadzu FT-IR equipment of DR8000 type. Each spectrum was collected at 4 cm^{-1} resolution with 32 scans. About 20 torr of purified NH_3 was introduced into each pretreated sample, stayed for 30 min at 473 K, evacuated at 473, 573, and 673 K each for 10 min. The IR spectra were obtained after each step of adsorption and desorption.

De-NOx activity of the sample was measured using a reactor of steady state. The mixture of 280 ppm NO, 640 ppm C_3H_8, and 10% O_2 balanced by Ar was introduced into a 5 cc stacked alumina having a particle size of 20–30#. The space velocity (SV) of the gas stream was mentained at 18000 h^{-1}. The measurement was carried out at 673 to 823 K. The gas components was analyzed by a NOx analyzer (Shimadzu NOA-305A) and a micro-GC having a column of poraplot (Chrompack CP-2002). 10% of H_2O was also introduced into the gas mixture to investigate the effect of water.

Results and Discussion

Porosity and Dehydration Properties

The N_2 adsorption isotherm of the sample shows a representative type II, having a closed point of desorption loop near $P/P_0 = 0.4$. The BET surface area and average pore width from Dollimore-Heal method of the sample is 350 m^2/g and 4 nm, respectively. Thus, NH_3 molecule with a molecular diameter less than 0.3 nm can adequately probe every acidic sites of this alumina. Figure 1 shows the TG and DSC curves of the sample. The weight loss of the sample until 973 K is around 11%, indicating the hydrophilic property of the sample. In the curve of DSC, a great endothermic peak can be observed around 473 K, indicating that most of adsorbed water can be removed at around 473 K. Besides, there is a slight endothermic peak around 773 K in the DSC curve. This desorbed species is special in comparison with the crystallized alumina, which should have

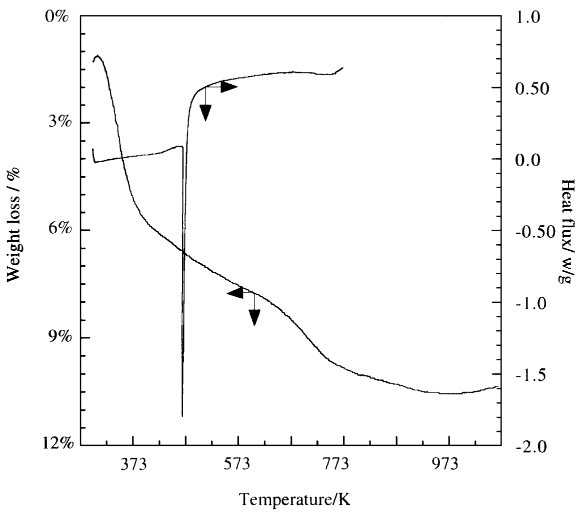

Figure 1. TG and DSA curves of the γ-alumina.

direct relationship with surface acidic sites and may influence the development of acidic sites around these temperatures.

NH_3 Differential Adsorption Heat at 473 K

Figure 2 shows the NH_3 differential adsorption heat (q_d) at 473 K by treatment procedure A. In comparison with pretreatment at 673–823 K, the q_d at 473 K-treatment is much lower, indicating the great shielding effect of reserved water on the surface acidic sites. When the treatment temperature rises, the NH_3 adsorption heat above 130 kJ/mol increases. The q_d values treated at 773 and 823 K agree almost with each other. A much evident difference of q_d between 673- and 823 K-treatment should be ascribed to the shielding effect of the slight amount of second group of adsorbed water on the strong acidic sites, as clearly shown by the DSC curve. On the other hand, the change of q_d below 110 kJ/mol with treatment temperature shows a complex property. Treatment at this temperature range leads to q_d making a round trip: the q_d decreases once a time at 723- and 773 K-treatment, and then recovers to a much enhanced values at 823 K-treatment. Atmospheric activation at this temperature range has no tremendous effects on the amount of total acidic sites above 70 kJ/mol.

Figure 3 shows the q_d change of the sample at treatment procedure B. A complete consistence of q_d at 723 K-treatment with that at 823 K-treatment is obtained. Surprisingly, the total amount of acidic sites increases two times by the operation of sufficient dehydration. Nevertheless, it is interesting to remark that the stronger active sites above 130 kJ/mol is not seriously changed in the two treatment procedures. Thus, slight reservation of water has little effects on the stronger

