Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

Investigation of NH_3 and NH_4^+ adsorbed on ZSM-5 Zeolites by Near and Middle Infrared Spectroscopy

Masato Takeuchi*, Tatsuya Tsukamoto, Atsushi Kondo, Masaya Matsuoka

[1]*Department of Applied Chemistry, Graduate School of Engineering*

Osaka Prefecture University

1-1, Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

*Corresponding author: Tel.: +81-72-254-9287; Fax: +81-72-254-9910

E-mail address: masato-t@chem.osakafu-u.ac.jp

Abstract

The adsorption states of NH_3 molecules and NH_4^+ ions on various sites, such as hydroxyl, H^+ and Na^+, of ZSM-5 zeolites with different SiO_2/Al_2O_3 ratios were investigated by near and middle infrared spectroscopy. For Na^+-type and siliceous ZSM-5 zeolites, only hydrogen-bonded NH_3 clusters were observed at 5021 and 4519 cm^{-1}, respectively, due to the lack of Brönsted acid sites. The NH_3 molecules interacting with the hydroxyl groups easily desorbed at room temperature (r.t.), while the molecules interacting with the Na^+ sites desorbed at 473 K. For the H^+-type ZSM-5, when NH_3 adsorption amount was small, the NH_4^+ formed on the H^+ sites as well as the NH_3 adsorbed on the H^+ (or possibly Al^{3+}) sites were independently observed at 4846 and 5044 cm^{-1}, respectively. As the amount of NH_3 adsorption increased, the NH_4^+ stabilized by the 2nd layer of NH_3 molecules as well as the hydrogen-bonded NH_3 clusters were observed at 4782 and 5017 cm^{-1}, respectively. The hydrogen-bonded NH_3 molecules desorbed at lower than 423 K but the NH_4^+ ions decomposed at 573 - 623 K to form Brönsted acid sites.

Keywords: NIR spectroscopy, adsorption of NH_3 and NH_4^+, Brönsted acid sites, ZSM-5 zeolite

Introduction

Surface acidity of solid acid catalysts has been widely evaluated by NH_3-TPD [1-3] and FT-IR measurements of the NH_3 [4-10] or pyridine [11-14] adsorbed on the surfaces. In recent years, the combination of IR mass spectroscopy and NH_3-TPD is becoming one of the most powerful techniques to clarify the acid sites of catalyst surfaces [15, 16]. In fact, all of the 4 vibration modes of a NH_3 molecule (symmetric stretching (ν_1): 3337 cm^{-1}, symmetric bending (ν_2): 950 cm^{-1}, asymmetric stretching (doubly degenerated) (ν_3): 3444 cm^{-1}, bending (doubly degenerated) (ν_4): 1627 cm^{-1}) are IR active [1, 4, 8-10]. On the other hand, although NH_4^+ also shows 4 vibration modes (symmetric stretching (ν_1): 3033 cm^{-1}, bending (doubly degenerated) (ν_2): 1685 cm^{-1}, asymmetric stretching (triply degenerated) (ν_3): 3134 cm^{-1}, bending (triply degenerated) (ν_4): 1397 cm^{-1}), only its ν_3 and ν_4 modes are IR active [1, 4, 7-8, 16]. However, when NH_3 molecules and NH_4^+ ions coexist on the catalyst surface, it is difficult to distinguish each stretching vibration mode of NH_3 and NH_4^+. For this reason, the ν_2 mode of NH_3 or ν_4 mode of NH_4^+ are generally chosen for MIR measurements. However, the ν_2 mode of NH_3 is sometimes hidden by the large absorption of the oxide lattice at 1100 - 1000 cm^{-1}. Moreover, many of the MIR absorptions of NH_3 and NH_4^+ overlap with those of the H_2O molecule.

On the other hand, near infrared (NIR) spectroscopy was first applied to measure the water content of grains in 1960s [17]. Recently, this technique has been widely applied in many fields such as mineralogy, food chemistry, pharmacology, and agriculture, etc [18-20]. In general, the absorption coefficients of the overtone and combination bands in the NIR region are about 10^{-3} times those of the fundamental vibrations in the MIR region. This advantage of NIR spectroscopy makes it possible to analyze various samples without dilution. For example, NH_3 aqueous solution shows NIR absorptions due to H_2O (5200 cm^{-1}: $\nu_{OH} + \delta$) and NH_3 (5020 cm^{-1}: $\nu_3 + \nu_4$, 4520 cm^{-1}: $\nu_2 + \nu_3$) (shown in Fig. S1 in supporting information).

Similarly, NH_4Cl aqueous solution shows NIR absorptions due to H_2O (5200 cm^{-1}: $\nu_{OH} + \delta$) and NH_4^+ (4660 cm^{-1}: $\nu_3 + \nu_4$) (shown in Fig. S2 in supporting information).

In this study, NH_3 molecules and NH_4^+ ions adsorbed on ZSM-5 zeolites with different SiO_2/Al_2O_3 ratios were investigated by NIR and MIR infrared spectroscopies. Especially, the differences between: (i) the adsorption of NH_3 on the silanol groups, Na^+ and H^+ sites; and (ii) formation of NH_4^+ by NH_3 adsorption on the H^+ sites have been discussed in detail. Furthermore, the stabilization of NH_4^+ by NH_3 clusters within the zeolite cavity was confirmed by NIR spectroscopy.

Experimental

NH_4/ZSM-5 (SiO_2/Al_2O_3 = 39, Na_2O = < 0.03 wt%), Na/ZSM-5 (SiO_2/Al_2O_3 = 23.8, Na_2O = 4.0 wt%) and H/ZSM-5 (SiO_2/Al_2O_3 = 1500, Na_2O = < 0.01 wt%) zeolites were purchased from Tosoh Co., Ltd (Tokyo, Japan). H/ZSM-5 (SiO_2/Al_2O_3 = 39) was prepared by calcination of NH_4/ZSM-5 at 723 K. The H/ZSM-5(39) was confirmed not to desorb NH_3 gas by TPD measurement.

Zeolite powder of ca. 80 - 130 mg was pressed into pellet form and placed in an in-situ FT-IR cell equipped with CaF_2 windows. Prior to NIR measurements, the zeolite samples were degassed at 723 K for 1.5 h, treated in O_2 (ca. 3 kPa) at 723 K for 1.5 h, and then degassed at 373 K for 1 h. Given amounts of NH_3 vapor were admitted into the cell, step by step, and the NIR absorption spectra of the NH_3 and NH_4^+ adsorbed on the zeolites were then recorded in diffuse reflectance mode by a FT-IR spectrometer (JASCO, FT/IR-660Plus, TGS detector, resolution: 4 cm^{-1}). At the same time, the MIR absorption spectra were recorded in the range of 4000 - 3000 cm^{-1}. The baseline was calibrated with desiccated KBr powder in the diffuse reflectance mode.

