

Research Article

Selective Nitration of Chlorobenzene by NO_2 in the Alkali Zeolite NaZSM-5

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Chlorobenzene was reacted with NO_2 , in the initially acid-free zeolite NaZSM-5, to yield para-chloronitrobenzene exclusively. The precursors were loaded sequentially into self-supporting pellets of the zeolite, contained within a stainless steel cell, from the gas phase. The reaction proceeds spontaneously at room temperature. It is, however, very temperature dependent and effectively ceases at zero degrees Celsius. The reaction was monitored *in situ* using FT-IR. The active nitrating agent is $\text{NO}_2^{\delta+}$ formed from the partial electron donation by the NO_2 to the Na^+ cations present in the zeolite lattice. Under the reaction conditions, chlorobenzene is not readily mobile through the pore system; thus, only the molecules adsorbed near a cation site react to form para-chloronitrobenzene.

1. Introduction

As part of a continuing investigation into employing heterogeneous catalysis to selectively produce small industrial intermediates, para-chloronitrobenzene was synthesized from chlorobenzene and NO_2 in the initially acid-free zeolite NaZSM-5.

Para-chloronitrobenzene is an intermediate in the production of fine chemicals, principally dyes, pesticides, and herbicides [1–3], where it is hydrogenated to para-chloroaniline before further processing. Chloronitrobenzenes are, however, highly toxic, causing methemoglobinemia [4, 5]. Given this toxicity, and their value as intermediates, the chloronitrobenzenes would seem to be ideal candidates for a study into selective synthesis in order to diminish byproducts.

ZSM-5 is a medium-pore pentasil zeolite [6, 7] with two perpendicular channel systems. One channel is straight with an elliptical cross-section of 0.55×0.51 nm, while the second forms a zigzag with dimensions of 0.56×0.53 nm [8]. Industrially, ZSM-5's most important process is to enhance the fraction of paraxylene during xylene isomerization [9–11]. This is thought to result from the aluminosilicate channel wall restricting the available transition state volume and enhancing the diffusion of the para isomer down the pores

[12]. The void space of the channel system is nearly perfectly sized to easily accommodate the adsorption and diffusion of para-substituted benzene rings, but is too restricted to allow easy movement of ortho- and metasubstituted species. ZSM-5 would thus be ideal for the selective formation of para-chloronitrobenzene.

Economic considerations for industrial intermediates favor selection of the least expensive form, hence NO_2 for nitrations. Traditional methods for the nitration of aromatic rings using NO_2 involve strong acids to generate NO_2^+ , which is the active entity in an electrophilic substitution of the ring [13, 14]. Use of solid acid catalysts, such as alumina/silica/metal oxide, achieves excellent conversions, but with limited ability to enhance the proportion of any isomer [15, 16]. Acid zeolites have been used successfully as solid acid catalysts to achieve nitration of aromatics with varying levels of selectivity [17–19]. The electrostatic fields of the Na^+ cations in NaZSM-5 are capable of enhancing the electrophilic character of small molecules adsorbed into the channel system [20]. Recently, it has been shown that nitrogen dioxide adsorbed in the pore system of NaZSM-5 will form $\text{NO}_2^{\delta+}$ from the partial electron donation by the NO_2 to the Na^+ cations present in the zeolite lattice. This $\text{NO}_2^{\delta+}$ is capable of nitrating small aromatics at room temperature

in the absence of acid protons in the zeolite lattice [21]. This would allow the use of NaZSM-5 as a heterogeneous nitration catalyst without a high-temperature acid activation step.

2. Experimental Section

The NaZSM-5 was prepared from small crystal commercial NH_4 -ZSM-5 (Zeolyst CBV 15014, lot no. 15014-1525-63) with a Si-Al ratio of 150. The zeolite was ion-exchanged using sodium acetate at room temperature until NH_4^+ peaks were no longer detectable by FT-IR. Also, there was no detectable Brønsted acid hydroxyl peak at 3611 cm^{-1} [22].