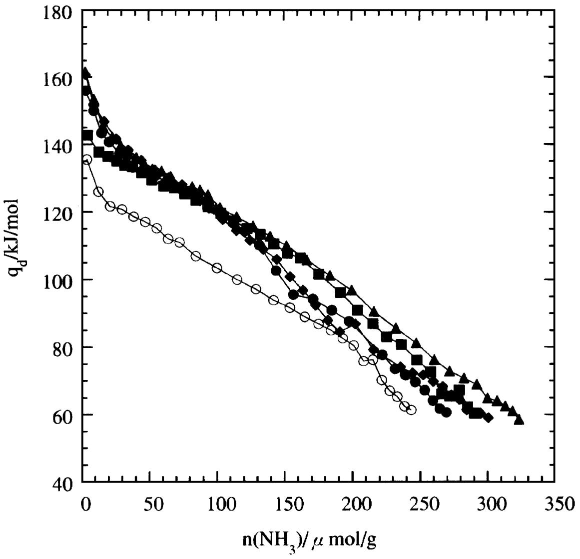

Figure 2. NH_3 differential adsorption heats at different activation temperatures using treatment procedure A. ○, 473 K; ■, 673 K; ●, 723 K; ◆, 773 K; ▲, 823 K.

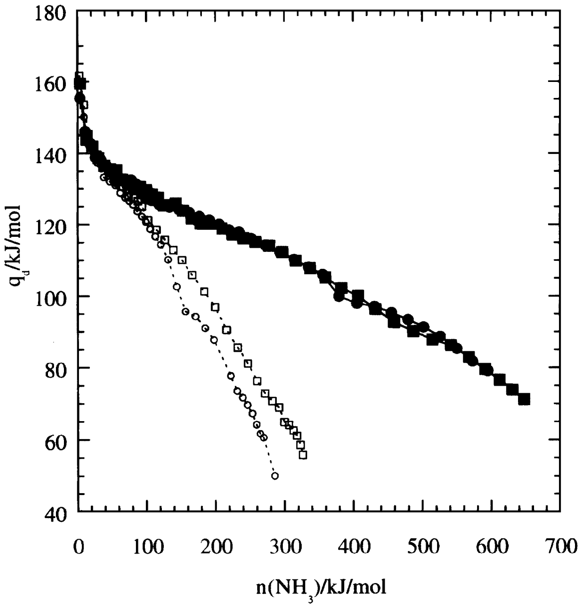

Figure 3. The NH_3 differential adsorption heats at different activation temperature using treatment procedure B. ●, 723 K; ▲, 823 K; ○, 723 K in procedure A; □, 823 K in procedure A.

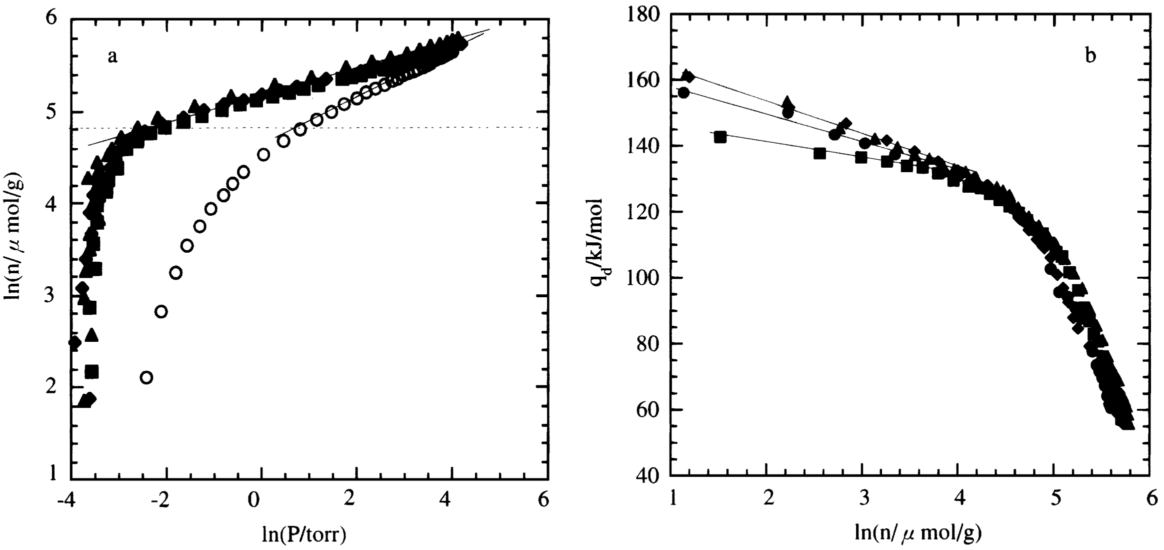

Figure 4. (a) The Freundlich plots of NH_3 adsorption and (b) changes of q_d with logarithm of adsorption amount using treatment procedure A. ○, 473 K; ■, 673 K; ●, 723 K; ◆, 773 K; ▲, 823 K.

acidic sites. The stronger active sites even can be activated at existence of slight water by elevating the activation temperature up to moderate temperature range. The slightly reserved water may exist on the surface of weak active sites and influence in a great deal the development of weak active sites.