Results and discussion

Figure 1 shows the NIR absorption spectra of the thermal decomposition process for the NH_4/ZSM-5(39) into the H/ZSM-5(39). For the NH_4/ZSM-5(39) before pretreatment (1a), three absorptions were observed at 5260, 5006 and around 4700 cm^{-1}. The absorption at 5260 cm^{-1} can be assigned to a ($\nu_{OH} + \delta$) combination band of the H_2O molecule within the zeolite cavities [6, 19]. Interestingly, although large amounts of H_2O molecules were adsorbed on the NH_4/ZSM-5(39), mainly less hydrogen-bonded H_2O molecules, almost in a gas-like phase [19, 21-22], were observed. This is why the pore size of the ZSM-5 zeolite is not large enough to form large hydrogen bond networks of H_2O clusters. The broad absorptions at 5006 and around 4700 cm^{-1} can be assigned to the ($\nu_3 + \nu_4$) combination band of the NH_3 molecules [23-27] and ($\nu_2 + \nu_3$) combination band of the NH_4^+ ions [28], respectively. When the NH_4/ZSM-5(39) was degassed at r.t., the absorption at 5260 cm^{-1} decreased and the absorptions of NH_3 (5046 cm^{-1}) and NH_4^+ (4700 cm^{-1}) were still unclear (1b). When the NH_4/ZSM-5(39) was degassed at 373 K, the absorption at 5260 cm^{-1} completely disappeared and two absorptions were observed at 5035 and 4848 cm^{-1} (1c). This means the H_2O molecules interacted with the NH_3 or NH_4^+ desorbed at 373 K and the latter two absorptions can be assigned to the isolated (or less hydrogen-bonded) NH_3 and NH_4^+ on the zeolite surface. As the degassing temperature increased up to 573 K, the isolated NH_3 and NH_4^+ decreased and two absorptions were observed at 4661 and 4375 cm^{-1} (1e). The peaks at 4661 and 4375 cm^{-1} can be assigned to the hydroxyl groups close to Al^{3+} (Brönsted acid sites) and the hydrogen-bonded silanol groups. As the degassing temperature increased up to 673 - 773 K, the isolated NH_3 and NH_4^+ completely disappeared and the absorption intensity at 4661 cm^{-1} increased (1g). The conversion process from NH_4^+-type

ZSM-5 to H^+-type ZSM-5 could be directly observed by NIR measurements.

Figure S3 shows the MIR absorption spectra of the NH_4/ZSM-5(39) obtained simultaneously with the NIR spectra in Fig. 1. The NH_4/ZSM-5(39) before pretreatment showed only a broad NIR absorption spectrum due to the large amounts of H_2O and NH_4^+ adsorbed on the surface (S3a). As the H_2O molecules desorbed, three absorptions were observed at 3740, 3374 and 3330 cm^{-1} (S3b - S3c). The peak at 3740 cm^{-1} is generally assigned to an isolated silanol group [4, 6-7, 9-10]. However, the NIR absorption at 4375 cm^{-1} clearly corresponded to the hydrogen bonded silanol groups [19, 21-22], the details of which will be discussed in Fig. S6. The absorption at 3300 - 3400 cm^{-1} can be assigned to the NH stretching vibration of NH_3 [4, 8-10]. No information about the NH_4^+ was obtained in the MIR region. As the NH_3 and NH_4^+ desorbed, two absorptions due to the silanol (3740 cm^{-1}) and Brönsted acid sites (3610 cm^{-1}) were clearly observed.

Figure 2 shows the NIR absorption spectra of the NH_3 adsorption (A) and desorption (B) processes on Na/ZSM-5(23.8). For the Na^+-type zeolite after pretreatment at 723 K (2a), a small peak was observed at 4569 cm^{-1}. This peak can be assigned to a ($\nu_{OH} + \delta$) combination band of the isolated hydroxyl groups [19, 21-22]. As the NH_3 adsorption amount increased (2b - 2e), the absorption intensity at 5021 and 4519 cm^{-1} monotonically increased. These absorption peaks can be assigned to the ($\nu_3 + \nu_4$) and ($\nu_2 + \nu_3$) combination bands of the hydrogen-bonded NH_3 molecules [23-27]. Even in the initial step of NH_3 adsorption, the isolated NH_3 molecule was not observed, suggesting the formation of uniform NH_3 clusters within the zeolite cavities. When the Na/ZSM-5(23.8) adsorbed with saturated amounts of NH_3 was degassed at r.t. to 423 K (2f - 2h), the absorption peaks due to the NH_3 molecules monotonically decreased. Then, as the degassing temperature increased up to 473 K, all of the NH_3 molecules were desorbed.

Figure S4 shows the MIR absorption spectra of the Na/ZSM-5(23.8) obtained simultaneously with the NIR spectra in Fig. 2. The Na/ZSM-5(23.8) after pretreatment showed a sharp peak at 3740 cm^{-1} (S4a). Along with the NIR absorption at 4569 cm^{-1}, the peak is obviously related to the isolated silanol groups [19, 21-22]. However, the ν_{OH} at 3740 cm^{-1} observed for the NH_4/ZSM-5(39) must be assigned to the hydrogen-bonded silanol groups in conjunction with the NIR measurements. As the amount of NH_3 adsorption increased, the NH stretching vibration modes of the NH_3 molecule were observed at 3250 - 3400 cm^{-1} (S4b - S4e). The desorption behavior of NH_3 closely corresponded with the results of NIR measurements. The NH_3 adsorption model for the Na^+-type ZSM-5 is proposed in Fig. 3. NH_3 molecules mainly adsorb on the Na^+ sites and isolated silanol groups to form a uniform NH_3 cluster within the zeolite cavity. The hydrogen-bonded NH_3 molecules with NH_3---Na^+ and silanol desorbed at r.t. but the NH_3 molecules directly interacting with Na^+ desorbed at 473 K.

Figure 4 shows the NIR absorption spectra of the NH_3 adsorption (A) and desorption (B) processes on the H/ZSM-5(1500). After pretreatment at 723 K (4a), the H/ZSM-5(1500) showed two absorption bands at 4556 and 4434 cm^{-1}, which can be assigned to the isolated and hydrogen-bonded hydroxyl groups, respectively [19]. As the NH_3 adsorption amount increased (4b - 4i), the absorption intensity at 5017 and 4505 cm^{-1} monotonically increased. Since Brönsted acid sites hardly exist on the H/ZSM-5(1500), the NH_3 molecules mainly interacted with the surface hydroxyl groups to form NH_3 clusters. When the H/ZSM-5(1500) adsorbed with saturated amounts of NH_3 was degassed at r.t. (4j - 4o), the NIR absorption due to the NH_3 molecules easily disappeared, suggesting a very weak interaction between the NH_3 molecules and the hydroxyl groups.

Figure S5 shows the MIR absorption spectra of the H/ZSM-5(1500) obtained simultaneously with the NIR spectra in Fig. 4. The H/ZSM-5(1500) after pretreatment showed two sharp peaks at 3725 and 3698 cm^{-1} (S5a) which could be assigned to the isolated and hydrogen-bonded silanol groups, respectively [4, 6-7, 9-10]. Each MIR absorption was closely related to the NIR absorption at 4556 and 4434 cm^{-1} [19]. As the NH_3 adsorption amount increased, the absorption due to the hydrogen-bonded silanol groups largely decreased, followed by the isolated silanol groups. However, absorption due to the NH_3 molecules was not clearly observed in the MIR region. Since the NH_3 molecules easily desorbed at r.t., the weak interaction between the NH_3 molecules and silanol groups was also confirmed by MIR measurements. The NH_3 adsorption model on the silica rich-type ZSM-5 is proposed in Fig. 5. In the initial adsorption step, NH_3 molecules adsorb onto the hydrogen-bonded silanol and then onto the isolated ones to form a uniform NH_3 cluster within the zeolite cavity.