The reactions were carried out using self-supporting pellets (6–9 mg, 12.5 mm dia.) of the zeolite contained in a stainless steel gas cell housed within a variable temperature vacuum cryostat (Oxford Instruments Model DNI714). The wafers were dehydrated overnight at 200°C (maximum cryostat temperature) under vacuum (varian turbomolecular pump Model V-60). 500 mtorr of chlorobenzene (Alfa Products, 98+%) was introduced into the 25°C gas cell, which was sealed after 5 s and allowed to equilibrate for 0.5 hours. The gas cell was then evacuated to a gas pressure of <5 mtorr and then brought to the reaction temperature and allowed to stabilize for 1.5 hours. 10.0 torr of room temperature NO_2 (Matheson, 99.5%) gas was released into the cell and then after thirty seconds the cell was closed. Time zero for the kinetics plots corresponds to the initial release of NO_2 into the sample cell.

The gas cell and the cryostat were fitted with KCl windows to allow the *in situ* collection of FT-IR spectra. These were collected using an IBM-Bruker IR-44 spectrometer. 100 scans at 1 cm^{-1} resolution were coadded and ratioed against a background of the empty dehydrated pellet at 25°C . Again, time zero for the kinetics is the initial release of NO_2 into the cell. 100 scans require approximately 100 s to collect on the IR-44 and thus each data point in the kinetics plot corresponds to a 100 s wide time slice.

The identity of the major reaction product was determined by comparison with authentic samples of ortho-, meta-, and para-chloronitrobenzene (Aldrich, 99+%, 98%, and 99% resp.) adsorbed into clean freshly dehydrated pellets.

3. Results and Discussion

The IR spectrum of the dehydrated NaZSM-5 pellet (see Figure 1) provides two windows for monitoring the species adsorbed onto the internal surface of the zeolite pore system. Details of the spectrum and the features present in the $>1300\text{ cm}^{-1}$ region have been previously reported [20, 21].

Chlorobenzene is readily adsorbed into the channel system of NaZSM-5 (see Figure 2 and Table 1). At 1959 and 1880 cm^{-1} and 1938 and 1861 cm^{-1} is a pair of weak C–H bend doublets of the aromatic ring. Comparison of these modes with those for benzene suggests that the lower frequency pair is associated with a polar environment, while the higher pair is associated with a nonpolar environment [22]. This would correspond to chlorobenzene adsorbed near a cation site and on the “cation free” silica lattice. Thus, there are two groups of

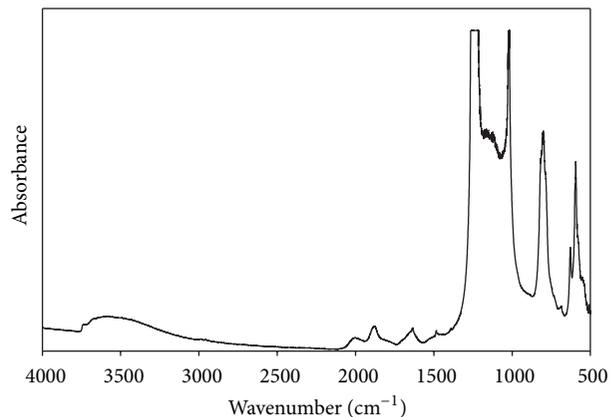


FIGURE 1: FT-IR spectrum of dehydrated NaZSM-5. Note: the effective windows for monitoring the adsorption and reaction of species on the zeolite surface are $>1300\text{ cm}^{-1}$ and $770\text{--}630\text{ cm}^{-1}$.

TABLE 1: FT-IR peaks for chlorobenzene adsorbed into NaZSM-5 at 25°C .