Acidic Sites Distribution

Figures 4(a) and (b) show the Freundlich plots of NH_3 adsorption and changes of q_d with logarithm of adsorption amount, respectively after treatment using procedure A. One can observe two branches of good linearity below NH_3 adsorption of 54 μmol/g (or $q_d > 130$ kJ/mol) and beyond NH_3 adsorption of 134 μmol/g (or $q_d < 110$ kJ/mol). Thus, the acidic sites of the γ-alumina can be assumed to be divided into two-dispersed energetic definitions of stronger and weaker acidic sites, either of which has the exponential energetic distribution. In order to confirm this consideration, we obtained an acid sites distribution from the experimental q_d changes with NH_3 adsorption using polynomial approximation and compared with the calculated exponential energetic distribution from NH_3 adsorption isotherm. Figure 5 shows the comparison of the two active site distribution. An excellent correspondence of two approaches is obtained in a prescribed energetic range. Furthermore, we can simply refer the property of binary energetic dispersion by approximation of a two-dispersed Freundlich model. Therefore, irrespective of an evidently continuous q_d change, the acid site distribution of alumina can be classified into two discontinuous energy patches with a transition field. Generally speaking, the strong and weak acidic sites of the γ-alumina are the Lewis and Brönsted sites, respectively. Take et al. have shown the difference in intensity of Lewis and Brönsted acidity using TPD and calorimetry, when a probe molecule is NH_3 (Take et al., 1981). The reason for the difference is ascribed to a greater rotational entropy freedom of NH_4^+ species. This also may give a reason to be able to express the difference of the two kinds of acidic sites from a complete q_d change containing both contributions.

NH_3 Adsorbed Species from FT-IR

FT-IR is a powerful method to figure out the sort of adsorbed species which cannot be distinguished by calorimetry. The treatment procedure A is of special. The NH_3 adsorbed species consequent on different acidic sorts need to be elucidated from FT-IR measurement. NH_3 adsorbed species on the γ-alumina from FT-IR has been studied in detail by Tsyganenko (Tsyganenko et al., 1975). Knozinger reviewed the NH_3 adsorbed species from FT-IR (Knozinger, 1976). The four kinds of adsorbed species were reported, that is, the Lewis acidic site formed by bonding with

