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Equilibrium and Dynamic Adsorption of Carbon Monoxide and Nitrogen on ZSM-5 with Different SiO_2/Al_2O_3 Ratio

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The adsorption of CO and N_2 in ZSM-5 with different SiO_2/Al_2O_3 ratio has been investigated both by static volumetric measurements and dynamic adsorption study. The adsorption capacity of CO and its selectivity over N_2 decreases with an increase in the SiO_2/Al_2O_3 ratio. ZSM-5 (25) showed highest selectivity for CO over N_2 whereas ZSM-5 (900) showed lowest CO selectivity. The dynamic adsorption study revealed that the breakthrough time of CO decreases while the dynamic adsorption capacity increases with an increase in CO percentage of gas mixture at fixed flow rate. The heat of adsorption for CO and N_2 decreases with an increase in SiO_2/Al_2O_3 ratio. The values for the Henry's constant, the Langmuir constant, and the slope are also reported for CO and N_2 adsorption isotherms on ZSM-5 having different SiO_2/Al_2O_3 ratio.

Keywords CO adsorption; dynamic adsorption; equilibrium adsorption; N_2 adsorption; ZSM-5

INTRODUCTION

The increase in CO and CO_2 concentration of atmosphere adds to global warming, and that has the potential for many devastating changes such as rising global temperatures and melting of ice glaciers leading to sea level rise. CO is a good source of carbon for C1 chemistry and has a number of industrial applications. The most likely options for CO separation and capture includes chemical absorption, chemical and physical adsorption, cryogenic distillation, and gas separation membranes. Gas separation using zeolites, activated carbon, and carbon molecular sieve potentially offers a cost-effective and environmentally friendly option (1–14).

An adsorption-based separation technique has been widely used in the chemical, petrochemical, and fertilizer industries to recover the gases especially CO, CH_4, H_2, and N_2 from their gas mixtures; and air and hydrocarbon separation (15–18). The adsorbents based on zeolites, activated carbons, alumina, and modified alumina are commercially used for CO recovery from mixtures by pressure/vacuum/temperature swing adsorption (19). The adsorption properties of zeolite based adsorbents can be influenced by their SiO_2/Al_2O_3 ratio, pore size, chemical composition, nature, and location of extra framework cations. The pore size of zeolite in combination with the chemical composition such as SiO_2/Al_2O_3 ratio and the nature of the extra framework cations determines the effectiveness of zeolite based adsorbents (20). The heat of adsorption for zeolite is generally lower. Consequently, stripping of the adsorbed molecules is easier and results in lower energy requirements for regeneration of the adsorbent. Therefore, zeolites are good candidates for the effective separation of CO from industrial waste gases (21). The best adsorbent for the application is determined by its capacity or by differences in intraparticle diffusivities (22–25). PVSA technology gained interest because of the low energy requirements and low capital investment cost (26).

A wide range of literature is available on the equilibrium and dynamic adsorption of CO and N_2 on different adsorbents. Many solid and liquid absorbents for CO separation have been reported (27). The copper-ammonium-salt liquor process wherein CO is absorbed at high pressure in an aqueous solution of copper-ammonium-salt by the formation of a copper-ammonium-CO complex is used for the recovery of CO (28). The COSORB process has also been used to recover CO, wherein the toluene solution containing aluminum copper (I) chloride ($AlCuCl_4$) selectively absorbs CO under mild conditions, and this process has substantial capital and operating advantages over the copper-ammonia-salt liquor process and the cryogenic process (29). In $AlPO_4$, the adsorption capacities for CO and N_2 were dependent on the size and geometry of the pore, as well as the molecular dimensions and polarity of the adsorbate (30). A double layer adsorbent column

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was used by Park et al. for hydrogen separation from a typical cracked gas mixture (H_2, CO_2, CH_4, CO) (31,32). Transition metal halide impregnated activated carbon has a high CO adsorption capacity. Huang have reported that Y type- zeolite-supported copper (I) ion adsorbs CO, and that the interaction between CO and the copper (I) ion is too strong to desorb CO (33). Hirai et al. have prepared a polystyrene-supported copper-aluminum complex and an activated carbon-supported copper(I) chloride, and reported that the effective CO adsorption was due to the formation of the complex between CO and copper (I) chloride, which is highly dispersed on the surface of the adsorbents (34). Two different coordination modes of CO in Na-ZSM-5 zeolites, the formation of $Na^+ \rightarrow CO$ and $Na^+ \rightarrow OC$ adducts between the adsorbed CO and extra-framework Na^+ ions have also been reported (35).

