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Reduction of methylene blue (MB) by ammonia in nanomordenite and mordenite zeolites: Method for the determination of ammonia concentration

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ABSTRACT

The increased encounter probability between ammonia and methylene blue dye(MB^+) incorporated in nanomordenite and Na-MOR zeolites demonstrated the reduction capacity of ammonia while present even at ppm level. The rate of reduction methylene blue dye by ammonia on the surface nanomordenite zeolite is faster than Na-MOR zeolite. Because nanomordenite zeolite with high silica(Si/Al=15) and surface area 400 (m^2/g) is referred to as hydrophobic support with respect to Na-MOR zeolite (Si/Al=6.5). On the other hand, the rate of color bleaching of MB^+ by ammonia was found to be fastest in proton form of nanomordenite and mordenite zeolites. The results obtained with the zeolites were also compared with non-ionic micelle(TX-100). The calibration graph is valid for wide range of concentrations in nanomordenite zeolite. The limit of detection (LOD) is 0.12mg ml^{-1}. This method is simple, sensitive and easy to carry out. By using only a UV-Visible spectroscopy, ammonia can be quantified.   © 2008 Trade Science Inc. - INDIA

INTRODUCTION

Zeolites are crystalline silico-aluminates with a very precise micro-porous structure and present some well-known general features responsible for their extensive applications in catalysis, adsorption and ion exchange[1]. These properties are related to the possibility of generating and regulating the acid-base and hydrophobic-hydrophilic character, and strong selective adsorption affinities. The properties of the zeolite depend mainly on the particular zeolite structure, framework composition, cation nature and pore structure, and can be easily modified[2]. Zeolite parameters such as particle size, surface area, pore diameter, mechanical strength, microbial resistance, thermal stability, chemical durability, hydrophobic/hydrophilic character, ease of regeneration, loading capacity and cost, will influence the behavior of the catalyst and its practical and technical applications[3].

In the some reaction, the water content of the support is another important parameter[4]. For example, from the electrochemical data was found that reduction reaction between MB^+ and NH_3 is thermodynamically allowed but dose not occur appreciably in water. A "kinetic barrier" arising from a low encounter probability due to the solvated nature of the reactants may explain why the reduction reaction is not observed on the experimental time scale. To remove this barrier and to increase the encounter probability in the methylene blue

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reduction by ammonia different micelles have been used[5]. But, there is problem associated with the use of micelle solutions. The dye molecules can be entrapped in the hydrocarbon core of the micelles and the rate of reduction is slow[6].

In the past decade, an increasing number of studies on the optical properties of dye-loaded zeolites were published[1]. The zeolite framework represents a host material exhibiting higher stability against organic solvents, acids and bases as well as a high resistance to temperature and radiation. The zeolite structure enables the access of dye molecules into the pores of the material host and also may provide anchoring sites to stabilize them[7-9].

Hydrophobic zeolites like dealuminated zeolites or zeolites with high Si/Al can be alternative supports for removing this barrier[10,11]. Hydrophobic zeolites are non-flammable, with stand temperature and can easily be regenerated[12-14]. Hydrophobic zeolites have been chosen to incorporated reducible organic compounds (MB+). In the next step, ammonia encounters the incorporated molecule and has been observed for the first time to play the role of a reductant. This observation has generated interest in developing a quantification technique for ammonia detection.

In general, colorimetric methods[15] are used for the determination of ammonia in aqueous environments. However, color or turbidity interferes with these methods and therefore, a time-consuming preliminary distillation step[16] is required before analysis. Thus, a fast and highly sensitive method is desired. At present, an ammonia selective electrode method[17,18] has been widely used for determining ammonia in environmental samples. However, this method is susceptible to interferences by amines[19]. A few years ago, a gas phase molecular adsorption method has been reported but this method is not quite as sensitive[20].