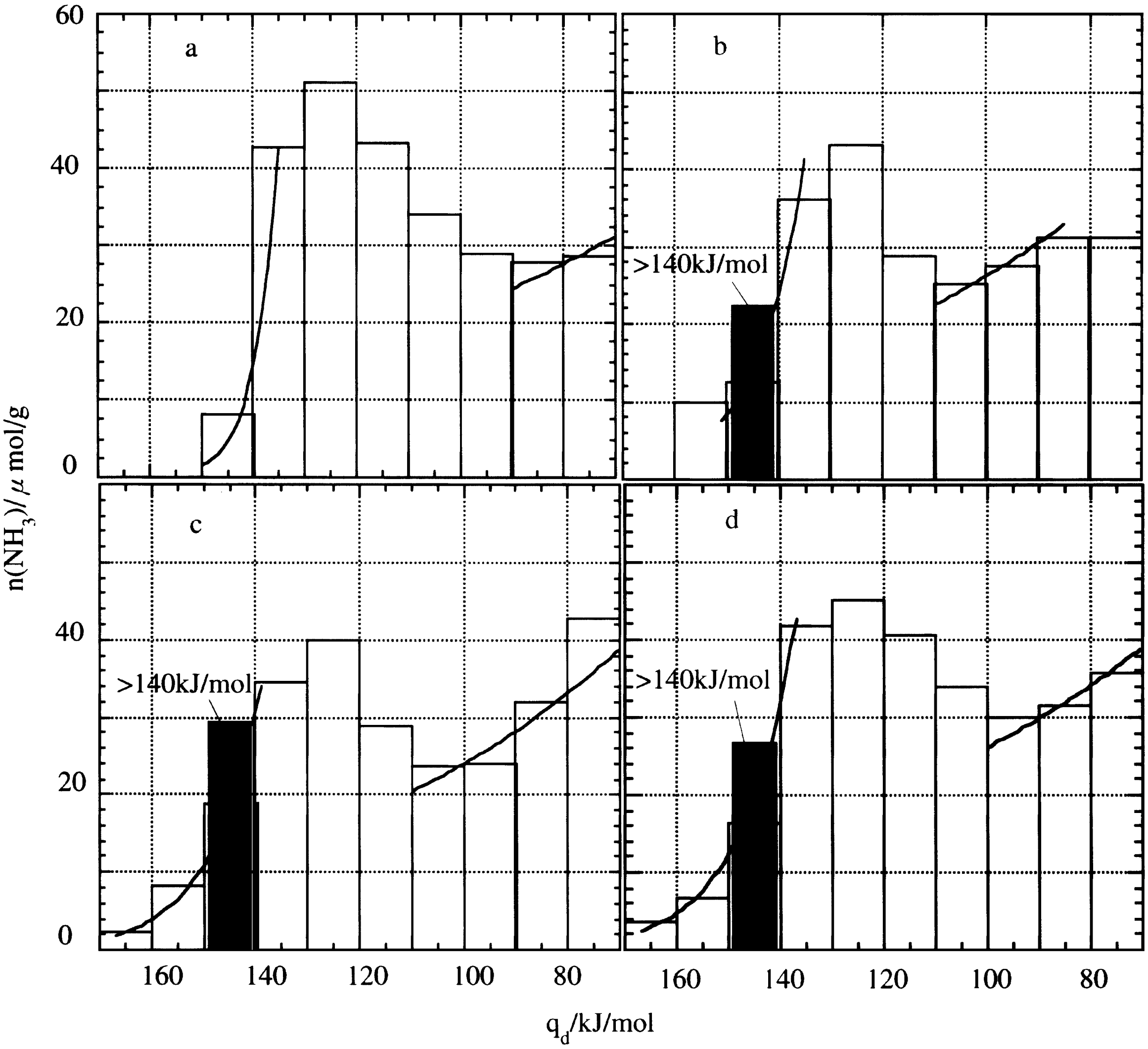

Figure 5. Apparent NH_3 adsorption site distribution at various activation temperatures after treatment using procedure A. (a) 673 K; (b) 723 K; (c) 773 K; (d) 823 K; the solid lines are from the energy distribution function by Freundlich equation.

a surface site of an electron donor, an NH_4^+ species formed by accepting a proton from the surface Brönsted acid site, a NH_2 species due to NH_3 dissociation adsorption, and the hydrogen-bonding adsorbed species. The position of all the IR absorption bands from the different researchers are not exactly the same perhaps due to slight change in chemical environment by using the different sample source or different sample treatment procedure. Table 1 reviews the main results on the classification of NH_3 adsorbed species.

Figure 6 shows the surface species of the alumina after treatment using procedure A. Appearance of surface OH— species around 3500–3900 cm^{-1} and disappearance of carbon-containing species at 1462 cm^{-1} and 1583 cm^{-1} due to the Na impurities beyond 673 K-treatment are detectable. The four of five kinds of surface —OH species ascribed by Busca (Morterra and Magnacca, 1996) are distinct after treatment beyond 673 K.

Figure 7 shows the changes of deformation modes of NH_3 molecules adsorbed on the surface of alumina treated in procedure A. When the alumina is equilibrated with gaseous NH_3, explicit Brönsted acidic species at 1700, 1481, and 1380 cm^{-1} are observable at 673–823 K-treatment. The peaks of these species decrease and almost disappear after desorption at 473 K.

Table 1. IR band position of deformation modes of NH_3 adsorbed on γ-Al_2O_3.

Frequency (cm^{-1})			Adsorbed species	Reference
	ν_{as}	ν_s		
1628		950	NH_3 gas	
		1100	$OH\cdots NH_3$	
1620		1280–1240	$\leftarrow NH_2H\cdots O$ or $\leftarrow NH_3$	(Tsyganenko, 1975)
	1560		NH_2	
	1510			
	1460		NH_4^+	
1620		1260–1285	$\leftarrow NH_3$	
	1390–1484		NH_4^+	(Knozinger, 1976)
	1510		NH_2	
	1560			
1700	1485		NH_4^+	(Shen et al., 1994)
	1395			
1620		1245	$\leftarrow NH_3$	

The Lewis acidic species at 1620 cm^{-1} and a broad peak or multi-peak groups at 1220–1280 cm^{-1} of the another reported range of Lewis species also appear after NH_3 adsorption. The intensity of Lewis species at 1620 cm^{-1} is much weakened and the broad and multi-peak groups at 1220–1280 cm^{-1} are clearly separated into three peaks at 1220, 1250, and 1290 cm^{-1} after desorption at 473 K. Since the equilibrium NH_3 adsorption at 20 torr is correspondent with the NH_3 adsorption on acidic sites with energy more than 70 kJ/mol, the weaker acidic sites of the alumina should be ascribed to the Brönsted property, and the stronger acidic sites to the Lewis property.