Position (cm^{-1})	Intensity	Identification*
3076	w	$\nu(\text{CH})$
2952	w	overtone
1959	w	
1938	w	
1880	w	
1861	w	
1582	m	$\nu(\text{CC})$
1479	s	$\nu(\text{CC})$
1445	m	$\nu(\text{CC})$
1349	w	$\nu(\text{CC})$
739	s	$\gamma(\text{CH})$
701	m	X-sens.r
684	m	$\phi(\text{CC})$

* Refer to [23].

adsorption sites. There are approximately 1.3 cations per unit cell for this ZSM-5 and, as may be observed from Figure 2, comparable loadings between the two sites.

Adsorption of NO_2 into the lattice immediately gives rise to strong peaks at 2910, 2048, 2005, 1915, 1902, 1830, 1742, 1709, 1687, and 1618 cm^{-1} (see Figure 3). Formation of N_2O_4 is enhanced in the lattice compared with the gas phase. The peaks at 1742 and 1830 cm^{-1} correspond to the symmetric and asymmetric, ONONO_2 , forms [24]. The proportion of the asymmetric forms grows slightly over the course of the reaction. The intensity of the symmetric N_2O_4 band at 1742 cm^{-1} decreases with time indicating that N_2O_4 is consumed during the reaction.

There are overtones and combination bands above 2800 cm^{-1} . At 1902 cm^{-1} there is a peak appropriate for NO [25]. This peak grows over the course of the reaction and also if a fresh pellet is exposed only to NO_2 but there is no evidence for the formation of N_2O_3 nor N_2O_5 . A possible explanation is selective adsorption of trace impurity NO , found in the

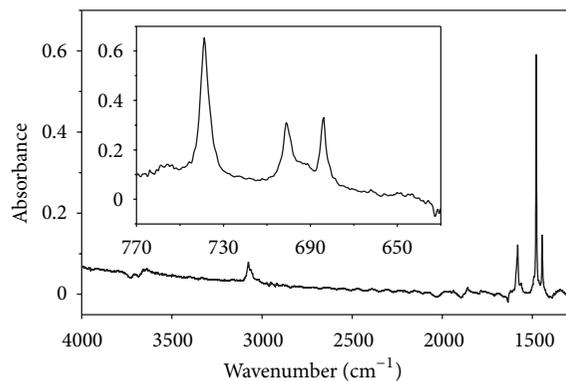


FIGURE 2: FT-IR difference spectrum ((zeolite + chlorobenzene) – empty zeolite) of chlorobenzene adsorbed into NaZSM-5 at 50°C.

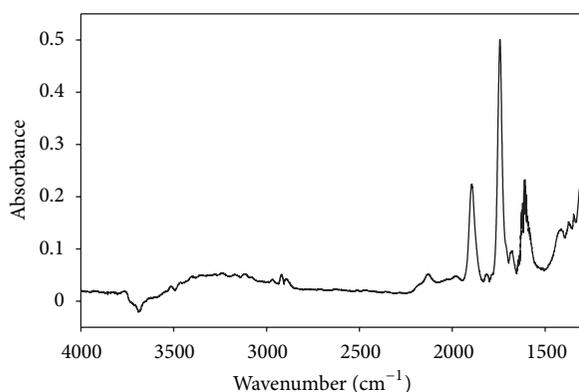


FIGURE 3: FT-IR difference spectrum of NO₂ adsorbed into a clean dehydrated NaZSM-5 pellet at 50°C.

NO₂, from the gas phase, and that the adsorption on the zeolite internal surface under these conditions inhibits N₂O₃ formation. NO₂⁺ is not visible at 2350 cm⁻¹ and NO₂⁻ is undetectable at 1244 cm⁻¹ because of the ZSM-5 framework [26, 27].

The bands between 2000 and 2100 cm⁻¹ are broad and result from NO₂^{δ+} with increasing δ values on going to higher wave number [22]. These species are formed by partial electron donation to the Na⁺ cations. During the reaction, the intensity of these bands is diminished (see Figure 4, traces c and d).