Figure 6 shows the NIR absorption spectra of the NH_3 adsorption (A) and desorption (B) processes on H/ZSM-5(39). When the H/ZSM-5(39) was pretreated at 723 K (6a), absorption due to the hydroxyl groups (Brönsted acid sites) was clearly observed at 4661 cm^{-1}. In the initial stage of NH_3 adsorption (6b - 6d), the ($\nu_3 + \nu_4$) and ($\nu_2 + \nu_3$) combination bands of the NH_3 molecules could be observed at 5044 and 4559 cm^{-1}. These can be assigned to an isolated NH_3 molecule directly interacting with the H^+ site or possibly Al^{3+} sites (Lewis acid sites). After the absorption intensities at 5044 and 4846 cm^{-1} leveled off, two absorptions which could be assigned to the hydrogen-bonded NH_3 clusters were newly observed at 5017 and 4846 cm^{-1} (6e - 6j). At the same time as the molecularly adsorbed NH_3 was observed, the ($\nu_2 + \nu_3$) combination band of a NH_4^+ ion could be observed at 4846 cm^{-1} and the absorption due to the Brönsted acid sites at 4661 cm^{-1} decreased (6b - 6h). These results clearly indicate the formation of NH_4^+ by NH_3 adsorption on the H^+ site. Interestingly, as the NH_3 adsorption amount increased further, the ($\nu_2 + \nu_3$) combination band of NH_4^+ shifted to 4782 cm^{-1} (6i - 6j), suggesting stabilization of the NH_4^+ ions by 2nd layer adsorption of the NH_3 molecules. When H/ZSM-5(39) adsorbed with saturated amounts of NH_3 was degassed at r.t., the NH_3 molecules interacting with NH_4^+ (4782 cm^{-1}) easily desorbed (6k). As the degassing temperatures increased up to 423 K, the hydrogen-bonded NH_3 molecules (5017 cm^{-1}) desorbed and isolated NH_3 molecules (5044 cm^{-1}) were left on the H/ZSM-5(39) (6l - 6m). As the degassing temperatures increased up to 473 - 523 K, absorption due to the Brönsted acid sites was observed again at 4661 cm^{-1} (6n - 6o). When H/ZSM-5(39) was degassed at 573 K, the absorptions due to NH_3 (5044 cm^{-1}) and NH_4^+ (4846 cm^{-1}) disappeared and the absorption due to the Brönsted acid sites completely recovered (6p).

Figure S6 shows the MIR absorption spectra of H/ZSM-5(39) obtained simultaneously with the NIR spectra in Fig. 6. After pretreatment at 723 K, H/ZSM-5(39) showed two peaks at 3740 and 3612 cm^{-1} (S6a), which can be assigned to the silanol and hydroxyl close to the Al^{3+} sites (Brönsted acid sites), respectively [4, 6-7, 9-10]. However, since the NIR absorption due to silanol was observed at 4375 cm^{-1}, the ν_{OH} at 3740 cm^{-1} should be assigned to the silanol groups which may interact with the hydroxyl of the Brönsted acid sites. As the NH_3 adsorption amount increased, absorption due to the Brönsted acid sites largely decreased, followed by the silanol groups. MIR absorption due to the NH_3 molecules was also not clearly observed. When H/ZSM-5(39) adsorbed with saturated amounts of NH_3 was degassed at temperatures higher than 373 K, MIR absorptions due to the Brönsted acid sites and silanol groups recovered (S6m - S6p), corresponding to the conversion of NH_4^+ into the H^+ sites. The NH_3 adsorption model on the H^+-type ZSM-5 is summarized in Fig. 7. It is notable that NIR investigations make it possible to directly observe the formation of NH_4^+ by NH_3 adsorption on the H^+ sites of the zeolite as well as multi-layer adsorption of the NH_3 molecules.

Conclusions

NH_3 molecules and/or NH_4^+ ions adsorbed on various ZSM-5 zeolites were successfully investigated by NIR and MIR spectroscopies. For the NH_4^+-type ZSM-5 before pretreatment, hydrated NH_3 and NH_4^+ as well as less hydrogen-bonded H_2O molecules were observed. As the degassing temperatures increased up to 673-773 K, isolated NH_3 and NH_4^+ were desorbed and the Brönsted acid sites were clearly observed. For the Na^+-type and siliceous ZSM-5, only hydrogen-bonded NH_3 clusters were observed since Brönsted acid sites do not exist on their surfaces. However, the NH_3 molecules interacting with the silanol groups easily desorbed at r.t., while the molecules interacting with the Na^+ sites desorbed at 473 K. For the H^+-type ZSM-5, the formation of NH_4^+ by NH_3 adsorption on the H^+ sites as well as isolated NH_3 molecules, which may interact with the H^+ or Al^{3+} sites, were successfully observed simultaneously. As the amount of NH_3 adsorption increased further, the NH_4^+ stabilized by the 2nd layer of NH_3 molecules as well as hydrogen-bonded NH_3 clusters were formed within the zeolite cavities.

Acknowledgements

This work was supported by the Grant-in-Aid for Young Scientists (A) (Grant No.: 24686093) KAKENHI of the Japan Society for the Promotion of Science (JSPS).

References

[1] N. Katada, T. Miyamoto, H.A. Begum, N. Naito, M. Niwa, A. Matsumoto, K. Tsutsumi, Strong acidity of MFI-type ferrisilicate determined by temperature-programmed desorption of ammonia, *J. Phys. Chem. B*, 2000, **104**, 5511.

[2] A.N. Il'ichev, V.A. Matyshak, V.N. Korchak, Y.B. Yan, ESR and TPD study of the interaction of nitromethane and ammonia with HZSM-5 and CuZSM-5 zeolites, *Kinetics and*

Catalysis, 2001, **42**, 97.

[3] C.Y. Liu, K. Aika, Ammonia adsorption on ion-exchanged Y-zeolites as ammonia storage material, *J. Jpn. Petrol. Inst.*, 2003, **46**, 301.

[4] M.R. Basila, T.R. Kantner, The infrared spectrum of ammonia adsorbed on silica-alumina, *J. Phys. Chem.*, 1967, **71**, 467.

[5] J. Howard, J.M. Nicolt, Fourier-transform infrared studies of copper-containing Y zeolites Dehydration, reduction and the adsorption of ammonia, *J. Chem. Soc., Faraday Trans I*, 1989, **85**, 1233.

[6] A. Zecchina, F.rancesco Geobaldo, G. Spoto, S. Bordiga, G. Ricchiardi, R. Buzzoni, G. Petrini, FTIR investigation of the formation of neutral and ionic hydrogen-bonded complexes by interaction of H-ZSM-5 and H-Mordenite with CH_3CN and H_2O: Comparison with the H-Nafion superacidic system, *J. Phys. Chem.*, 1996, **100**, 16584.

[7] A. Zecchina, L. Marchese, S. Bordiga, C. Pazè, E. Gianotti, Vibrational spectroscopy of NH_4^+ ions in zeolitic materials: An IR study, *J. Phys. Chem. B*, 1997, **101**, 10128.

[8] H. Kamata, K. Takahashi, C.U. Ingemar Odenbrand, Surface acid property and its relation to SCR activity of phosphorus added to commercial $V_2O_5(WO_3)/TiO_2$ catalyst, *Catal. Lett.*, 1998, **53**, 65.

[9] V. Bolis, C. Busco, S. Bordiga, P. Ugliengo, C. Lamberti, A. Zecchina, Calorimetric and IR spectroscopic study of the interaction of NH_3 with variously prepared defective silicalites Comparison with ab initio computational data, *Appl. Surf. Sci.*, 2002, **196**, 56.

[10] M. Armandi, V. Bolis, B. Bonelli, C. Otero Areán, P. Ugliengo, E. Garrone, Silanol-related and unspecific adsorption of molecular ammonia on highly dehydrated silica, *J. Phys. Chem. C*, 2011, **115**, 23344.

[11] E. P. Parry, An infrared study of pyridine adsorbed on acidic solids. Characterization of surface acidity, *J. Catal.*, 1963, **2**, 371.

[12] M. Maache, A. Janin, J.C. Lavalley, Acidity of zeolites Beta dealuminated by acid leaching: An FTIR study using different probe molecules (pyridine, carbon monoxide), *Zeolites*, 1993, **13**, 419.

