J. Chem. Eng. Data **2002,** *47,* 587−589

Adsorption of Nitrous Oxide on Silicalite-1

Johan C. Groen,*,† Javier Pérez-Ramírez,‡ and Weidong Zhu‡

Applied Catalyst Characterization, Industrial Catalysis, DelftChemTech, Delft University of Technology, Julianalaan 136, 2628 BL, Delft, The Netherlands

The adsorption of nitrous oxide (N_2O) on silicalite-1 has been investigated using a volumetric method. The adsorption isotherms are for the first time reported at temperatures in the range of 273 K to 398 K and at pressures up to 120 kPa. The Langmuir isotherm appropriately fits the equilibrium data. The thermodynamic properties such as the Henry's law constant and enthalpy associated with the adsorption are derived to characterize interactions between adsorptive and adsorbent.

Introduction

Nitrous oxide (N_2O) has been identified as a greenhouse gas (150 times stronger than CO_2) and a contributor to the destruction of ozone in the stratosphere.[1,2] The concentration of this pollutant in the atmosphere is steadily increasing, mainly caused by anthropogenic activities, such as agriculture, chemical production, and combustion (stationary and mobile) processes. Emissions from the chemical industry, mainly adipic acid and nitric acid production, can be effectively reduced in the short term.[2,3] Control of N_2O emissions in these cases usually involves a catalytic process, either by an *end-of-pipe* treatment (direct N_2O decomposition into N_2 and O_2 or N_2O reduction with hydrocarbons or ammonia) or by the reuse of N_2O in the tail gas for other reactions to valuable products. All these processes are catalyzed by metal-loaded MFI-type zeolites, including ZSM-5 and silicalite-1.[4−8] Reutilization of N_2O consists of its use as a selective and valuable oxidant in the environmental benign and sustainable industrial manufacture of fine and intermediate chemicals, such as phenol (from benzene) or methanol (from methane).[7,8] The recovery of N_2O can be easily applied in exhausts from adipic acid plants, which are characterized by high N_2O concentrations (>30 vol %). In other sources such as nitric acid plants, where diluted N_2O streams are present (0.05 vol % to 0.2 vol %), the selective adsorption of N_2O on metal ion-exchanged ZSM-5 has been proposed to produce a concentrated stream of N_2O (>5 vol %).[9]

This work addresses the fundamental science of this important process. The application of MFI-type zeolite either as a catalyst or as an adsorbent in the different processes described above makes the acquisition of adsorption isotherms of N_2O in this zeolitic material very important and useful for practical design and understanding of adsorption, diffusion, and reaction. Adsorption equilibrium is, on one hand, the key information for the design of practical separation processes based on adsorption mechanisms. The adsorption isotherm data are, on the other hand, of utmost importance for modeling the catalytic kinetics. However, up to now there has been hardly any data available concerning the adsorption properties of N_2O on silicalite-1.

This paper presents experimental results for the adsorption of N_2O on silicalite-1 determined by a volumetric method. Different thermodynamic properties, like the enthalpy and the Henry's law constant associated with adsorption, are presented to characterize interactions between adsorptive and adsorbent.

Experimental Section

Adsorption. A Micromeritics ASAP 2010 gas adsorption analyzer (stainless steel version) was used to accurately measure the gas uptake by the adsorbent in the pressure range from 0.1 kPa to 120 kPa. The instrument was equipped with a molecular drag vacuum pump and two different pressure transducers (1.33 kPa, uncertainty <0.15% of reading and 133 kPa, uncertainty <0.1% of full scale) to enhance the sensitivity in the low-pressure range, which is especially useful in adsorption studies on microporous materials. The static-volumetric technique is used to determine the volume of gas adsorbed at different partial pressures: upon adsorption a pressure decrease is observed in the gas phase, which is a direct measure of the amount adsorbed.

The sample cell was loaded with 240 mg of silicalite-1 crystals. Prior to the adsorption measurements the crystals were outgassed in situ in vacuum at 623 K for 16 h to remove any adsorbed impurities. The obtained dry sample mass was used in the calculation of isotherm data. Adsorption measurements were subsequently done at different temperatures from 273 K to 398 K. The temperature was controlled within ±0.3 K using an ice−water mixture to fix the temperature at 273 K and a circulating oil bath to control the temperatures up to 398 K. Five different temperatures were used to reduce the uncertainty in the derived adsorption parameters (273 K, 298 K, 323 K, 373 K, and 398 K).

The gaseous adsorptive nitrous oxide, obtained from Hoekloos with a specified purity over 99%, was used without further purification. Helium was obtained as an ultra-high-purity gas (>99.995%, Air Products) and was used to determine the free space of the sample cell.