Carbon monoxide is usually obtained by separation from synthesis gases produced by catalytic conversion or partial oxidation of natural gas, oils, or other hydrocarbon feedstock. In addition to carbon monoxide, these gases contain primarily hydrogen and methane but are often contaminated with significant amounts of nitrogen derived from the feed or added during processing. Conventional cryogenic separation processing leaves nitrogen as an impurity in the carbon monoxide, which, for both environmental and processing reasons, is unacceptable for some uses of carbon monoxide. The problem of nitrogen contamination of the carbon monoxide product is becoming an increasing problem with the usage of more marginal feed stock in front end reforming processes. In view of this, there is a demand for efficient and effective removal of contaminant nitrogen from carbon monoxide-containing feeds. The separation of nitrogen from carbon monoxide is relatively difficult compared to the removal of hydrogen or methane (36). Carbon dioxide, methane, and nitrogen adsorption on zeolite ZSM-5 has been studied by few researchers but a systematic study on the effect of SiO_2/Al_2O_3 ratio on adsorption properties of carbon monoxide and nitrogen in zeolite ZSM-5 has not been reported yet (37–39). Herein, we report the CO and N_2 adsorption on the ZSM-5 having different SiO_2/Al_2O_3 ratio, both by volumetric equilibrium adsorption measurements and dynamic adsorption study. Volumetric adsorption measurements of CO and N_2 up to 1 atmospheric pressure at 288 K and 303 K were carried out while dynamic adsorption studies are carried out for CO and N_2 with different CO percentage in gas mixture and at a fixed flow rate of $100\,cm^3/min$.

EXPERIMENTAL

Materials

The sodium form of ZSM-5 with SiO_2/Al_2O_3 ratio 25, 40, 100, 400, and 900 in powder form was procured from Zeochem, Switzerland and is used as received. ZSM-5 (25), ZSM-5 (40), ZSM-5 (100), ZSM-5 (400), and ZSM-5 (900) represent ZSM-5 with SiO_2/Al_2O_3 ratio of 25, 40, 100, 400, and 900 respectively. For preparing zeolite extrudes, 20% clay by weight was used as binder. The average length and diameter of extrudes is 5 mm and 3 mm respectively. Ultra high-purity (>99.99%) CO (Ultra pure gases India Pvt. Ltd., Vadodara, India) and N_2 (Inox Air Products Ltd, Maharashtra, India) were used in all adsorption measurements.

Methods

ZSM-5 samples were analyzed by powder X-ray diffraction (PXRD) using Cu $K\alpha$ radiation (1.54056 Å) in the 2θ range of 5–65° (Philips, X'pert MPD PW3123 diffractometer).

Equilibrium Adsorption Measurements

CO and N_2 adsorption was measured at 288 K and 303 K using a static volumetric system ASAP 2020 Surface area and pore size analyzer, (Micromeritics Inc., USA). Prior to the adsorption measurements, the samples were dried at 353 K for 24 hours in oven. The samples were further activated *in-situ* by increasing the temperature at a heating rate of $1\,K\,min^{-1}$ up to 673 K under vacuum (5×10^{-3} mmHg) and the temperature and vacuum was maintained for 8 hours before the sorption measurements. The adsorption data is fitted in Langmuir, Langmuir-Freundlich, and Virial equation. The values for Henry's constant, *K*, were determined from the first Virial coefficient. The adsorption capacity, the selectivity, and the isosteric heat of adsorption were determined from the adsorption isotherms measured at 288 K and 303 K. The specific surface area of the ZSM-5 samples was determined from N_2 adsorption isotherm at 77.35 K.