Figure 8 shows the changes of reserved NH_3 species at 773- and 823 K-pretreatment with further elevating temperature. Both the species at 1620 and 1220 cm^{-1} disappear after evacuation at 573 K. However, the species at 1250 and 1290 cm^{-1} remain on the surface. These two species should represent two NH_3 species adsorbed on two different Lewis acidic sites. Reservation of these Lewis acidic species even at a rather

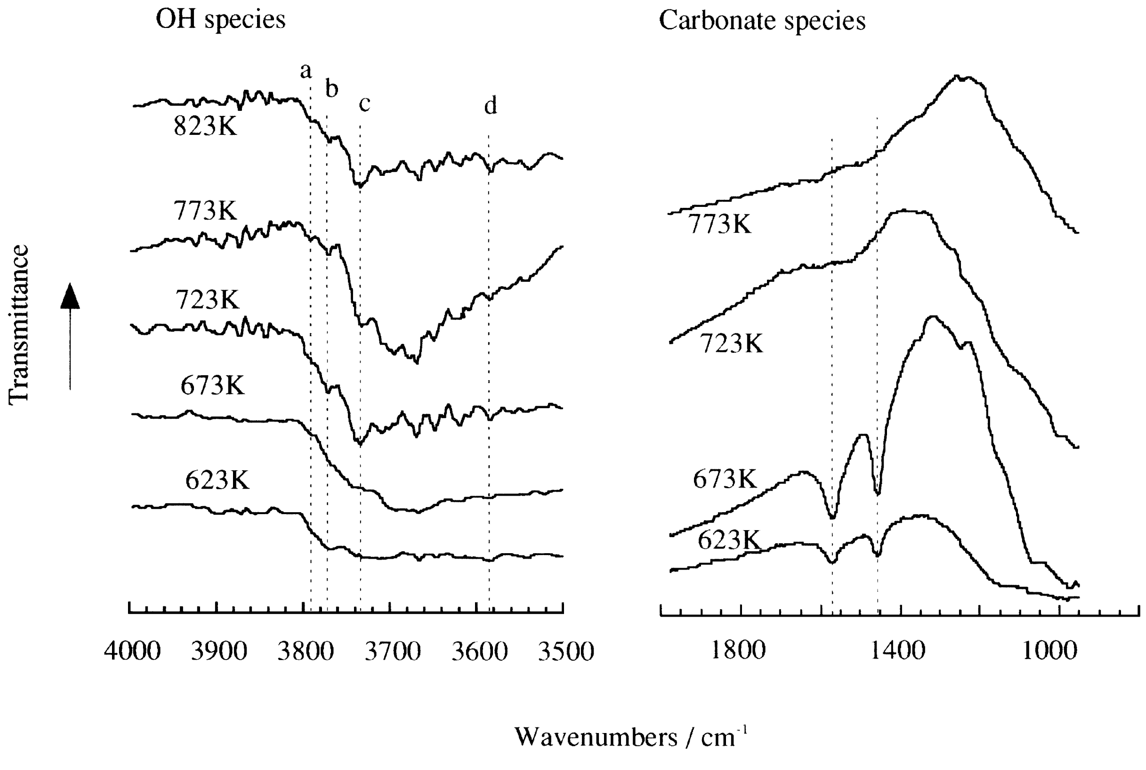

Figure 6. Development of surface species with activation temperatures after treatment using procedure A. (a) Al(IV)—OH; (b) □—O—Al(IV)—OH; (c) □—O—Al(VI)—OH or Al(VI)—OH; (d) $(Al)_3$—OH by Busca's definition where □ represents the defective site.