[13] T. Barzetti, E. Selli, D. Moscotti, L. Forni, Pyridine and ammonia as probes for FTIR analysis of solid acid catalysts, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 1401.

[14] B. Chakraborty, B. Viswanathan, Surface acidity of MCM-41 by in situ IR studies of pyridine adsorption, *Catal. Today*, 1999, **49**, 253.

[15] K. Suzuki, T. Noda, N. Katada, M. Niwa, IRMS-TPD of ammonia: Direct and individual measurement of Brønsted acidity in zeolites and its relationship with the catalytic cracking activity, *J. Catal.*, 2007, **250**, 151.

[16] M. Niwa, K. Suzuki, N. Katada, T. Kanougi, T. Atoguchi, Ammonia IRMS-TPD study on the distribution of acid sites in mordenite, *J. Phys. Chem. B*, 2005, **109**, 18749.

[17] J.R. Hart, K.E. Norris, C. Golumbic, Determination of the moisture content of seeds by Near-infrared spectrophotometry of their methanol extracts, *Cereal Chem.*, 1962, **39**, 94.

[18] P. Williams, K. Norris, “Near-Infrared Technology in the Agricultural and Food Industries 2nd Ed.”, American Association of Cereal Chemists, St. Paul, Minnesota, USA, 2001.

[19] J. M. Chalmers, P. R. Griffiths, “Handbook of Vibrational Spectroscopy Vol. 3”, Wiley, 2002.

[20] T. Theophile, “Infrared Spectroscopy - Life and Biomedical Sciences”, InTech, 2012.

[21] M. Takeuchi, L. Bertinetti, G. Martra, S. Coluccia, M. Anpo, States of H_2O adsorbed on oxides: An investigation by near and mid infrared spectroscopy, *Appl. Catal. A: Gen.*, 2006, **307**, 13.

[22] M. Takeuchi, G. Martra, S. Coluccia, M. Anpo, Evaluation of the adsorption states of H_2O on oxide surfaces by vibrational absorption: -Near and middle infrared spectroscopy-, *J.*

Near Infrared Spectrosc., 2009, **17**, 373.

[23] E. Gianotti, V. Dellarocca, L. Marchese, G. Martra, S. Coluccia, T. Maschmeyer, NH_3 adsorption on MCM-41 and Ti-grafted MCM-41. FTIR, DR UV–Vis–NIR and photoluminescence studies, *Phys. Chem. Chem. Phys.*, 2002, **4**, 6109.

[24] W. Zheng, D. Jewitt, R. Kaiser, Infrared Spectra of Ammonia – water ices, *Astrophys. J. Suppl. Series*, 2008, **125**, 1.

[25] P. Predeep, "Optoelectronics - Devices and Applications", InTech, 2012.

[26] Š. Urban, N. Tu, K. Narahari Rao, G. Guelachvili, Analysis of High-resolution Fourier transform spectra of $^{14}NH_3$ at 2.3 μm, *J. Mol. Spectrosc.*, 1989, **133**, 312.

[27] L.R. Brown, J.S. Margolis, Empirical line parameters of NH_3 from 4791 to 5294 cm^{-1}, *J. Quant. Spectrosc. Radiat. Transfer*, 1996, **56**, 283.

[28] C.M. Canal, A. Saleem, R.J. Green, D.A. Hutchins, Remote identification of chemicals concealed behind clothing using near infrared spectroscopy, *Anal. Methods*, 2011, **3**, 84.

Figure captions

Fig. 1 NIR absorption spectra of NH_4/ZSM-5(39) with different degassing temperatures: (a) before pretreatment; and degassed at (b) r.t., (c) 373 K, (d) 473 K, (e) 573 K, (f) 673 K, and (g) 773 K.

Fig. 2 NIR absorption spectra of: (A) NH_3 adsorption and (B) desorption processes on Na/ZSM-5(23.8); (a) after pretreatment at 723 K, (b - e) adsorption; (b) 0.094 → 0.001 kPa, (c) 0.408 → 0.001 kPa, (d) 1.50 → 0.02 kPa, (e) 1.50 → 1.50 kPa, (f - i) degassed at (f) r.t., (g) 373 K, (h) 423 K, and (i) 473 K.

Fig. 3 Proposed model of NH_3 adsorption on the Na^+-type zeolite.

Fig. 4 NIR absorption spectra of: (A) NH_3 adsorption and (B) desorption processes on the H/ZSM-5(1500); (a) after pretreatment at 723 K, (b - i) adsorption; (b) 0.011 → 0.000 kPa, (c) 0.020 → 0.001 kPa, (d) 0.053 → 0.002 kPa, (e) 0.110 → 0.003 kPa, (f) 0.220 → 0.006 kPa, (g) 0.405 → 0.027 kPa, (h) 0.770 → 0.189 kPa, (i) 1.50 → 0.93 kPa, (j - o) degassed at r.t., (j) 0.90 kPa, (k) 0.48 kPa, (l) 0.25 kPa, (m) 0.10 kPa, (n) 0.022 kPa, and (o) 0.000 kPa.

Fig. 5 Proposed model of NH_3 adsorption on the siliceous zeolite.

Fig. 6 NIR absorption spectra of: (A) NH_3 adsorption and (B) desorption processes on the H/ZSM-5(39); (a) after pretreatment at 723 K, (b - j) adsorption; (b) 0.023 → 0.000 kPa, (c) 0.098 → 0.000 kPa, (d) 0.193 → 0.000 kPa, (e) 0.203 → 0.000 kPa, (f) 0.288 → 0.000 kPa, (g) 0.392 → 0.000 kPa, (h) 0.745 → 0.001 kPa, (i) 1.50 → 0.022 kPa, (j) 1.50 → 0.316 kPa, (k - p) degassed at (k) r.t., (l) 323 K, (m) 423 K, (n) 473 K, (o) 523 K, (p) 573 K.

Fig. 7 Proposed model of NH_3 adsorption on the H^+-type zeolite.