The ammonia selective electrode method has also been applied in combination with flow-injection systems. Apart from direct sensing of ammonia, the electrodes have also been used as transducers for monitoring enzymatic reactions during which ammonia is released or consumed. The determination of urea, which by catalytic action of urease, is hydrolyzed to give ammonia and carbon dioxide, is a representative example [21]. Ammonia electrodes can also be exploited to monitor the binding of antigens to antibodies[22]. Despite the utility of present day electrochemical ammonia sensors, they have some disadvantages: (1) they do not lend themselves to miniaturization; (2) it is not easy to sterilize them; (3) their performance can be affected by surface potentials, resulting in drifting signal; (4) as in other potentiometric methods, a reference electrode is required, along with is troublesome liquid-liquid junction.

For the determination of the air vapor concentration (AVC) of ammonia several methods are available, but none is rapid, simple and sensitive for practical applications. The Berthelot reaction[23] is time consuming and unsuitable for AVC studies. The AVC of ammonia can be determined by other methods[24] but none of them is suitable for use as a personal dosimeter. Other techniques that include molecular absorption, gas chromatography with chemiluminescence detection and fluorimetric methods[25,26] are well-documented but require sophisticated apparatus.

The assay of ammonia has found increasing importance in the diagnosis of several disease states, such as hepatic coma, Eck·s fistula and Rey·s syndrome[27]. Higher dosages of ammonia may cause iritis, bronchoc onstriction and dyspnca[28]. Hence the detection of ammonia is very important not only for air quality studies but also for diagnostic purposes.

In this paper, it is reported for the first time a simple demonstration of the unusual reducing capability of ammonia that leads to a cost effective and sensitive UV-vis spectroscopy method for the determination of ammonia concentration. This method utilizes the quantitative color bleaching of methylene blue by ammonia in nanomordenite(Si/Al=15) and Na-mordenite(Si/Al=6.5) zeolites. The decrease in color intensity of MB+ is a direct measure of the ammonia concentration and hence is suitable for routine analysis. Ammonia concentration can be detected at the parts-per-million (ppm) level. Possible interferences have been investigated and the standard deviation of the method has been estimated to be ±2%. The results obtained with the zeolites were also compared with TX-100 micelle.

EXPERIMENTAL

Reagents

Ammonia solution(0.1M) was prepared from a stock ammonia solution(17M) by proper dilution methods using distilled water and standardized by standard

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HCl solution. MB+ reagent was of analytical grade from Merck. Stock solution of MB+(1.0×10^{-5}) was prepared in water. Poly (oxyethylene) iso-octyl phenyl ether (Triton X-100 or TX-100) was purchased from Aldrich. The Na- mordenite(Na-MOR) and nanomordenite zeolites were synthesized in our laboratory based on the described procedure in the literature, respectively [29,30].All other reagents were of analytical grade from Merck or Sigma.

Sample preparation and treatments

Methylene blue loaded samples (MB-NaMOR and MB-nanomordenite) were prepared by ion exchange method. To obtain MB-NaMOR and MB-nanomor denite samples 3 grams of zeolites were lightly ground and immersed in 150ml of an aqueous solution of 1.0×10^{-5}M methylene blue and the solids were shaken. Samples of MB-NaMOR and MB-nanomordenite were synthesis after 24h. The samples were carefully washed with hot deionized water for several times to removed occlude materials and surface-adsorbed species. Samples also, were cleaned with using an ultrasonic cleaner. Then the solids were oven dried at 70 ºC for 5 h. The quantity of the adsorbed MB+ was estimated to be 1.13×10^{-3} mmol/g Na-MOR and 2.8×10^{-3} mmol/g nanomordenite.

Characterization

All UV-visible absorption spectra were recorded in a Shimadzu UV-1650 PC spectrophotometer equipped with 1cm quartz cell.

The crystallinity of the samples was checked by X-ray diffractometer(Philips PW 1840) with Cu-Kαradiation at room temperature. XRD patterns were recorded using an automatic divergence slit system.

Chemical analysis of the mordenite and nanomordenite were done by energy dispersive X-ray analysis(EDX) joined to a Philips XL 30 scanning electron microscopes. The water content of the samples was determined by gravimetry. From EDX data unit cell composition of the Na-MOR and nanomordenite were $Na_{7.4}[(AlO_2)_{7.4}(SiO_2)_{40.6}].23.7H_2O$ and $Na_{0.3}TEA_{3.2}[(Al)_{3.5}(Si)_{92.5}(O)_{192}].10H_2O$, respectively.