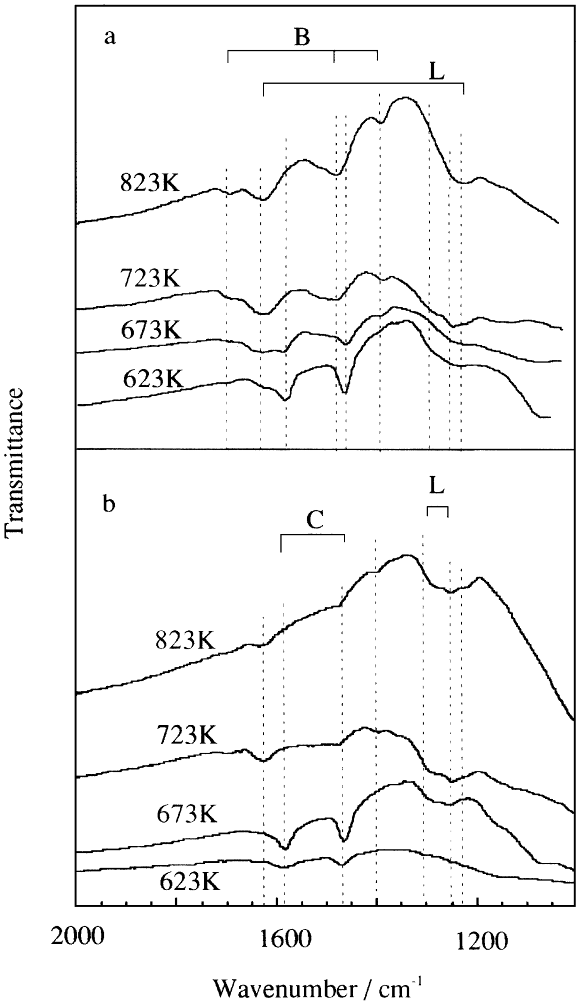

Figure 7. Changes of acidic sites with NH_3 adsorption at 473 K at various activation temperature after treatment of procedure A. (a) after adsorption for 30 min in 20 torr NH_3; (b) after desorption for 10 min.

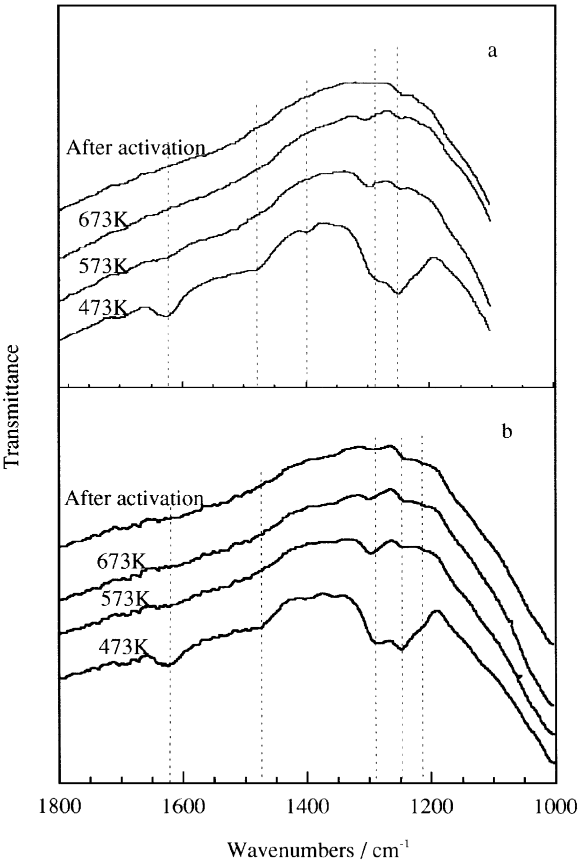

Figure 8. Changes of acidic site with desorption temperature. (a) 773 K-; (b) 823 K-activation after treatment using procedure A.

elevated temperature gives an evidence of a rather sharp energetic distribution of Lewis acidic sites, as already shown by acid site distribution. Thus, FT-IR also confirms that the Lewis acidic sites of the alumina are much evidently energetically distributable. Furthermore, interaction of NH_3 with the surface metal ion of a stronger electron donor should result in a species of higher wavenumbers. It is apparent that the relative intensity of peak at 1290 cm^{-1} over that at 1250 cm^{-1} is greater at 823 K-treatment than at 773 K-treatment. Thus, 823 K-treatment leads to formation of greater amounts of stronger Lewis acidic sites although this is not quite differentiable from change of q_d. Besides, Tsyganenko mentioned a scheme that coordinated NH_3 molecules can interact with oxygen of surface hydroxyl species. If this consideration is true, the interaction may lead to slight lowing of position of ν_s of the coordinated NH_3 molecules. As the position of the species at 1290 cm^{-1} shifts to the higher wavelength number at higher evacuation temperature, this species may strongly have relationship with the surface hydroxyl groups which still remain on the surface after treatment using procedure A.

On the Relationship of Acidic Sites Distribution and De-NOx Activity

Figure 9 shows the changes of conversions of NO and C_3H_8 at various reaction temperatures. The alumina has a greater conversion activity for C_3H_8 than for NO. The NO conversion shows a peak around 773 K. Figure 10 shows the changes of various acidic sites