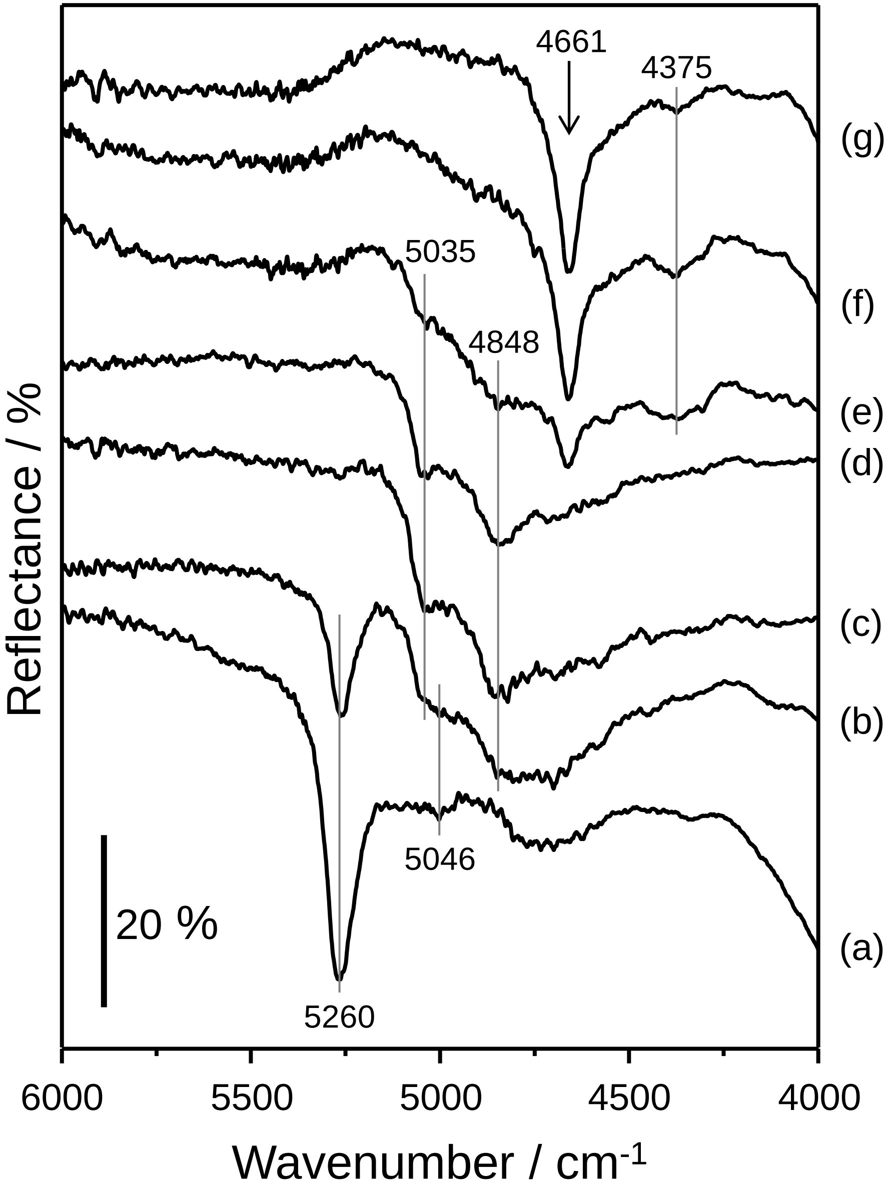

4661
4375
5035
4848
5046
5260
(g)
(f)
(e)
(d)
(c)
(b)
(a)
20 %
Reflectance / %
6000
5500
5000
4500
4000
Wavenumber / cm-1

Figure 1

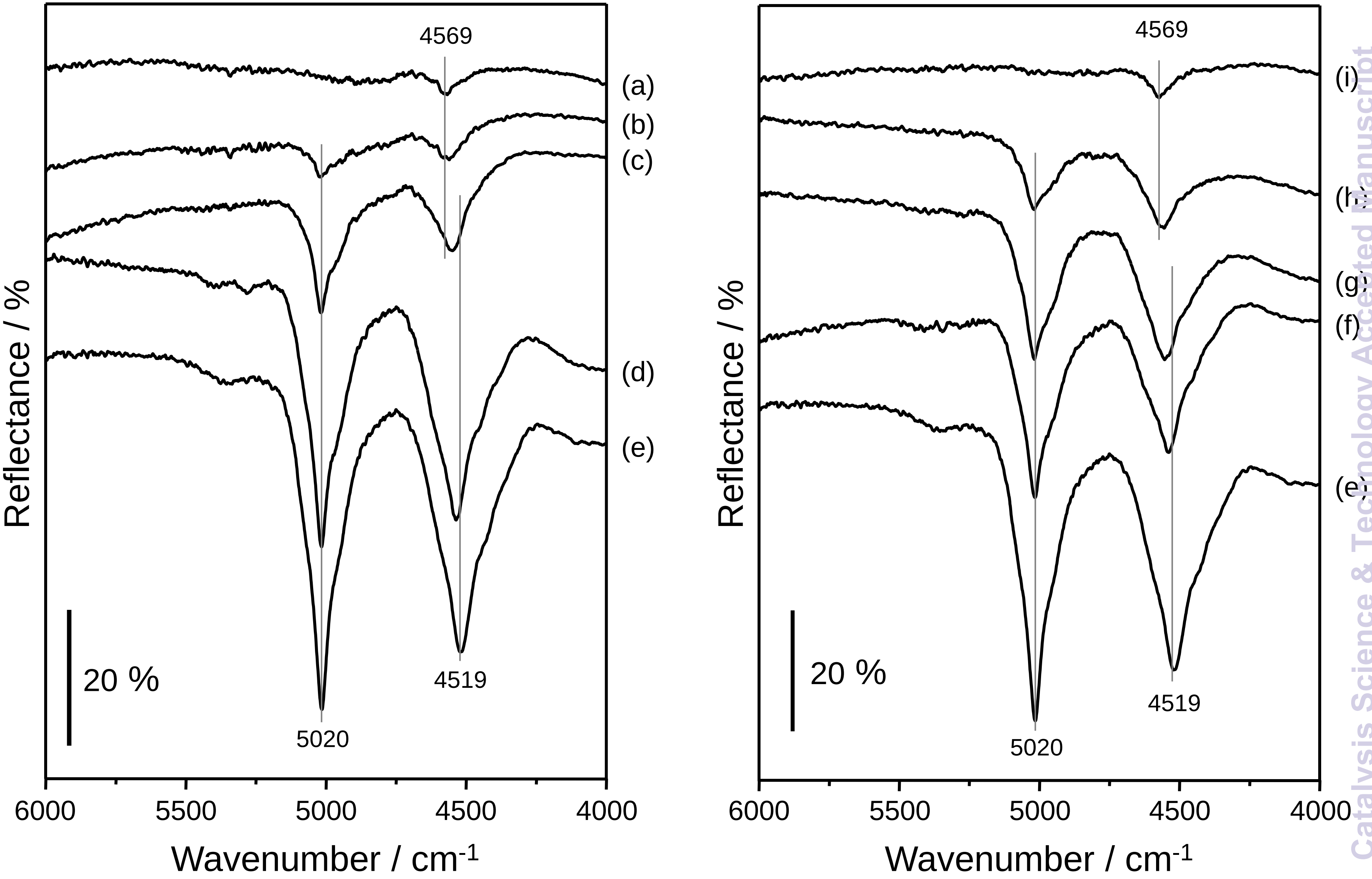
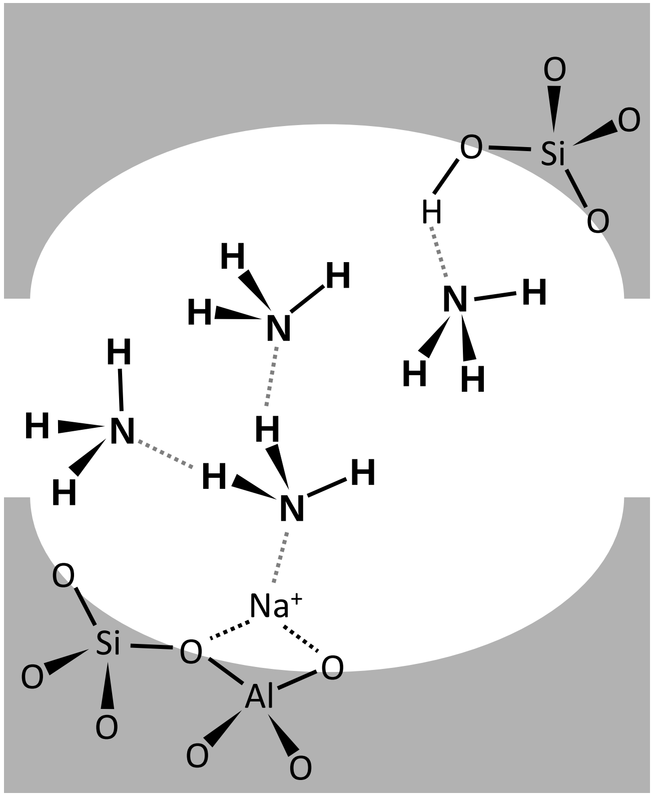