Dynamic Adsorption Measurements

The single column breakthrough setup for studying the dynamic adsorption of gases was designed and assembled locally. Prior to generating breakthrough curves, zeolite ZSM-5 was *in-situ* activated by increasing the temperature at a heating rate of $1\,K\,min^{-1}$ up to 623 K under N_2 flow and the temperature and the flow was maintained for 12 hours to remove moisture and all adsorbed gases. Different feed compositions (1.6% CO and 98.4% N_2, 6% CO and 94% N_2, 12% CO and 88% N_2, 20% CO and 80% N_2) were ascertained by analyzing the feed gas by gas chromatograph. 45.3 g of anhydrous zeolite ZSM-5 (25) extrude was used for dynamic adsorption studies at 303 K and 1 atm pressure. Desorption was carried out countercurrently under N_2 flow at the same temperature and pressure, to check the easiness of desorption. No considerable change in temperature occurred during the adsorption and the desorption cycle. The raffinate was analyzed by gas chromatograph, (Chemito Inc., model 7610) having a molecular sieve column and thermal conductivity detector (TCD). The flow rate of helium used as a carrier gas was maintained at $40\,cm^3/min$.

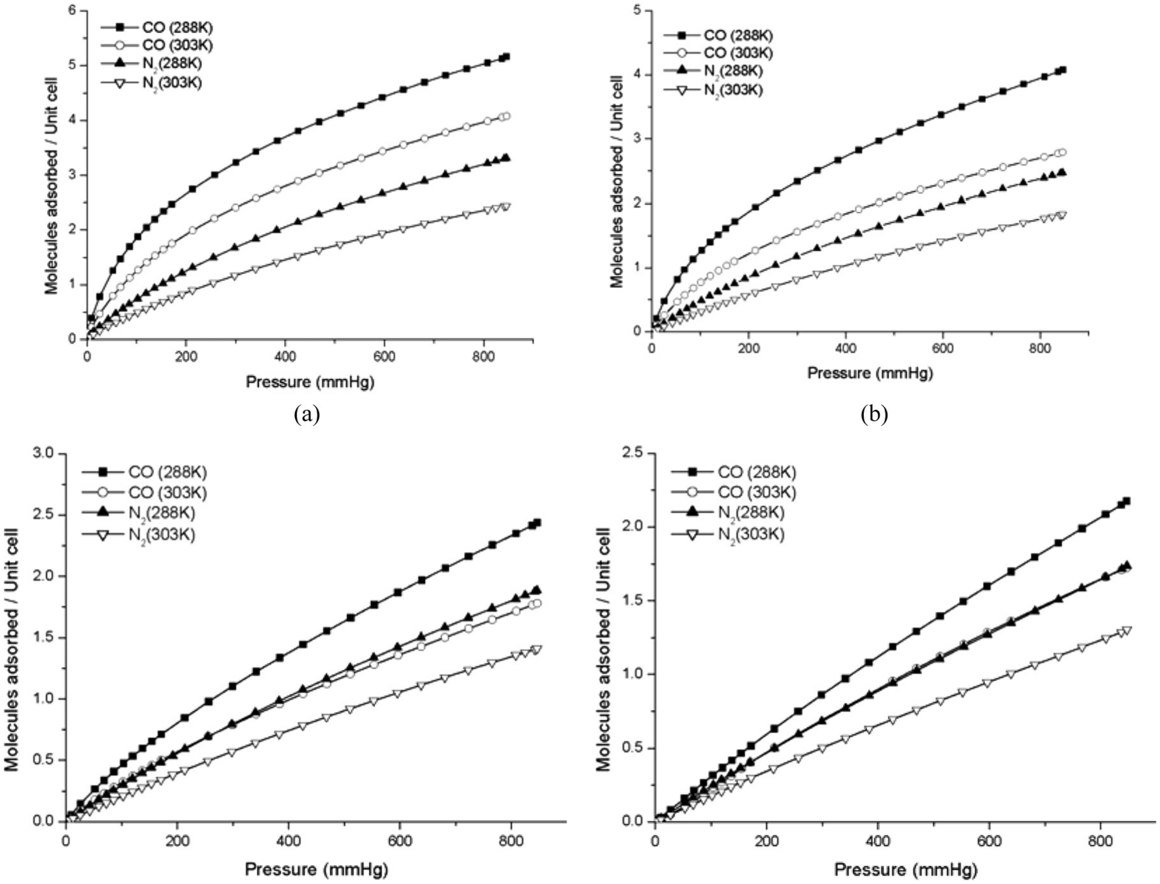
TABLE 1
Surface area and the chemical composition of ZSM-5 having different silica alumina ratio