RESULTS AND DISCUSSION

Absorption spectra were measured with a double-beam spectrophotometer on both homogeneous solution and dilute dispersions of zeolites. Because of the small particle size and the high dilution good quality, transmission spectra could be measured. When necessary, a dye - free diluted zeolites dispersion was used to determine the baseline. To measure the spectra of zeolites containing methylene blue cation, about 1mg of MB-Na zeolites dispersed in 2mL of water. The UV-visible spectrum of MB-nanomordenite shows a λ_{max} at 655nm(Figure 1) and similar result was obtained for MB-NaMOR zeolite. The other spectra were taken as follows: 1mg MB-zeolites was mixed 2mL of distilled water and different amounts 1-800μL of an aqueous ammonia solution(0.1M) were added. UV-vis spectra of MB-zeolites show the decrease in the absorbance value at 655 nm with increasing ammonia solution(0.1M) in the range 1-800μL(Figure 1).
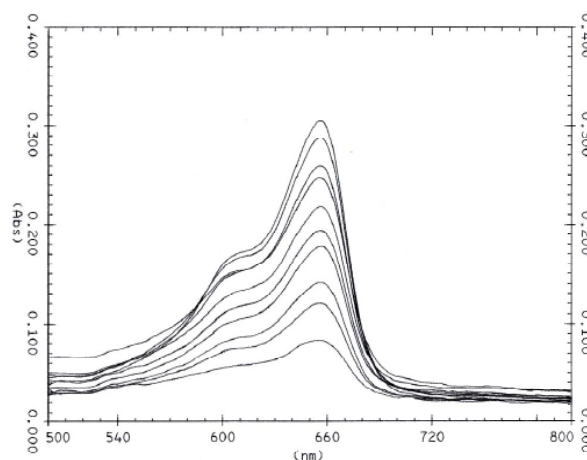

Figure 1 : UV-vis spectra of the reduction of MB by varing amounts of ammonia in nanomordenite zeolite. Inset shows the absorbance *vs.* concentration of ammonia (ppm) plot
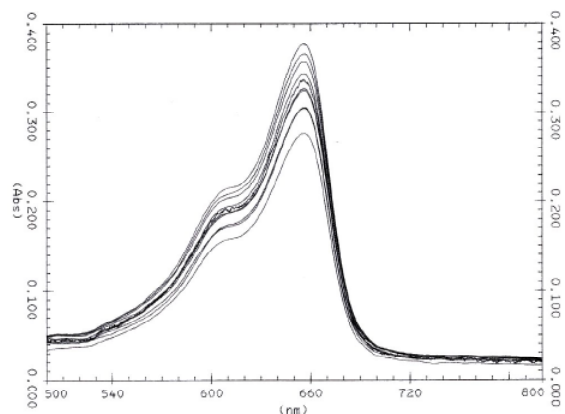

Figure 2 : UV-visible spectra the reduction of MB by varying amounts of ammonia in TX-100 micelle

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In an other stoppered cuvette 2mL of TX-100 (0.2M) and 50μL methylene blue(9.0×10^{-3}M) were placed. The solution showed a λ_{max} at 655nm. Then this solution was mixed with 1-800μL of an aqueous ammonia solution(0.1M). After 2min(the time required for manipulation) the decrease in the absorbance value of the micelle-stabilized dye(MB$^+$) was monitored at 655nm (Figure 2). The bleaching of MB$^+$ color gives a quantitative measure of the ammonia concentration present in the zeolites.

Methylene blue is a water-soluble non-toxic cationic dye, which is blue in color and upon reduction, it become colorless. The optical spectrum of MB$^+$ in water shows two 665 and 610 nm bands which correspond to the monomeric and dimeric form of MB in water, respectively(Figure 3). In zeolite samples (Nanomor denite and Na-MOR) and TX-100 micelle its λ_{max} shifts to 655 and 605nm.