4569
(a)
(b)
(c)
(d)
(e)
20 %
4519
5020
Reflectance / %
6000
5500
5000
4500
4000
Wavenumber / cm-1
4569
(i)
(h)
(g)
(f)
(e)
20 %
4519
5020
Reflectance / %
6000
5500
5000
4500
4000
Wavenumber / cm-1

Figure 2



5021, 4519 cm^{-1}	hydrogen bonded NH_3 cluster
3740 cm^{-1}	isolated silanol

Figure 3

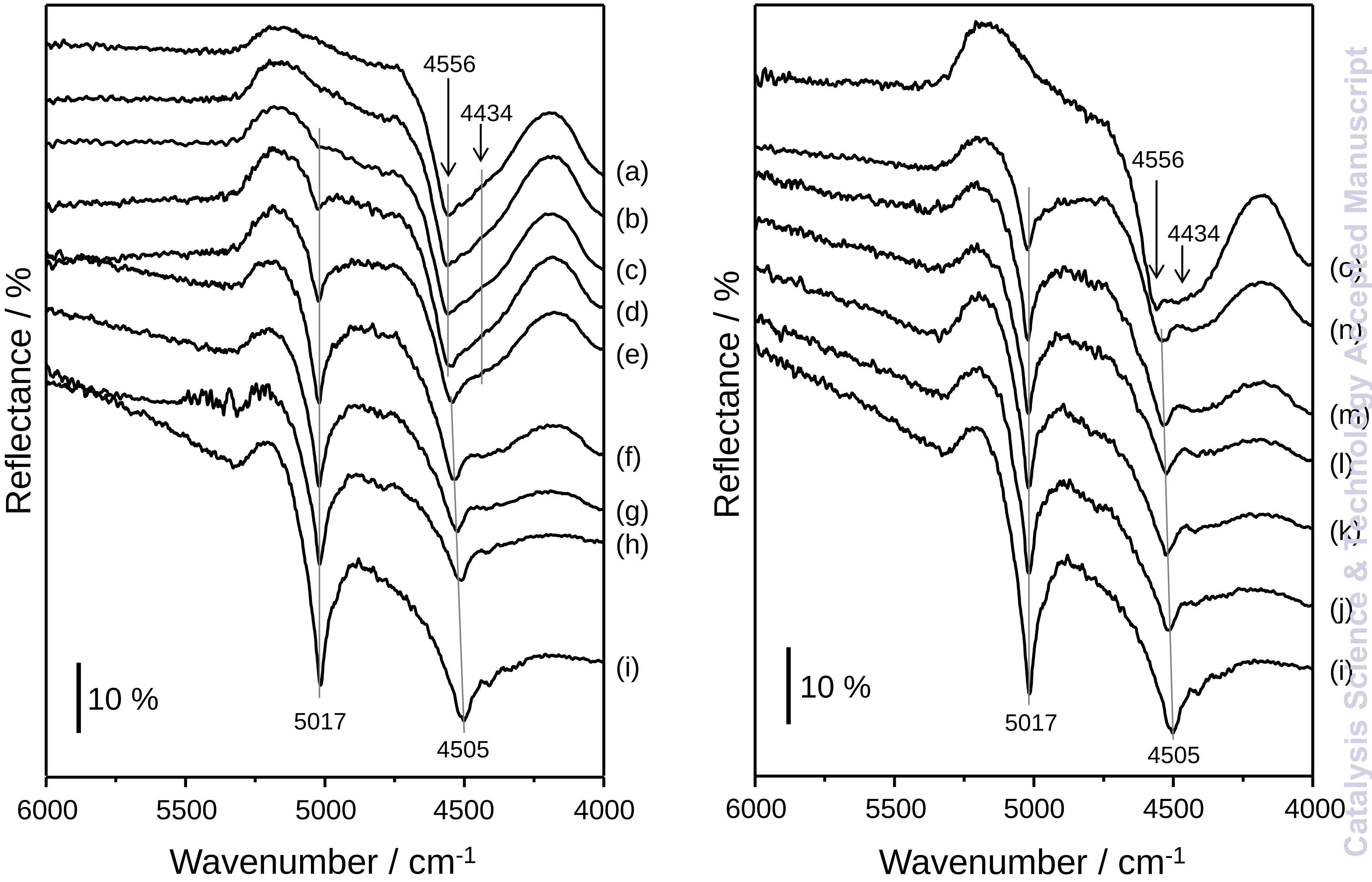
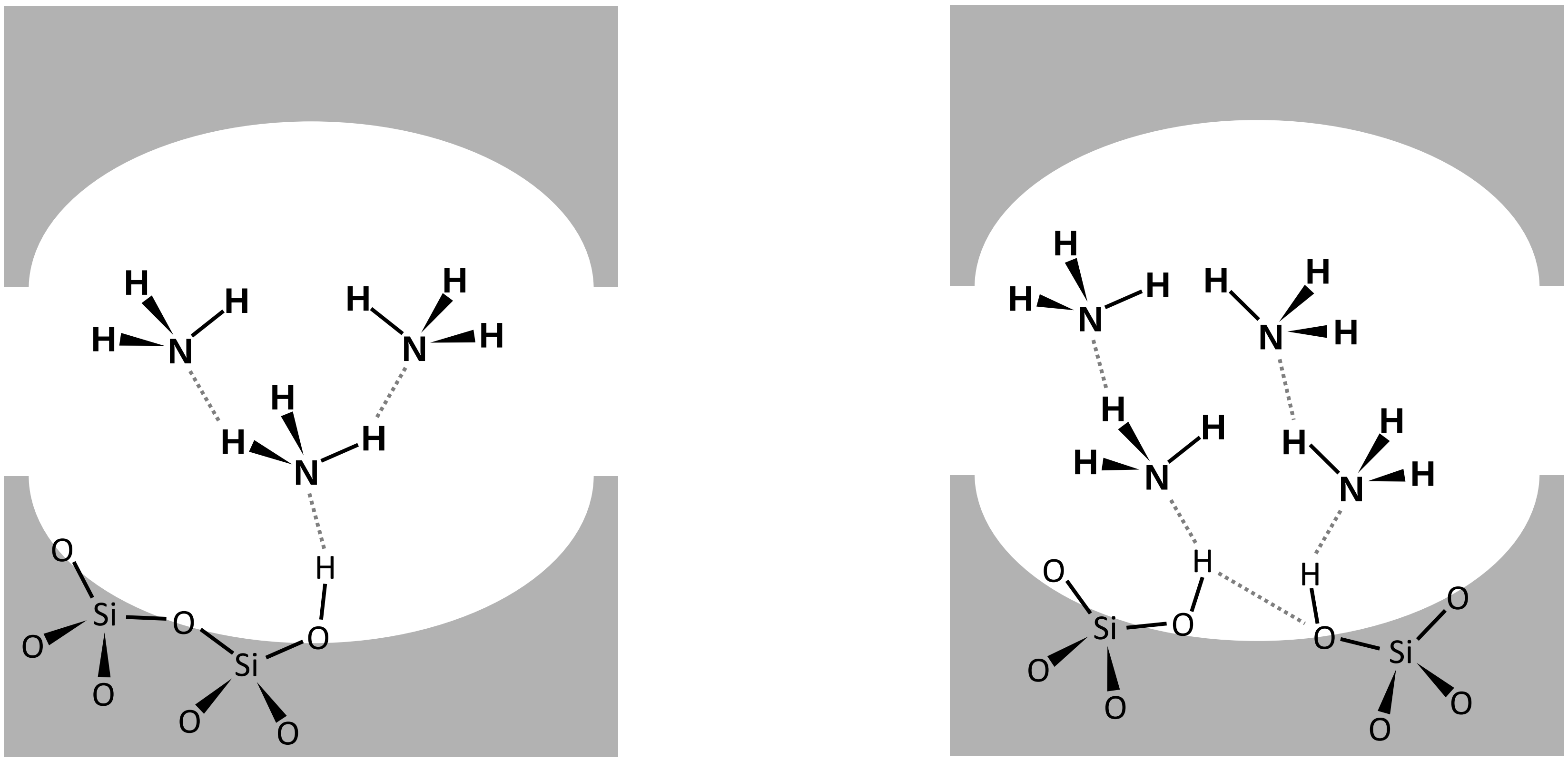