Adsorbent	Composition of anhydrous ZSM-5, wt%			BET surface area, m^2/g
	Na_2O	Al_2O_3	SiO_2	
ZSM-5 (25)	3.72	6.12	90.16	371
ZSM-5 (40)	2.41	3.97	93.61	379
ZSM-5 (100)	1.0	1.65	97.35	348
ZSM-5 (400)	0.26	0.42	99.32	334
ZSM-5 (900)	0.12	0.19	99.69	315

RESULTS AND DISCUSSION

The PXRD patterns of samples showed a highly crystalline nature of ZSM-5. The chemical composition and surface area of ZSM-5 with different SiO_2/Al_2O_3 ratio is given in Table 1. The equilibrium adsorption capacity of CO and N_2 on ZSM-5 having a different SiO_2/Al_2O_3 ratio was obtained from the adsorption isotherms at 288 and 303 K. The adsorption isotherms of CO and N_2 at 288 and 303 K (Figs. 1 (a–d)) tend to become linear with an increase in SiO_2/Al_2O_3 ratio of ZSM-5. The number of molecules of CO and N_2 adsorbed per unit cell of ZSM-5 with different SiO_2/Al_2O_3 ratio at 288 K, 303 K, and at 101.3 kPa was calculated. The adsorption capacities of CO and N_2 increased with decrease in SiO_2/Al_2O_3 ratio; however, the adsorption capacity of CO was higher than that of N_2. As the number of cations per unit cell increases, the adsorption capacity increases for both the gases.

The adsorption data were fitted into the Langmuir and the Langmuir-Freundlich model; and the values of the slope, the Langmuir constant (*b*), and the Langmuir-Freundlich parameter (*n*) for the adsorption of CO and N_2 on ZSM-5 having different SiO_2/Al_2O_3 ratio, at 288 and 303 K are given in Table 2. The decrease in slope and Langmuir constant *b* for CO and N_2 with an increase in SiO_2/Al_2O_3 ratio is in agreement with the decrease in adsorption capacity. With an increase in SiO_2/Al_2O_3 ratio the Langmuir-Freundlich parameter *n* reaches 1 and it



(a)

(b)

(c)

(d)

FIG. 1. (a) CO and N_2 adsorption isotherms at 288 and 303 K for ZSM-5 (40); (b) CO and N_2 adsorption isotherm at 288 and 303 K for ZSM-5 (100); (c) CO and N_2 adsorption isotherm at 288 and 303 K for ZSM-5 (400); (d) CO and N_2 adsorption isotherm at 288 and 303 K for ZSM-5 (900).

TABLE 2

Langmuir and Langmuir–Freundlich parameters for N_2 and CO adsorption isotherms in ZSM-5 with different silica alumina ratio

	288 K				303 K			
Sample	Slope	$b \times 10^{-3}$ ($mmHg^{-1}$)	Variance $\times 10^{-3}$	n	Slope	$b \times 10^{-3}$ ($mmHg^{-1}$)	Variance $\times 10^{-3}$	n
Langmuir–Freundlich parameters for N_2								
ZSM-5 (25)	0.069	1.847	0.79	1.13	0.036	1.01	0.23	1.08
ZSM-5 (40)	0.063	1.512	0.111	1.19	0.034	1.00	0.07	1.14
ZSM-5 (100)	0.029	0.938	0.363	1.10	0.016	0.59	0.08	1.05
ZSM-5 (400)	0.015	0.378	0.055	1.05	0.009	0.28	0.03	1.03
ZSM-5 (900)	0.011	0.195	0.118	1.04	0.008	0.16	0.09	1.04
Langmuir parameters for N_2								
ZSM-5 (25)	0.040	1.39	13.50	–	0.024	0.89	3.22	–
ZSM-5 (40)	0.029	1.17	16.77	–	0.019	0.88	5.23	–
ZSM-5 (100)	0.019	0.84	3.18	–	0.012	0.58	0.52	–
ZSM-5 (400)	0.012	0.41	0.56	–	0.008	0.30	0.10	–
ZSM-5 (900)	0.010	0.23	0.29	–	0.007	0.18	0.16	–
Langmuir–Freundlich parameters for CO								
ZSM-5 (25)	0.441	10.22	0.72	1.39	0.237	5.90	15.14	1.28
ZSM-5 (40)	0.415	8.25	7.57	1.55	0.195	4.78	1.94	1.39
ZSM-5 (100)	0.224	4.30	11.85	1.47	0.091	3.16	3.40	1.29
ZSM-5 (400)	0.040	0.50	0.36	1.21	0.024	0.44	0.21	1.17
ZSM-5 (900)	0.015	0.20	0.21	1.04	0.006	0.26	0.40	0.93
Langmuir parameters for CO								
ZSM-5 (25)	0.129	4.28	284.48	–	0.089	3.04	121.05	–
ZSM-5 (40)	0.088	3.46	254.48	–	0.055	2.45	85.58	–
ZSM-5 (100)	0.054	2.36	137.85	–	0.032	1.90	28.73	–
ZSM-5 (400)	0.017	0.69	10.21	–	0.012	0.60	3.58	–
ZSM-5 (900)	0.012	0.25	0.49	–	0.010	0.24	1.12	–