The nitration of chlorobenzene using NO₂ proceeds spontaneously at room temperature. The chlorobenzene and NO_x bands decrease in intensity with a concomitant growth of peaks at 3128, 2855, 1955, 1911, 1835, 1605, 1582, 1514, 1423, 1348, and 1316 cm⁻¹. Comparison with authentic samples adsorbed into NaZSM-5 indicates that the sole chloronitrobenzene product is para-chloronitrobenzene. The bands at 1955 and 1835 cm⁻¹ correspond to symmetric and asymmetric ONONO₂, respectively.

Comparison of the spectrum for an authentic sample of para-chloronitrobenzene adsorbed into NaZSM-5 (see Table 2) with that for the reaction product reveals that the authentic sample has two peaks at 1528 and 1514 cm⁻¹ in the region of the –NO₂ asymmetric stretch, while the product

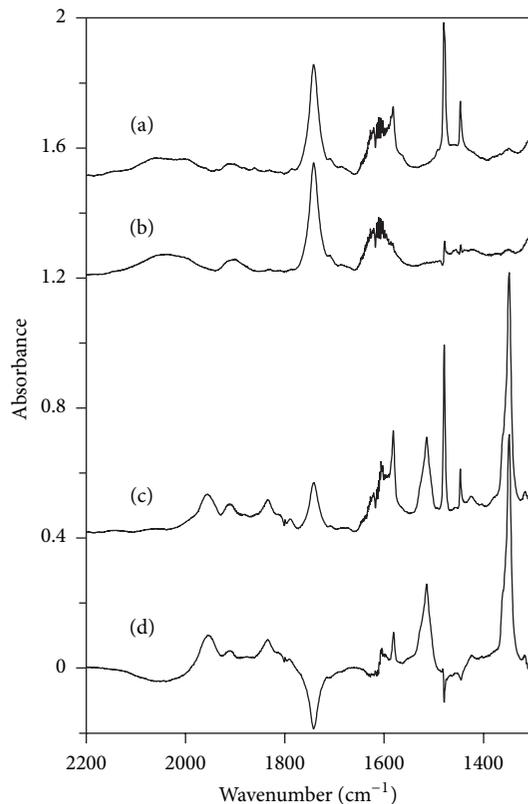


FIGURE 4: FT-IR spectra of chlorobenzene and NO₂ in NaZSM-5 at 50°C: (a) at time $t = 0$; (b) difference between zeolite + chlorobenzene (Figure 2) and zeolite + chlorobenzene + NO₂ (trace a) highlighting the NO₂ bands under the initial reaction conditions; (c) after 240 min of reaction; (d) difference between time $t = 0$ (trace a) and $t = 240$ min (trace c).

spectrum has only a single peak at 1514 cm⁻¹. The discrepancy arises from the adsorption of chloronitrobenzene onto the two sites (cation-free and cation) during the preparation of the authentic sample while populating only the cation site during the reaction.

The reaction is highly temperature dependent. Less than 5% of the chlorobenzene is consumed at 0°C, which increases to 27% (along with 64% of the N₂O₄) at 50°C. Figures 5 and 6 illustrate these trends over the course of the reaction. At higher temperatures, reduced adsorption into the lattice increases the percent completion, but diminishes the absolute yield of product. At 100°C, essentially all of the adsorbed chlorobenzene is found on the cation-associated sites.

Para-chloronitrobenzene was obtained as the sole product for the reaction of NO₂ with chlorobenzene under the reaction conditions. These results illustrate the selectivity that may be obtained using zeolite catalysis and carefully selecting the reaction conditions. The three conditions of importance are a mild nitrating agent and the loading of the zeolite to maximize reaction on the internal surface and temperature.

The active nitrating species is NO₂^{δ+} formed by the interaction of adsorbed NO₂ with the electrostatic fields of the poorly shielded Na⁺ cations in the NaZSM-5 lattice [22].

TABLE 2: FT-IR peaks for para-chloronitrobenzene adsorbed into NaZSM-5 at 25°C.