Reflectance / %
4556
4434
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
10 %
5017
4505
6000
5500
5000
4500
4000
Wavenumber / cm-1
Reflectance / %
4556
4434
(o)
(n)
(m)
(l)
(k)
(j)
(i)
10 %
5017
4505
6000
5500
5000
4500
4000
Wavenumber / cm-1

Figure 4



4556 cm^{-1} 3725 cm^{-1}	isolated silanol
5017, 4505 cm^{-1}	hydrogen bonded NH_3 cluster

4434 cm^{-1} 3698 cm^{-1}	hydrogen bonded silanol
5017, 4505 cm^{-1}	hydrogen bonded NH_3 cluster

Figure 5

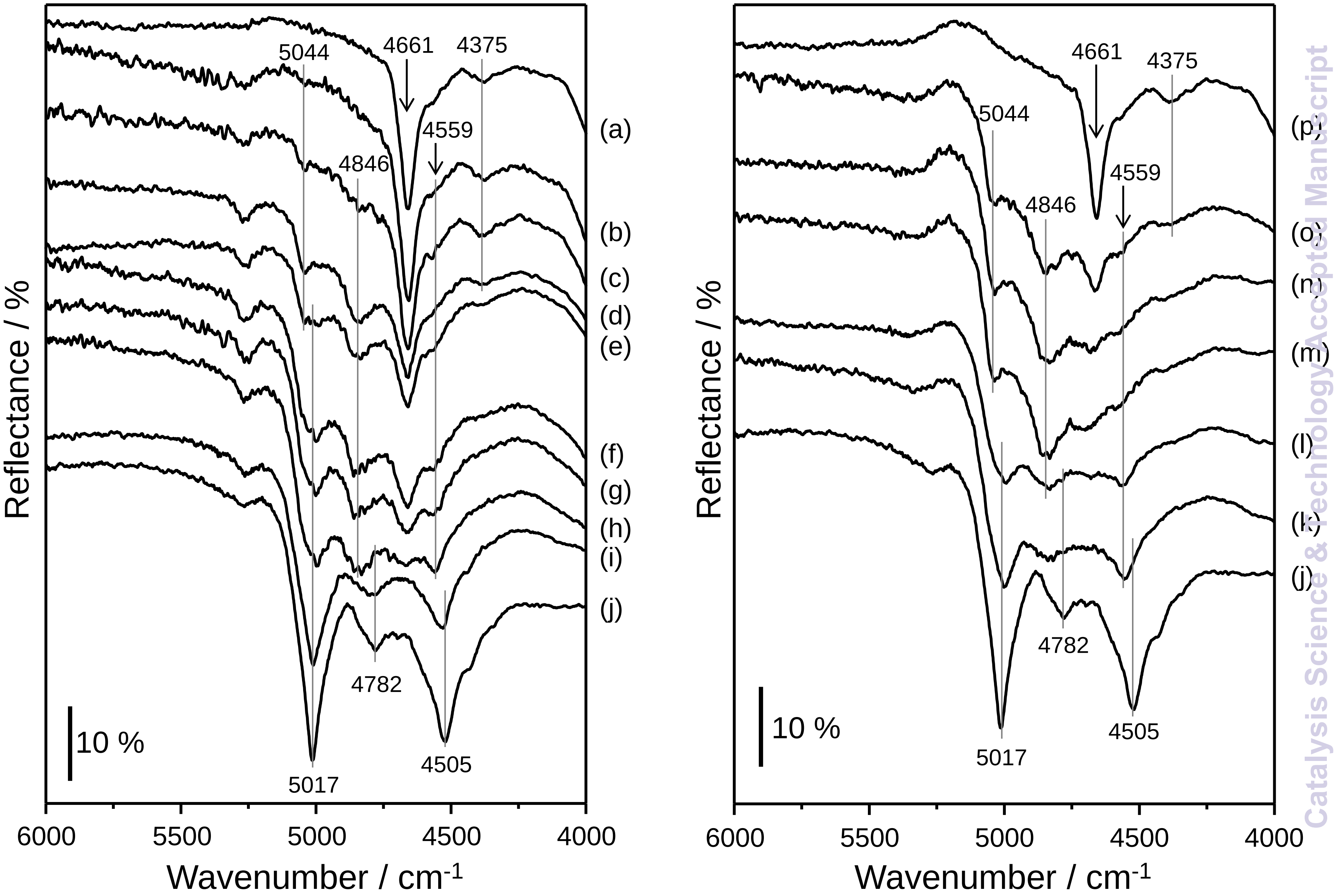
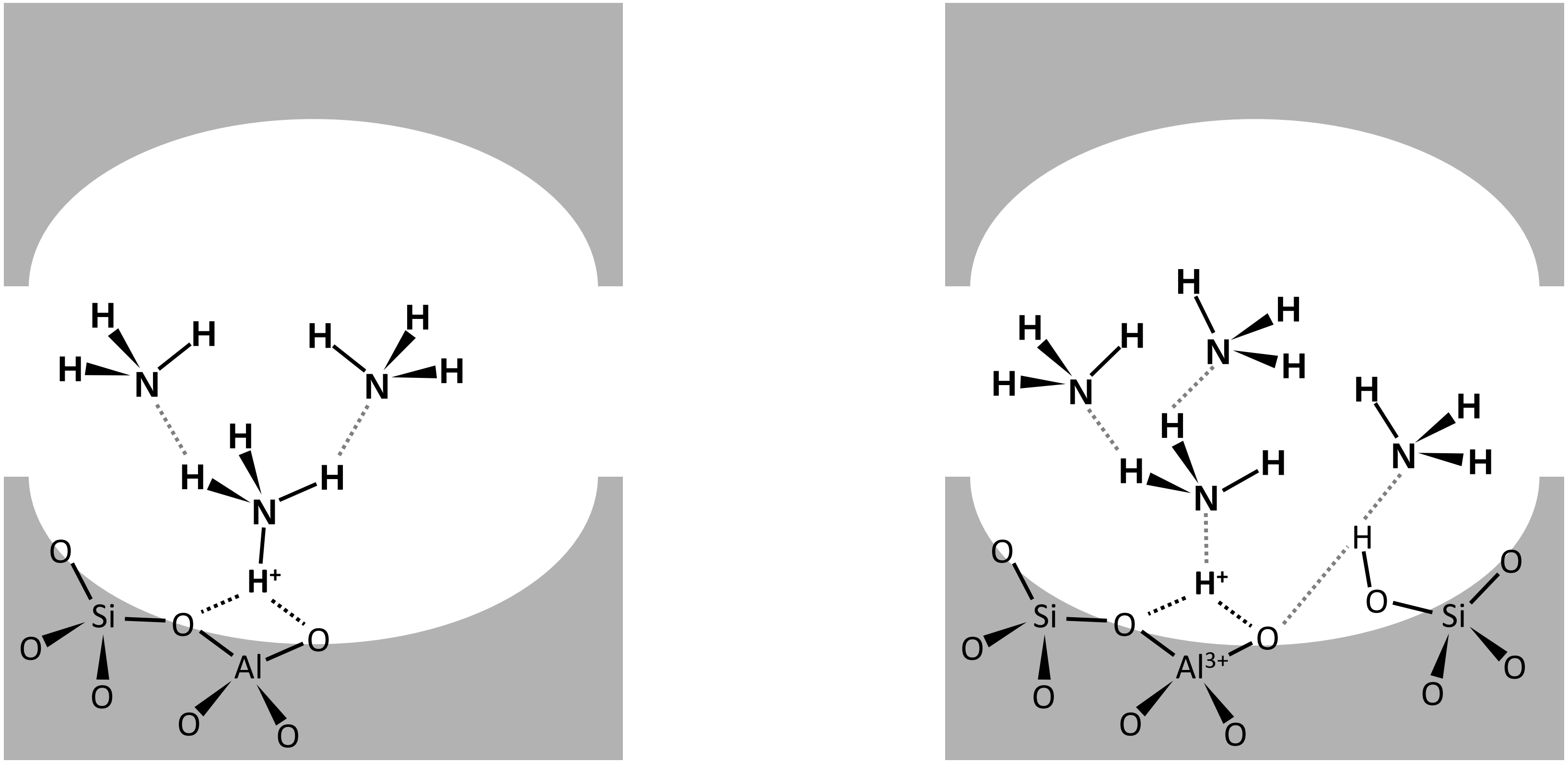