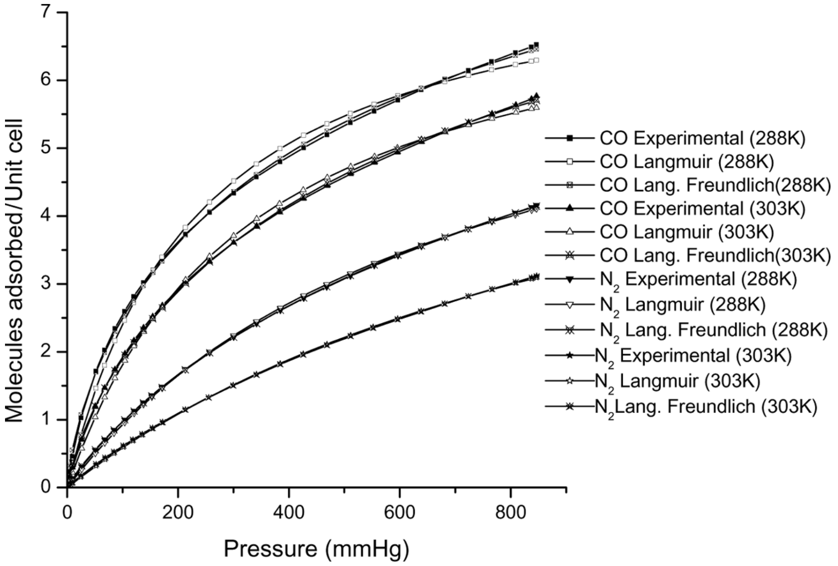


FIG. 2. CO and N_2 adsorption isotherm with Langmuir and Langmuir-Freundlich model fitting at 288 and 303 K for ZSM-5 (25).

TABLE 3
Heat of adsorption, virial coefficient and Henry's constant at 288 and 303 K on ZSM-5 having different silica alumina ratio

	Heat of adsorption ($-\Delta H$) kJ/mole		Henry's constant K (10^{-5} cm^{3}g^{-1}Pa^{-1})				A virial coefficient			
			CO		N_2		CO		N_2	
Adsorbent	CO	N_2	288 K	303 K	288 K	303 K	288 K	303 K	288 K	303 K
ZSM-5 (25)	33	26.8	205	105	42	22	1.16	1.95	2.89	3.55
ZSM-5 (40)	30	25.3	185	82	40	21	1.39	2.21	2.92	3.51
ZSM-5 (100)	28	23.2	107	60	16	9.6	1.95	2.52	3.87	4.36
ZSM-5 (400)	25	19	18	11	9	5.8	3.76	4.26	4.42	4.86
ZSM-5 (900)	23	19.5	8	5	7	4.8	4.98	4.98	4.71	5.05

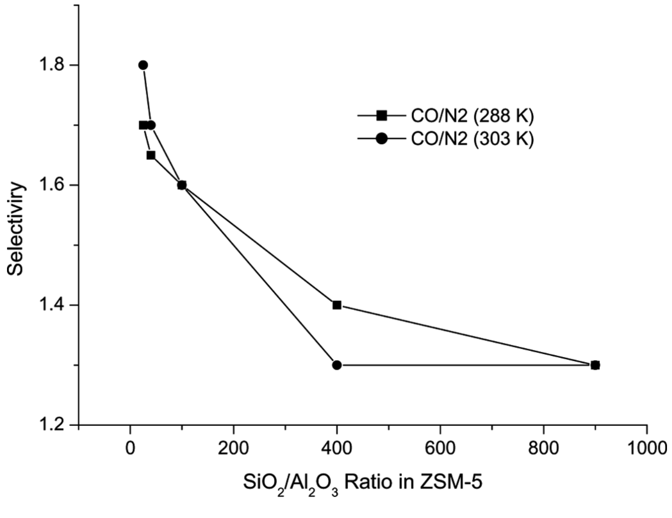


FIG. 3. CO selectivity over N_2 adsorption at 288 and 303 K for ZSM-5 having different silica alumina ratio.