Adsorbent. The silicalite-1 crystals with a ratio Si/Al > 1300 were synthesized in-house. The template inside the silicalite-1 crystals was removed by calcination at 873 K for 12 h. The apparent density of the sample was 1.76 g cm^{-3}, and the adsorption of N_2 indicated an accessible

---

* To whom correspondence should be addressed. Tel.: +31 (0) 15 278 4371. Fax: +31 (0) 15 278 4452. E-mail: j.c.groen@tnw.tudelft.nl.

† Applied Catalyst Characterization.

‡ Industrial Catalysis.

10.1021/je015527l CCC: $22.00

Table 1. Experimental Isotherm Data for N_2O on Silicalite-1

p / kPa	q / mol kg^{-1}	p / kPa	q / mol kg^{-1}	p / kPa	q / mol kg^{-1}	p / kPa	q / mol kg^{-1}	p / kPa	q / mol kg^{-1}
$T = 273$ K		$T = 298$ K		$T = 323$ K		$T = 373$ K		$T = 398$ K	
0.13	0.018	0.14	0.008	0.14	0.003	0.15	0.000	0.16	0.000
0.64	0.082	0.70	0.036	0.67	0.015	0.75	0.004	0.76	0.001
1.6	0.185	1.4	0.066	1.7	0.036	1.7	0.009	1.7	0.004
3.3	0.340	3.4	0.149	3.3	0.070	3.4	0.019	3.4	0.009
6.4	0.596	6.7	0.276	6.6	0.132	6.7	0.037	6.7	0.020
10.0	0.844	10.8	0.416	10.0	0.193	10.1	0.055	10.0	0.031
14.1	1.069	13.4	0.497	12.9	0.241	13.2	0.072	13.3	0.040
16.7	1.197	16.7	0.596	16.7	0.303	16.7	0.090	16.7	0.051
20.1	1.337	20.0	0.688	20.0	0.355	20.0	0.107	20.0	0.061
23.6	1.456	23.4	0.773	23.4	0.404	23.4	0.123	23.4	0.071
27.0	1.559	26.8	0.853	26.7	0.452	26.7	0.139	26.7	0.081
30.4	1.649	30.2	0.927	30.1	0.498	30.1	0.154	30.1	0.091
33.9	1.728	33.6	0.997	33.4	0.542	33.4	0.169	33.4	0.100
37.3	1.797	37.0	1.061	36.8	0.584	36.7	0.184	36.7	0.109
40.7	1.857	40.4	1.122	40.2	0.625	40.1	0.199	40.1	0.118
44.0	1.909	43.8	1.178	43.6	0.664	43.4	0.213	43.4	0.127
46.7	1.949	46.7	1.223	46.7	0.699	46.7	0.226	46.7	0.136
50.0	1.994	50.0	1.272	50.0	0.735	50.0	0.240	50.0	0.145
53.4	2.034	53.4	1.317	53.4	0.769	53.4	0.253	53.4	0.154
56.7	2.070	56.7	1.360	56.7	0.803	56.7	0.266	56.7	0.162
60.0	2.104	60.0	1.400	60.0	0.835	60.0	0.278	60.0	0.170
63.4	2.135	63.3	1.438	63.4	0.865	63.4	0.291	63.4	0.179
66.7	2.163	66.7	1.474	66.7	0.894	66.7	0.303	66.7	0.187
70.0	2.190	70.0	1.507	70.0	0.923	70.0	0.315	70.0	0.195
73.4	2.215	73.3	1.539	73.4	0.950	73.4	0.326	73.4	0.202
76.7	2.238	76.7	1.569	76.7	0.976	76.7	0.337	76.7	0.209
80.0	2.259	80.0	1.597	80.0	1.001	80.0	0.348	80.0	0.217
83.3	2.279	83.3	1.623	83.4	1.025	83.4	0.359	83.4	0.224
86.7	2.298	86.7	1.648	86.7	1.049	86.7	0.369	86.7	0.230
90.0	2.315	90.0	1.672	90.1	1.071	90.0	0.379	90.0	0.236
93.4	2.332	93.3	1.694	93.3	1.093	93.4	0.389	93.4	0.242
96.7	2.347	96.7	1.716	96.7	1.114	96.7	0.398	96.7	0.249
100.0	2.362	100.0	1.736	100.0	1.133	100.0	0.407	100.0	0.255
103.4	2.375	103.3	1.755	103.3	1.151	103.4	0.415	103.3	0.260
106.7	2.388	106.7	1.773	106.7	1.170	106.7	0.424	106.7	0.266
110.0	2.401	110.0	1.790	110.0	1.189	110.0	0.433	110.0	0.271
113.4	2.413	113.3	1.807	113.4	1.206	113.4	0.441	113.3	0.276
116.7	2.424	116.7	1.821	116.7	1.222	116.7	0.450	116.7	0.281
120.0	2.434	120.0	1.836	120.0	1.237	120.0	0.458	120.0	0.286

microporous void volume of 0.179 cm^3 g^{-1} and a microporous area of 372 m^2 g^{-1}.