Position (cm ⁻¹)	Intensity	Identification*
3128	w	ν_1
2855	w	$\nu_3 + \nu_{17}$
1911	w	$2 \nu_{11}$
1605	w	ν_2
1582	m	ν_{16}
1514	s	$\nu_{12}, \nu_{as}(\text{NO}_2)$
1481	m	ν_{26}
1424	w	ν_{34}
1348	s	$\nu_3, \nu_s(\text{NO}_2)$
1316	w	$\nu_{38} + \nu_5$
745	m	$\nu_{40}, \gamma(\text{NO}_2)$
742	m	$\nu_{40}, \gamma(\text{NO}_2)$
678	w	ν_{13}

* Refer to [28].

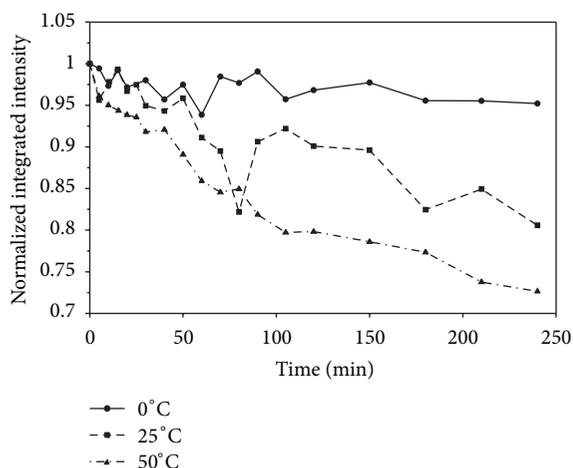


FIGURE 5: Normalized integrated peak intensities as a function of time for the 1445 cm⁻¹ mode of chlorobenzene at 0°C, 25°C, and 50°C.

The $\text{NO}_2^{\delta+}$ are less reactive than the NO_2^+ produced using acid zeolites such as HZSM-5 which, under the experimental conditions, eliminates secondary nitration.

Reaction on the internal surface is enhanced by the sequential loading of reagents. Evacuating the sample cell after loading chlorobenzene essentially removes gas phase and physisorbed external surface molecules. After the loading of NO_2 , the full zeolite channels prevent rapid and extensive diffusion within the pores (the two adsorption site populations do not intermix) suggesting that the movement to the external surface is also minimized.

Temperature plays a nonlinear role in the efficiency and selectivity of the reaction (see Figure 7). Increasing the temperature enhances the rate of formation of $\text{NO}_2^{\delta+}$ [22] and hence the rate of nitration, as well as enhancing the rate of reagent diffusion, possibly increasing the percent conversion. However, increasing temperature also reduces the amount of

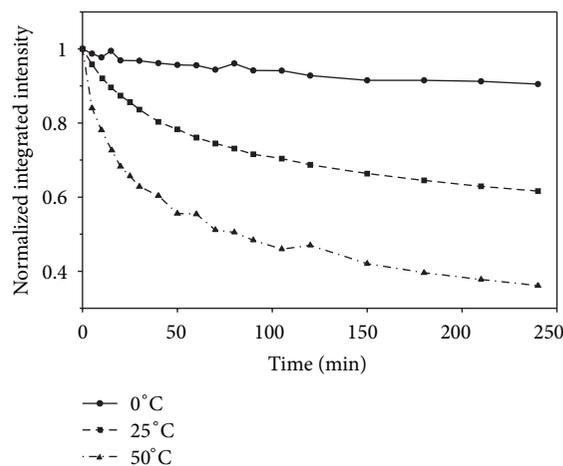


FIGURE 6: Normalized integrated peak intensities as a function of time for the 1742 cm⁻¹ mode of N_2O_4 at 0°C, 25°C, and 50°C.