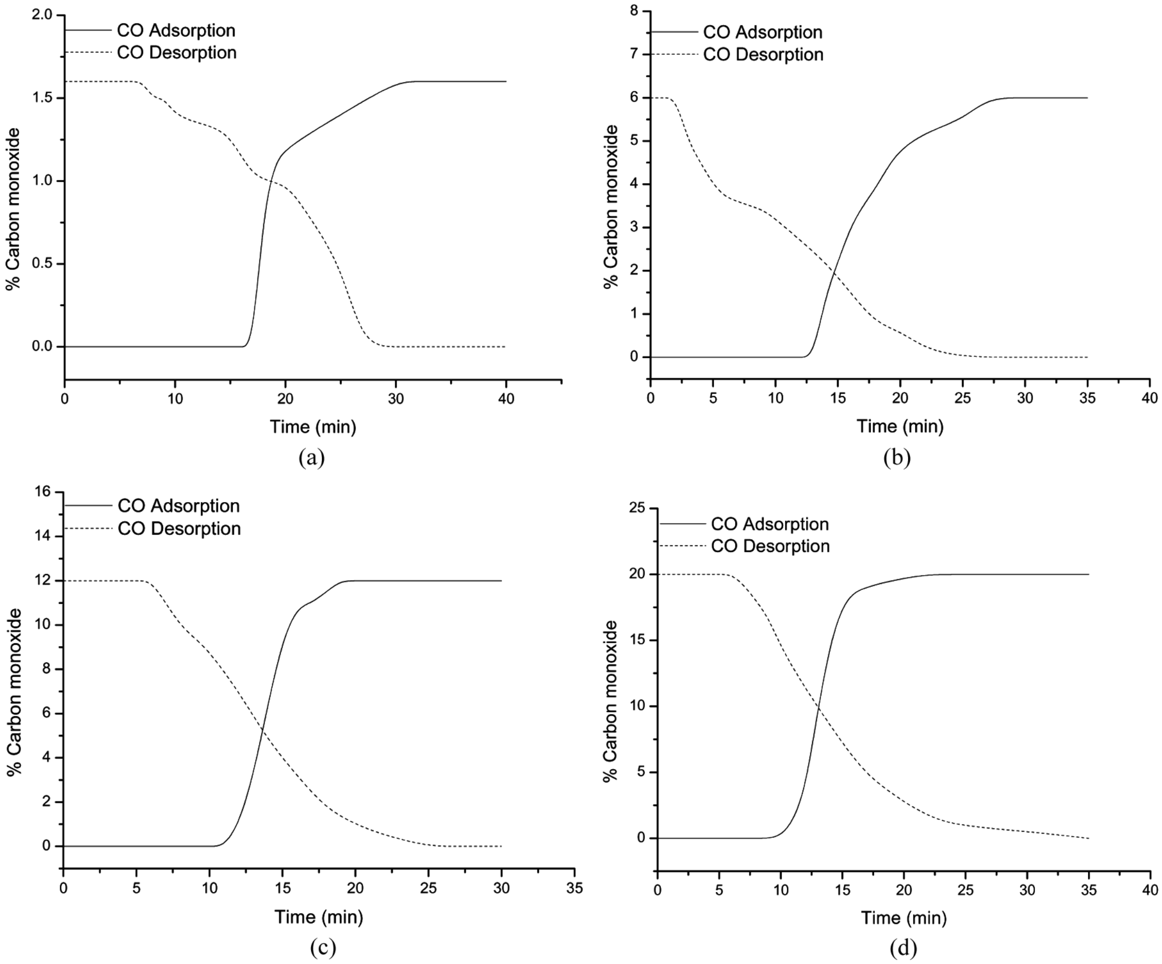
showed CO adsorption capacity of ZSM-5 tend to dependent on pressure. Both the Langmuir and Langmuir-Freundlich model fitted well for nitrogen adsorption while the Langmuir-Freundlich model is best fitted for carbon monoxide adsorption at 303 K (Fig. 2). The variance is low in the Langmuir-Freundlich model fitting. The CO and N_2 adsorption data obtained at 288 and 303 K were also fitted in Virial equation (Table 3). The Henry's constant K for the adsorption of CO and N_2 decreased while Virial coefficient A increases with increase in the SiO_2/Al_2O_3 ratio. The magnitude of Henry's constant was higher for CO as compared to N_2 attributed to the strong interaction of CO molecule with the sodium cations of the ZSM-5. The ZSM-5 (25) had the highest value of Henry's constant for both the gases studied. The isosteric heat of adsorption for CO and N_2 (Table 3) decreases with an increase in the SiO_2/Al_2O_3 ratio due to decrease in numbers of the sodium cations per unit cell. The heat of adsorption for CO was higher than that of N_2 may be due to a strong interaction of CO with sodium cations.