Results and Discussion

Isotherms. The isotherm data of N_2O adsorbed on silicalite-1 are presented in Table 1. The isotherms were reversible over the complete pressure range investigated. For the sake of clarity, the desorption data are omitted.

For any practical application, the experimental data should be described by an analytical expression including adjustable parameters as a function of temperature. Various empirical methods have been proposed to fit isotherm data. In many cases, however, it may not be easy to determine a set of isotherm parameters that can represent all the experimental data at multiple temperatures with good accuracy.

The determined isotherms of N_2O on silicalite-1 exhibit a type-I adsorption isotherm (Brunauer classification) over the temperature and pressure range studies, as shown in Figure 1. For adsorption on heterogeneous adsorbents such as zeolites, the Langmuir model is often used to fit isothermal data.[10]

$$q = q_{\mathrm{sat}}\frac{Kp}{1 + Kp} \qquad (1)$$

where q is the amount adsorbed, q_{sat} is the saturation amount adsorbed, K is the equilibrium constant, and p is the pressure. The Langmuir equation can describe the isotherm data well, also included in Figure 1. Because of its simplicity in form and its correct behavior at low and high pressures, the Langmuir model is usually recommended as the first choice of isotherm equations for fitting adsorption data, especially for engineering purposes. The estimated values of the adsorption parameters in the Langmuir model are listed in Table 2. The fitted values of equilibrium parameters show the temperature dependence. In principle, the saturation amount adsorbed, q_{sat}, should stay constant in the Langmuir model. However, the results in Table 2 show that q_{sat} is a function of temperature and decreases with temperature in the range from 273 K to 323

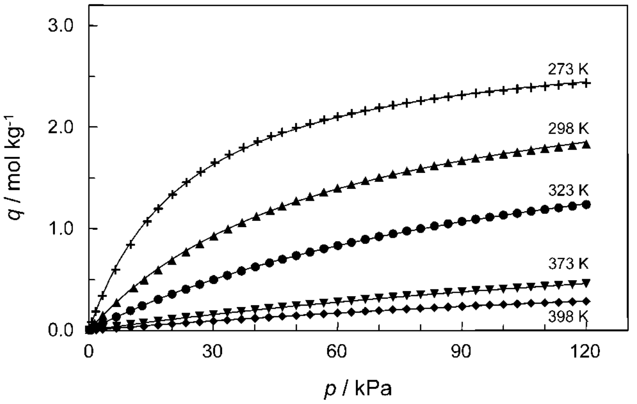

Figure 1. Adsorption isotherms of N_2O on silicalite-1 at different temperatures. Lines are the Langmuir isotherm model fits.

Table 2. Fitted Values and Standard Deviations of Adsorption Equilibrium Constants (Eq 1) and the Estimated Values of the Henry's Law Constant (Eq 3)

T	q_{sat}	$K \times 10^2$	σ_{model}[a]	$K_H \times 10^2$
K	mol kg^{-1}	kPa^{-1}	mol kg^{-1}	mol kg^{-1} kPa^{-1}
273	2.934 ± 0.006	4.173 ± 0.029	0.009	13.09
298	2.769 ± 0.011	1.684 ± 0.015	0.008	5.028
323	2.469 ± 0.010	0.847 ± 0.006	0.003	2.191
373	1.332 ± 0.010	0.439 ± 0.005	0.001	0.589
398	1.012 ± 0.027	0.335 ± 0.012	0.002	0.334

[a] Standard deviation model: $\sqrt{\sum_n (q_{cal} - q_{exp})^2/(n-j)}$, for j fitting parameters.

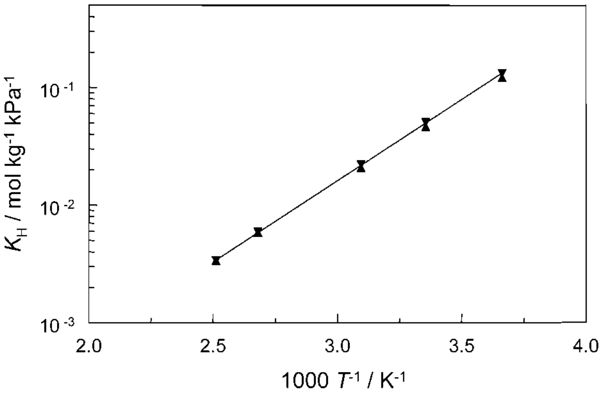

Figure 2. ln K_H vs 1/T plot for the studied adsorptive by silicalite-1. ▲, K_H data from eq 2; ▼, K_H data from eq 3.