In water, the rate of reduction of MB$^+$ by NH$_3$ has been observed to be negligibly small and it takes a long time to observe an appreciable change in color of the dye. A similar observation was noted in the case of the MB$^+$-ascorbic acid reaction in water in the absence of any surfactant[31]. In a like wise fashion, the slow reaction of NH$_3$ with MB$^+$ in water is thought to be due to low encounter probability. For increase the encounter probability in the MB$^+$ reduction by NH$_3$, nanomordenite and Na-MOR zeolites with different Si/Al ratio (nanomordenite Si/Al=26.5 and Na-MOR Si/Al=6.5) were used. The results obtained with the zeolites were also compared with TX-100 micelle. The order of reaction, reduction of MB$^+$ with NH$_3$ in zeolites and TX-100 is (Figure 4):

Rate MB-nanomordenite>Rate MB-NaMOR>Rate TX-100 and the rate constant values are 8.6×10^{-2}, 5.28×10^{-2} and 2.63×10^{-5}min^{-1}, respectively. That is, the rate of color bleaching of MB$^+$ was found to be fastest in the nanomordenite and Na-MOR zeolites. The site of incorporation of dye molecules depends on their relative hydrophobic and hydrophilic tendencies and electrostatic interactions.

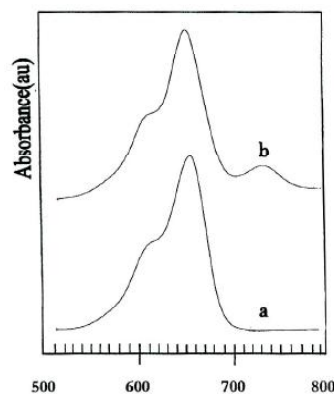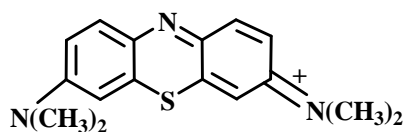The cationic form of methylene blue has the structure

Figure 3 : Electronic spectra of MB in: (a) water and (b) hydrochloric acid
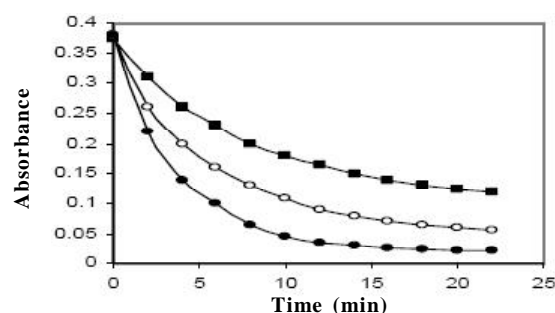

Figure 4 : Absorbance vs. time plot for the reduction of MB by ammonia in (a) TX-100, (b) Na-MOR and (c) Nanomo rdenite

and the minimum effective kinetic size is ca. 0.7×1.6nm[32]. On the other hand, in a previous study, we observed that intercalation or encapsulation MB$^+$ into channel mordenite(channel diamer 0.65-0.7nm) took about after 3-4 days[33,34].Therefore, MB cation is exchanged on the surface of the nanomordenite and Na-MOR zeolites after 24h. One would therefore expect the MB cation to be unable to enter the channel structure of nanomordenite.

The study have been shown that methylene blue is exchange on the surface of the zeolites by both electrostatic and hydrophobic interactions[35], whereas MB$^+$ is bound to near the surface of the non-ionic TX-100 micelle (short penetration) by hydrophobic forces[5,36,37]. Then, insignificant color bleaching of the dye was observed in TX-100 with respect to zeolites. This might be due to short penetration of the dye in the TX-100 micelle due to hydrophobic interactions. This might be the reasons for the low collision probability between MB$^+$ and NH$_3$.

Zeolite framework composition

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The result shows that, the rate of reaction MB^+ reduction by NH_3 in nanomordenite zeolite is faster than Na-MOR. One of the most important parameters in the zeolite framework composition is its Si/Al ratio. In fact, the aluminum content of the crystalline network will determine the global framework charge, as well as the amount of cations in the structure, and will drastically influence the hydrophobic/hydrophilic character of the structure.