The selectivity of CO over N_2 decreased with an increase in SiO_2/Al_2O_3 ratio of ZSM-5 (Fig. 3). The decrease in selectivity was due to the strong interaction of CO with sodium ions (which decreases with an increase in SiO_2/Al_2O_3 ratio) due to its higher quadrupole moment and polarizability (19). The selectivity of CO over N_2 in ZSM-5 with SiO_2/Al_2O_3 ratio of 25, 40, 100, 400, and 900 was 1.8, 1.7, 1.6, 1.3, 1.3 respectively at 303 K and 1.7, 1.6, 1.6, 1.4, 1.3 at 288 K. The CO selectivity over N_2 decreased up to SiO_2/Al_2O_3 ratio of 400 while in ZSM-5

TABLE 4
Dynamic adsorption parameters for CO and N_2 mixtures*

Feed gas composition, in %	$N_2 = 80 \pm 1$ $CO = 20 \pm 1$	$N_2 = 88 \pm 1$ $CO = 12 \pm 1$	$N_2 = 94 \pm 1$ $CO = 6 \pm 1$	$N_2 = 98.4 \pm 1$ $CO = 1.6 \pm 1$
Break through time (min)	9	11	13	16
Dynamic adsorption capacity (cm^3/g)	4	2.9	1.7	0.6

*Column characteristic: Column capacity = 140 cm^3, Column length = 20 cm. Inner diameter = 3 cm, weight of adsorbent = 45.3 g and gas flow rate = 100 ml/min.



(a) (b) (c) (d)

FIG. 4. Breakthrough curves for CO and N_2 adsorption at 303 K for ZSM-5 (25) using gas mixture (a) 1.6% CO and 98.4% N_2; (b) 6% CO and 94% N_2; (c) 12% CO and 88% N_2; and (d) 20% CO and 80% N_2.

(400) and ZSM-5 (900) the selectivity was almost the same due to a small number of sodium cations per unit cell.

The breakthrough measurements in ZSM-5 (25) with different CO percentage in the gas mixture were carried out at 303 K. The breakthrough parameters are given in Table 4 and Figs. 4 (a–d) shows the breakthrough curves of CO adsorption and desorption for four different CO and N_2 mixture; 1.6% CO and 98.4% N_2; 6% CO and 94% N_2; 12% CO and 88% N_2; 20% CO and 80% N_2, respectively. The CO breakthrough time for these gas mixtures at 100 cm^3/min feed flow rate was 16, 13, 11, and 9 minutes, respectively. In ZSM-5 (25) the breakthrough time of CO decreased on increasing the CO% while the dynamic capacity of CO increased with increasing the CO%. In ZSM-5 (25), the dynamic capacity of CO decreased from 4.0 to 0.6 cm^3/g when the CO percentage is decreased from 20% to 1.6%. This decrease in the dynamic adsorption capacity may be due to the long length of the unused bed. The adsorbed carbon monoxide is easily desorbed by a countercurrent purging of nitrogen at 100 cm^3/min.