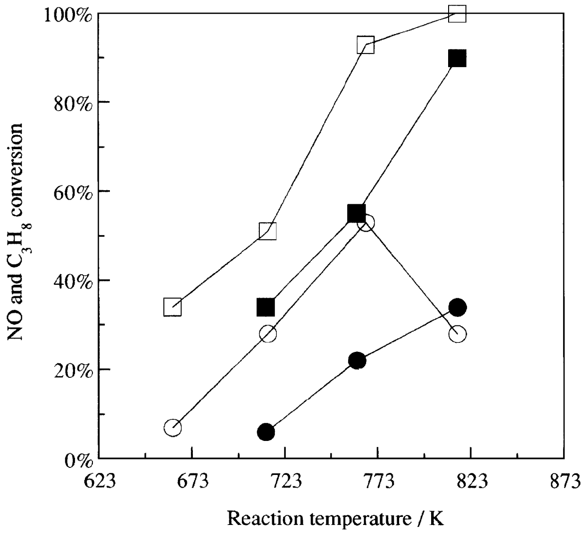

Figure 9. De-NOx activity of the γ-alumina in reaction of 640 ppm $C_3H_8 + 280$ ppm NO+ 10% O_2 balanced by Ar with SV = 18000 h^{-1}. ○ and ●, NO without water and with 10% water; □ and ■, C_3H_8 without water and with 10% water respectively.

with activation temperature. Apparently, the Lewis acid sites with energy more than 130 kJ/mol increases with the activation temperature. However, the Brönsted acid sites with energy between 70 and 90 kJ/mol shows a peak at 773 K although the changing amount is small. Thus, it seems as if there is an intuitive consistency between changes of acid sites and those of conversions of C_3H_8 and NO. Generally, the selective De-NOx reaction using hydrocarbons as reductants can be considered to progress in two parallel reactions:

$$C_3H_8 + O_2 \rightarrow CO_2 + H_2O \qquad (1)$$

$$C_3H_8 + NO + O_2 \rightarrow N_2 + CO_2 + H_2O \qquad (2)$$

Equation (2) is a by-reaction of C_3H_8 burning, e.g., Eq. (1). N_2 is formed through formation of intermediate products such as —CNO. According to the Arrhenius equation, the mountain shape of NO conversion may be owing to the consumption of C_3H_8 by Eq. (1) if the activation energy for Eq. (1) is greater than that of Eq. (2). However, measurement of acid site distribution