Two sodium forms of zeolites, with different framework compositions, were tested. The Si/Al ratio for as-synthesized nanomordenite and Na-MOR determined by EDX/SEM were 15 and 6.5 respectively. Nanomordenite zeolite with high silica carries less framework charge and is commonly referred to as hydrophobic support and with high surface area is a good median for adsorption ammonia. The opposite holds true for high alumina zeolites such as Na-MOR that is labeled hydrophilic character[10]. Hence nanomordenite zeolite has high hydrophilic character with respect to Na-MOR zeolite and the rate of reaction MB^+ reduction by NH_3 increase on the surface of the hydrophobic nanomordenite. Serralhe et.al reported similar observation for some zeolites (such as Na-mordenite and nanomordenite Na-Y and Na-ZSM-5…) as supports for an enzymatic alcoholysis reaction. They resulted that the Si/Al ratio of the framework revealed to be important parameters. They showed that, zeolites with a high Si/Al ratio present higher hydrophobic character[38].

The nature of the cation in the zeolite structure, which will affect the water binding to the zeolite, will influence the amount of water that must be present in the reaction media. Meininghaus et.al has been reported[14] that, stronger interactions were observed between the water and charge balancing sodium ions as compared with Bronsted acid sites. They showed that, higher temperature were necessary for the regeneration of a nanomordenite zeolite. Furthermore, its capacity for water was greater, resulting in stronger hydrophilicity. However, the proton form resulted in chemical conversion during thermal regeneration then its capacity for water was smaller, resulting in stronger hydrophobicity. Serralhe and et.al has been reported[38] that, zeolites containing cations with a higher charge density will bind water more tightly and they are stronger hydrophilicity. These reports are similar to the results obtained by Adlercreutz[4], in this study of the water effect on the alcoholysis activity of chymotrypsin on different supports.

Calibration graph and other statistical parameters

The analytical utility of this study was investigated using the calibration curve for variable amounts of ammonia addition. The ammonia dependent decrease in absorbance of the dye(due to the reduction MB^+ by NH_3) gives a quantitative measure of ammonia concentration in solution. The plot is linear in the range of $0.049\text{-}2.8 \times 10^{-3}$M of ammonia(due to the addition of 1-800µL of 0.1M ammonia to 1mg of MB-zeolite in 2 mL water). The methylene blue content in the nanomordenite zeolite is 2.8×10^{-3}. The absorbance values, A, are related to the concentration ammonia, C_{NH3}(mg/mL) by the equation:

$$A = -9.0 \times 10^{-4} C_{NH3} + 0.3345$$

with a correlation coefficient to 0.9809. The estimated for the standard deviation from 9 blank measurements is 4.8×10^{-5} absorbance units. The limit of detection (LOD) is 0.16 ppm and calculated as $LOD=3S_B/m$ where S_B is standard deviation of the blank and m is the slop of the calibration graph.

Interference by other species

Interferences due to various cations and anions were studied in detail. Large excesses of urea, boric acid, EDTA, nitrate, sulfate, chloride, carbonate, iodide ion, sodium ion, potassium ion and pyridine do not interfere at all in the determination. NH_4NO_3, NH_4Br, NH_4OOCH_3 did not react with the MB^+ incorporated in zeolites(nanomordenite and Na-MOR). However, a mixture of ammonium salts along with NaOH at room temperature reduced the blue color of the MB^+ incorporated in above zeolites quantitatively as in the case of NH_3. Hydrazin, aniline, dimethyl amine and triethyl amine interfere strongly.

CONCLUSION

This paper not only describes a method for ammonia determination via the color bleaching of the cationic dye MB^+ incorporated in nanomordenite zeolite but also explains the "zeolite catalyzed redox reaction". The cation of structure and framework composition of the zeolites has a marked influence on the catalytic reaction them. The results show that, reduction methylene blue

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by ammonia for zeolites with high Si/Al ratio is faster than zeolites with low Si/Al ratio. On the other hand, the nature of the cation in the zeolite will affect the water binding to the zeolite. The rate of color bleaching of methylene blue dye was found to be fastest in zeolites with respect to non-ionic micelles. Because cationic dyes diffuse into hydrocarbon core non-ionic micelles and encounter probability decreases between methylene blue and ammonia. But zeolites containing multiple adsorption sites, strong interaction with cationic dyes(MB^+)(hydrophobic and electrostatic force) and its organized structure are better than micelles for reduction reaction methylene blue by ammonia.

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