The adsorption capacity of CO and N_2 increases with an increase in the number of cations per unit cell of ZSM-5 framework. Among the five adsorbents studies, ZSM-5(25) showed the maximum adsorption capacities and heats of adsorption. Adsorbate molecules can interact with the zeolite surface through lattice oxygen atoms, accessible extra framework cations, and with Al and Si atoms. The Al and Si atoms present at the center of tetrahedra are not directly exposed to the adsorbate molecules. Consequently, their interactions with the adsorbate molecules were negligible. The principal interactions of these adsorbate molecules with the zeolite surface were with lattice oxygen atoms and extra framework cations. The electrostatic interactions between the adsorbate molecules and the extra framework cations of the zeolite depend on the quadrupole moments, the polarizability, and the dipole moment of the adsorbate molecules, CO

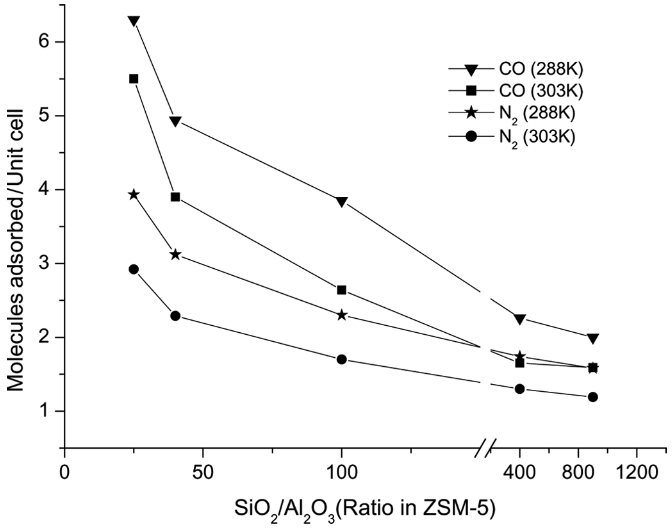


FIG. 5. CO and N_2 equilibrium adsorption capacities at 288 and 303 K for ZSM-5 having various silica alumina ratio.

is the polar molecule with higher quadrupole moments and polarizability than N_2 which is nonpolar. CO has quadrupole moment of 2.50×10^{-26} esu cm^2, polarizability 19.5×10^{-25} cm^3 and dipole moment of 0.112×10^{18} esu cm while N_2 has lower quadrupole moment of 1.52×10^{-26} esu cm^2, polarizability 17.6×10^{-25} cm^3 and zero dipole moment (19).

ZSM-5 having SiO_2/Al_2O_3 ratio of 25, 40, 100, 400, and 900 has CO adsorption capacities of 6.5, 5.0, 3.8, 2.3, 2.0 and 5.5, 3.9, 2.7, 1.7, 1.5 molecules/unit cell, at 288, 303 K respectively at 101.3 kPa. There was a decrease in adsorption capacity with an increase in SiO_2/Al_2O_3 ratio (Fig. 5) attributed to the decrease in the number of sodium cations per unit cell and electrostatic interaction. ZSM-5 with SiO_2/Al_2O_3 ratio of 25, 40, 100, 400 and 900 has N_2 adsorption capacities of 3.9, 3.1, 2.3, 1.7, 1.6 and 3, 2.3, 1.7, 1.3 1.1 molecules/unit cell at 288, 303 K, respectively at 101.3 kPa. Quadrupole moment and Polarizability of N_2 is lower than that of CO which produces electrostatic attraction towards the cationic sites of the adsorbent. As the adsorption of CO and N_2 is mainly governed by the electrostatic interactions, the CO and N_2 molecules may located close to the cations.

CONCLUSION

ZSM-5 (25) has higher carbon monoxide adsorption capacity than nitrogen. The pure gas adsorption capacity decreases with an increase in the system temperature for ZSM-5 having different SiO_2/Al_2O_3 ratio as expected from a physical adsorption system. The adsorption capacities and selectivity for carbon monoxide over nitrogen are very promising for ZSM-5 (25) as an adsorbent for the carbon monoxide separation from its mixture with nitrogen. The adsorption of binary gas mixtures of carbon monoxide and nitrogen with different composition showed competitive adsorption of carbon monoxide over nitrogen in adsorbent column. The breakthrough time decreases while the dynamic capacity increases with increasing carbon monoxide percentage. The adsorbed carbon monoxide desorbed completely under the countercurrent nitrogen flow.

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