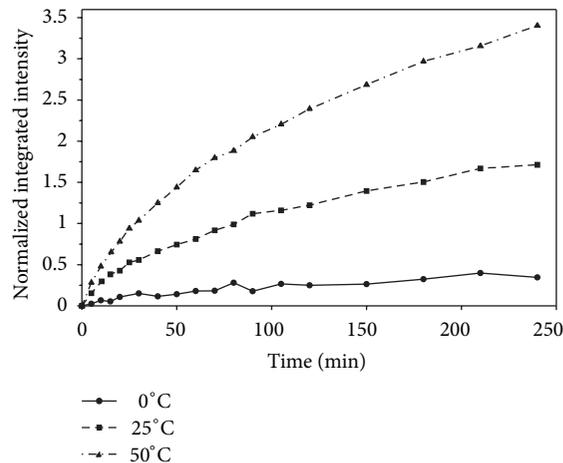


FIGURE 7: Normalized integrated peak intensities as a function of time for the growth of the asymmetric stretch of chloronitrobenzene at 1514 cm⁻¹ (a) 0°C; (b) 25°C; (c) 50°C.

NO_2 adsorbed into the ZSM-5 lattice, which will reduce the fraction of the nitration occurring on the internal surface. Even at 50°C, the amount of NO_2 available seems to be a limiting factor in the reaction. This is supported by studies using HZSM-5, where chloronitrobenzene yields dropped from 27.0 to 12.2% on raising the temperature from 125 to 250°C [18, 19].

4. Conclusions

Reaction under mild conditions of chlorobenzene and NO_2 in NaZSM-5 selectively and at good yield produced para-chloronitrobenzene. The results from this study along with those obtained in acid zeolites illustrate that the reaction conditions must be carefully chosen to maximize desired product yields and that the effects of some parameters (such as temperature) are nonlinear.