Reflectance / %
Wavenumber / cm-1
6000
5500
5000
4500
4000
10 %
5044
4661
4375
4559
4846
5017
4782
4505
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(p)
(o)
(n)
(m)
(l)
(k)
(j)

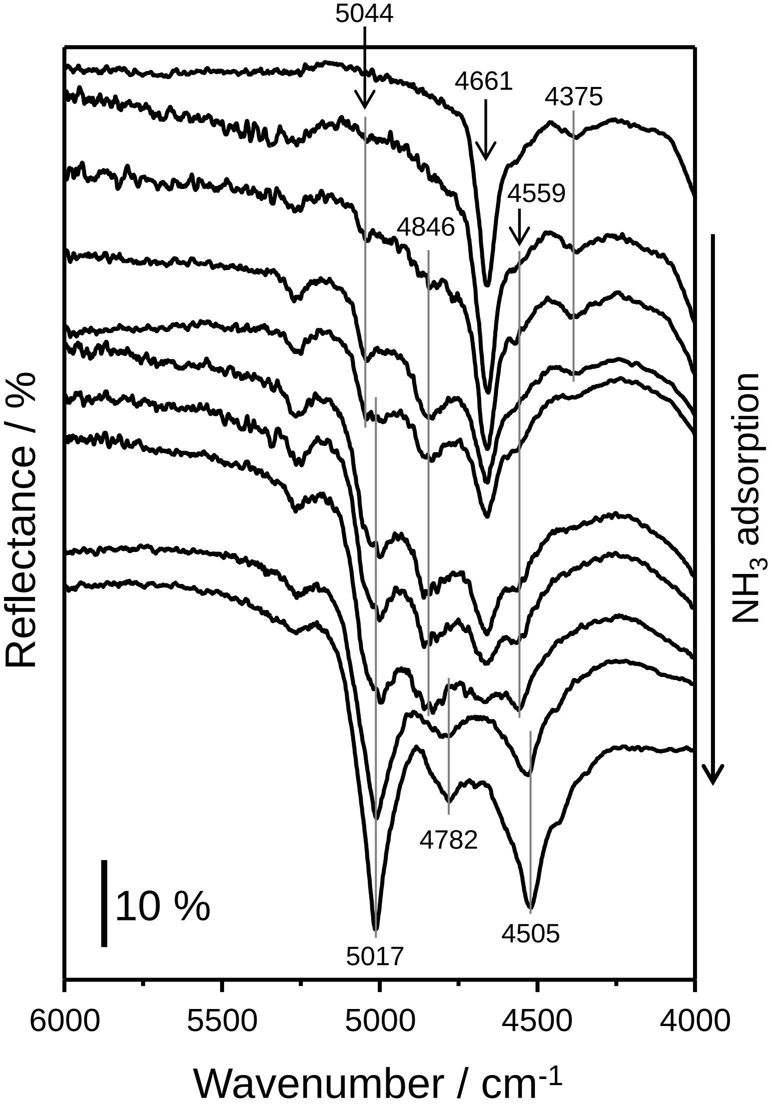
Figure 6

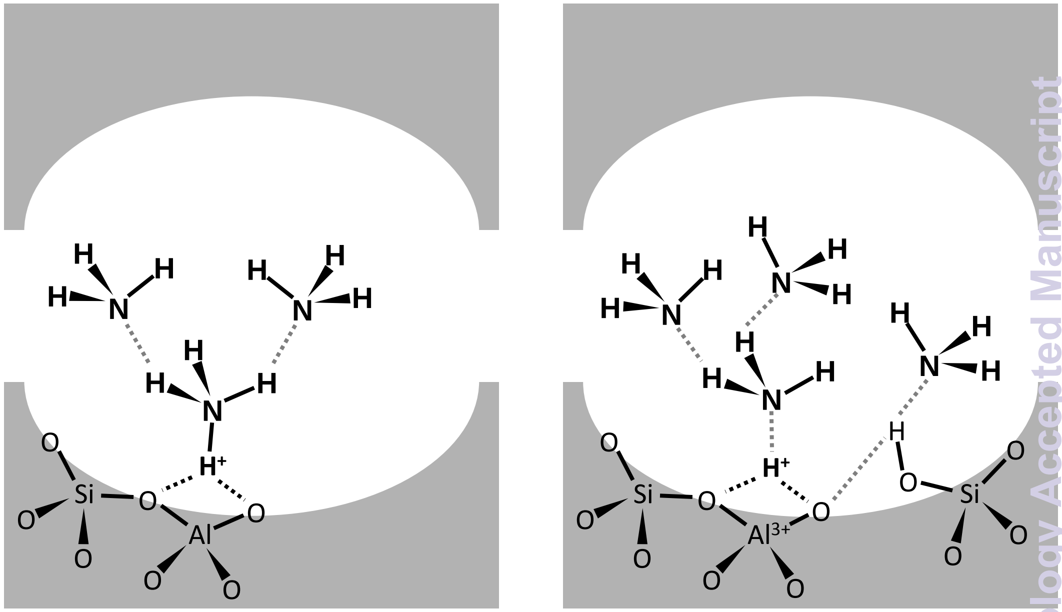


4661 cm^{-1}	Brönsted acid site (OH)
4846 cm^{-1}	isolated NH_4^+
4782 cm^{-1}	NH_4^+ stabilized by NH_3 cluster
5017, 4505 cm^{-1}	hydrogen bonded NH_3 cluster

4661 cm^{-1}	Brönsted acid site (OH)
5044 cm^{-1}	NH_3 interacted with H^+ sites
5017, 4505 cm^{-1}	hydrogen bonded NH_3 cluster
3740 cm^{-1}	silanol interacted with B-acid site

Figure 7





4661 cm^{-1}	Brönsted acid site (OH)
4846 cm^{-1}	isolated NH_4^+
4782 cm^{-1}	NH_4^+ stabilized by NH_3 cluster
5017, 4505 cm^{-1}	hydrogen bonded NH_3 cluster
5044 cm^{-1}	NH_3 interacted with H^+ sites
3740 cm^{-1}	silanol interacted with B-acid site

NH_4^+ formed by NH_3 adsorption on the H^+ sites of ZSM-5 zeolite as well as molecularly adsorbed NH_3 were simultaneously observed by near-infrared (NIR) spectroscopy. Furthermore, the formation of uniform NH_3 clusters within the cavities of Na^+-type and siliceous ZSM-5 were also observed.