K, while fitted q_{sat} data dramatically decrease at higher temperatures. This might be caused by a lack of higher loading data at higher temperatures.

Thermodynamic Properties. From the isotherm data a number of thermodynamic properties have been derived. The Henry's law constant, K_H, quantifies the extent of adsorption of a given adsorptive by a solid. The magnitude of K_H depends on both the properties of the adsorptive and solid. As a first estimate of the Henry's law constant, its value can be obtained from the fitting results for the Langmuir model,

$$K_H = q_{sat}K \tag{2}$$

An alternative way of representing the equilibrium data to extract the Henry's law constant makes use of the virial form of the thermodynamic equilibrium relation.[11]

$$K_H = \frac{q}{p}\exp\left(2A_1 q + \frac{3}{2}A_2 q^2 + \frac{4}{3}A_3 q^3 + ...\right) \tag{3}$$

where K_H is the Henry's law constant, q the amount adsorbed, p the equilibrium pressure, and A_i the virial coefficient. It is evident that ln(p/q) vs q should approach linearity at low loadings, thus providing a straightforward extrapolation to determine the Henry's law constant K_H. The K_H values obtained in this way at the different temperatures, included in Table 2, can be described with the integrated form of the van't Hoff equation,

$$K_H = K_{H0}\exp\left(\frac{-\Delta H°}{RT}\right) \tag{4}$$

From the observed linearity of the ln K_H vs 1/T plot, Figure 2, the enthalpy of adsorption at zero coverage, $\Delta H°$, and the pre-exponential factor, K_{H0}, are determined. The estimated values of $\Delta H°$ and K_{H0} are -26.5 kJ mol^{-1} and 1.14×10^{-6} mol kg^{-1} kPa^{-1}, respectively. It is interesting to note that the derived values of K_H by eqs 2 and 3 are consistent, as shown in Figure 2. This also indicates the quality of the model fits.

Conclusion

The equilibrium adsorption data of nitrous oxide (N_2O) on silicalite-1 have been accurately measured by a volumetric technique. The isotherms are for the first time reported in the temperature range from 273 K to 398 K and at pressures up to 120 kPa. The Langmuir isotherm expression appropriately fits the equilibrium data. The reported experimental data might be useful for the design and modeling of processes involving (i) N_2O conversions on MFI-based catalysts, including catalytic decomposition, selective catalytic reduction, or selective catalytic oxidation processes or (ii) selective adsorption in metal-based zeolites at room temperature to concentrate tail-gas streams containing N_2O. This includes adsorption, diffusion, and reaction kinetics.

Literature Cited

(1) Rodhe, H. A comparison of the contribution of various gases to the greenhouse effect. *Science* **1990**, *248*, 1217−1219.

(2) Centi, G.; Perathoner, S.; Vanazza, F. Catalytic control of non-CO_2 greenhouse gases. *CHEMTECH* **1999**, *12*, 48−55.

(3) Kapteijn, F.; Rodríguez-Mirasol, J.; Moulijn, J. A. Heterogeneous catalytic decomposition of nitrous oxide. *Appl. Catal. B* **1996**, *9*, 25−64.

(4) Pérez-Ramírez, J.; Kapteijn, F.; Mul, G.; Moulijn, J. A. Superior performance of *ex*-framework FeZSM-5 in direct N_2O decomposition in tail-gases from nitric acid plants. *Chem. Commun.* **2001**, 693−694.

(5) Mauvezin, M.; Delahay, G.; Kisslich, F.; Coq, B.; Kieger, S. Catalytic reduction of N_2O by NH_3 in presence of oxygen using Fe-exchanged zeolites. *Catal. Lett.* **1999**, *62*, 41−44.

(6) Centi, G.; Vazzana, F. Selective catalytic reduction of N_2O in industrial emissions containing O_2, H_2O and SO_2: behavior of Fe/ZSM-5 catalysts. *Catal. Today* **1999**, *53*, 683−693.

(7) Hoelderich, W. Environmentally benign manufacturing of fine and intermediate chemicals. *Catal. Today* **2000**, *62*, 115−130.

(8) Panov, G. I. Advances in oxidation catalysis; oxidation of benzene to phenol by nitrous oxide. *CATTECH* **2000**, *4*, 18−31.

(9) Centi, G.; Generali, P.; dall'Olio, L.; Perathoner, S. Removal of N_2O from industrial gaseous streams by selective adsorption over metal-exchanged zeolites. *Ind. Eng. Chem. Res.* **2000**, *39*, 131−137.

(10) Barrer, R. M. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; John Wiley & Sons: New York, 1982.

(11) Ross, S.; Olivier, J. P. *On Physical Adsorption*; John Wiley & Sons: New York, 1964.

Received for review October 15, 2001. Accepted February 25, 2002.

JE015527L