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References

- [1] Y. Z. Chen and Y. C. Chen, "Hydrogenation of Para-chloronitrobenzene over nickel borides," *Applied Catalysis A*, vol. 115, no. 1, pp. 45–57, 1994.
- [2] B. Coq, A. Tizani, and F. Figueras, "Particle size effect on the kinetics of *p*-chloronitrobenzene hydrogenation over platinum/alumina catalysts," *Journal of Molecular Catalysis*, vol. 68, pp. 331–345, 1991.
- [3] H. H. Szmato, *Organic Building Blocks of the Chemical Industry*, John Wiley & Sons, New York, NY, USA, 1989.
- [4] T. Yoshida, "Determination of *p*-chloronitrobenzene in plasma by reversed-phase high-performance liquid chromatography," *Journal of Chromatography B*, vol. 570, pp. 321–318, 1991.
- [5] G. S. Travlos, J. Mahler, H. A. Ragan, B. J. Chou, and J. R. Bucher, "Thirteen-week inhalation toxicity of 2- and 4-chloronitrobenzene in F344/N rats and B6C3F1 mice," *Fundamental and Applied Toxicology*, vol. 30, no. 1, pp. 75–92, 1996.
- [6] R. J. Argauer and G. R. Landolt, "Crystalline zeolite zsm-s and method," U.S. Patent 3702886, 1972.
- [7] F. G. Dwyer and E. E. Jenkins, "Crystalline silicates and method of preparing the same," U.S. Patent 3941871, 1976.
- [8] D. H. Olson, G. T. Kokotailo, S. L. Lawton, and W. M. Meier, "Crystal structure and structure-related properties of ZSM-5," *Journal of Physical Chemistry*, vol. 85, no. 15, pp. 2238–2243, 1981.
- [9] R. W. Neuzil, "Aromatic hydrocarbon separation by adsorption," U.S. Patent 3558730, 1973.
- [10] R. W. Neuzil, "Aromatic hydrocarbon separation by adsorption," U.S. Patent 3558732, 1973.
- [11] J. J. Ward, "Molecular sieve catalysis," in *Applied Industrial Catalysis*, B. B. Leach, Ed., vol. 3, p. 271, Academic Press, New York, NY, USA, 1984.
- [12] J. Kärger and D. M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids*, John Wiley & Sons, New York, NY, USA, 1992.
- [13] J. March, *Advanced Organic Chemistry*, John Wiley & Sons, New York, NY, USA, 3rd edition, 1985.
- [14] S. Takenaka, T. Nishida, and J. Kanemoto, "Process for preparing mononitrochlorobenzene," U.S. Patent 4476335, 1984.
- [15] I. Schumaker and K. B. Wang, "Vapor phase nitration of aromatic compounds," U. S. Patent 4415744, 1983.
- [16] I. Schumaker, "Vapor phase nitration of aromatic compounds," U. S. Patent 4618733, 1986.
- [17] N. V. Testova, L. V. Malysheva, K. G. Ione, E. A. Paukshtis, and N. F. Salakutdinov, "Gas phase nitration of aromatic hydrocarbons on zeolite catalysts. The role of acid sites and peculiarities of the reaction course," in *Proceedings of the International Meeting "Zeolite Catalysis for the Solution of Environmental Problems"*, pp. 137–154, Yaroslavl, Russia, 1992.
- [18] N. F. Salakutdinov, K. G. Ione, E. A. Kobzar, and L. V. Malysheva, "Gas-phase nitration of aromatic-compounds through nitrogen-dioxide on zeolites," *Zhurnal Organicheskoi Khimii*, vol. 29, pp. 546–558, 1993.
- [19] L. V. Malysheva, E. A. Paukshtis, and K. G. Ione, "Nitration of aromatics by nitrogen oxides on zeolite catalysts: comparison of reaction in the gas phase and solutions," *Catalysis Reviews*, vol. 37, pp. 179–226, 1995.
- [20] S. J. Kirkby and H. Frei, "Highly selective photochemical and thermal chlorination of benzene by Cl₂ in NaZSM-5," *Journal of Physical Chemistry B*, vol. 102, no. 37, pp. 7106–7111, 1998.
- [21] S. J. Kirkby, "Acid free nitration of benzene and toluene in zeolite NaZSM-5," *ISRN Physical Chemistry*. In press.
- [22] H. P. Wang, T. Yu, B. A. Garland, and E. M. Eyring, "Benzene in Zeolite ZSM-5 studied by diffuse reflectance infrared spectroscopy," *Applied Spectroscopy*, vol. 44, no. 6, pp. 1070–1073, 1990.
- [23] D. H. Whiffen, "Infra-red summation bands of the out-of-plane C-H bending vibrations of substituted benzene compounds," *Spectrochimica Acta*, vol. 7, pp. 253–263, 1955.
- [24] R. V. St. Louis and B. Crawford Jr., "Infrared spectrum of matrix-isolated NO₂," *Journal of Chemical Physics*, vol. 42, pp. 857–864, 1965.
- [25] M. Katoh, T. Yamazaki, H. Kamijo, and S. Ozawa, "Infrared studies on nitrogen oxides adsorbed on alkali metal ion-exchanged ZSM-5 zeolites," *Zeolites*, vol. 15, no. 7, pp. 591–596, 1995.
- [26] J. W. Nebgen, A. D. McElroy, and H. F. Klodowski, "Raman and infrared spectra of nitronium perchlorate," *Inorganic Chemistry*, vol. 4, no. 12, pp. 1796–1799, 1965.
- [27] D. E. Milligan and M. E. Jacox, "Matrix-Isolation Study of the Interaction of Electrons and Alkali Metal Atoms with Various Nitrogen Oxides. Infrared Spectra of the Species NO⁻, NO₂⁻, and N₂O₂⁻," *Journal of Chemical Physics*, vol. 55, pp. 3404–3418, 1971.
- [28] J. H. S. Green and D. J. Harrison, "Vibrational spectra of benzene derivatives-X: monosubstituted nitrobenzenes," *Spectrochimica Acta A*, vol. 26, pp. 1925–1937, 1970.



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