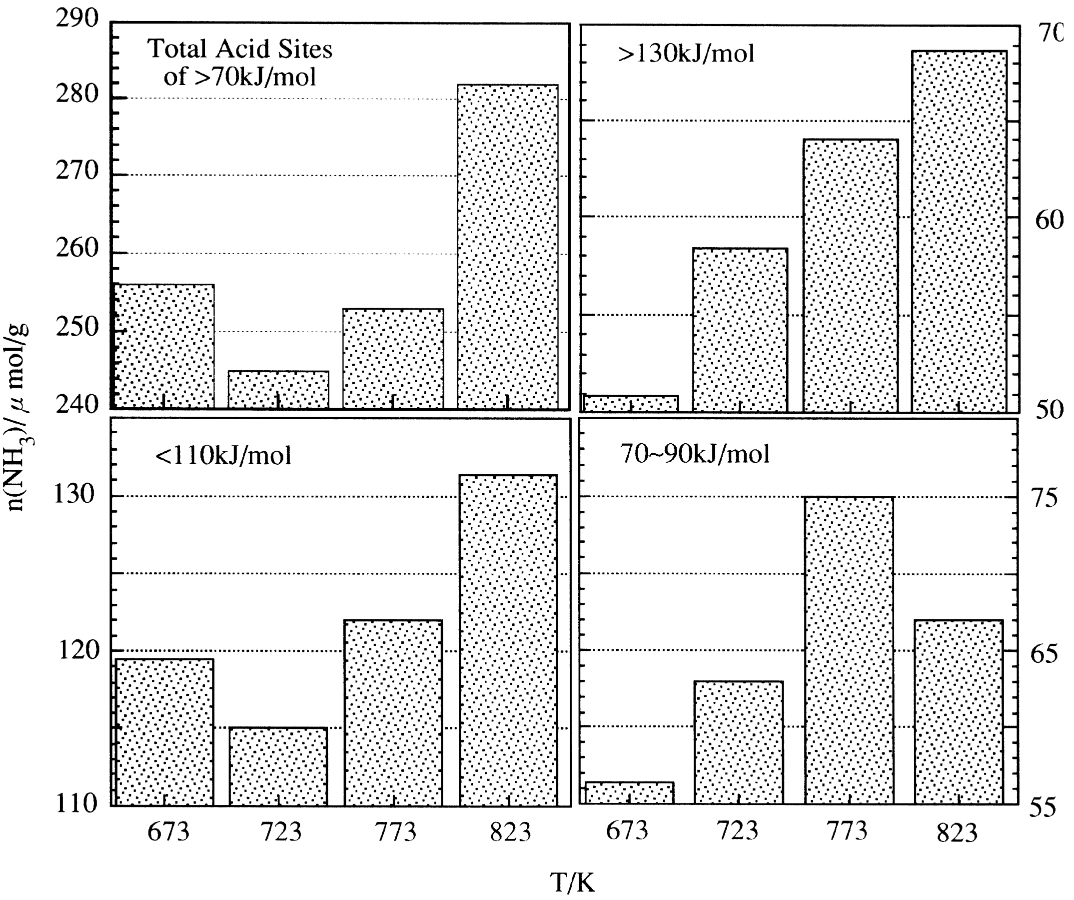

Figure 10. Dependency of apparent NH_3 adsorption sites on activation temperature after treatment using procedure A.

indicates a distinct change in acidic sites even in the moderate temperature region when the surface of the alumina is not clean. Formation of surface intermediates from which water is also produced by both Eqs. (1) and (2) may lead to a real reaction surface not clean. The profile of acidic sites of the real reaction surface are greatly changeable, as can be assumed from the result by treatment using procedure A. The change of acid sites may influence the De-NOx activity in ability to form an intermediate surface product. In Fig. 9, conversions of C_3H_8 and NO at existence of 10% H_2O is also shown. The conversions of both C_3H_8 and NO are decreased by addition of water. However, water has a greater negative effect on NO conversion since recovery of C_3H_8 conversion is much faster than that of NO conversion. This again indicates a possibility of relationship of Brönsted acid sites with NO conversion since Brönsted acid sites are greatly influenced by the surface adsorbed water. However, probing acid sites by procedure A does not always represent the in-situ surface states on which a De-NOx reaction undergoes. Further researches are being undergone for obtaining a more reliable conclusion.

Conclusion

Measurement of NH_3 differential adsorption heat shows that γ-alumina has a binary acidic site distribution of Lewis and Brönsted, both of which are of the exponential function. Lewis acidic sites have a much sharper distribution than that of Brönsted acidic sites. Lewis acidic sites can be easily activated in air even at moderate temperature range. Degree of dehydration has a great influence on the development of Brönsted acidic sites of a hydrophilic alumina. The increase of stronger Lewis acidic sites and its interaction with surface —OH species are confirmed from FT-IR. Changes of acidic sites distribution of the alumina may be possible to influence the De-NOx activity by influencing formation of the surface intermediates.

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References

Auroux, A., “Acidic Characterization by Microcalorimetry and Relationship with Reactivity,” *Topics in Catal.*, **4**, 71–89 (1997).

Cardona-Martinez, N. and J.A. Dumesic, “Application of Adsorption Microcalorimetry to the Study of Heterogeneous Catalysis,” *Adv. Catal.*, **38**, 149–244 (1992).

Carniti, P., A. Gervasini, and A. Auroux, “Energy Distribution of Surface Acid Sites of Metal Oxides,” *J. Catal.*, **150**, 274–283 (1994).

Hamada, H., “Selective Reduction of NO by Hydrocarbons and Oxygenated Hydrocarbons over Metal Oxide Catalysts,” *Catal. Today*, **22**, 21–40 (1994).

Knozinger, H., “Specific Poisoning and Characterization of Catalytically Active Oxide Surfaces,” *Adv. Catal.*, **25**, 184–271 (1976).

Morterra, C. and G. Magnacca, “A Case Study: Surface Chemistry and Surface Structure of Catalytic Aluminas, as Studied by Vibrational Spectroscopy of Adsorbed Species,” *Catal. Today*, **27**, 497–532 (1996).

Shen, J.S., R.D. Cortright, Y. Chen, and J.A. Dumesic, “Microcalorimetric and Infrared Spectroscopic Studies of γ-Al_2O_3 Modified by Basic Metal Oxides,” *J. Phys. Chem.*, **98**, 8067–8073 (1994).

Spiewak, B.E., B.E. Handy, S.B. Sharma, and J.A. Dumesic, “Microcalorimetric Studies of Ammonia Adsorption on γ-Al_2O_3, HNa-Y Zeolite, and H-Mordenite,” *Catal. Letters*, **23**, 207–213 (1994).

Take, J., H. Matsumoto, S. Okada, H. Yamaguchi, K. Tsutsumi, H. Takahashi, and Y. Yoneda, “Comparison of IR Method and Calorimetric Method in Determination of Acid Sites on Solid Surfaces,” *Shokubai*, **23**, 344–346 (1981).

Tsyganenko, A.A., D.V. Pozdnyakov, and V.N. Filimpnpv, “Infrared Study of Surface Species Arising from Ammonia Adsorption on Oxide Surfaces,” *J. Mol. Structure*, **29**, 299–318 (1975).