Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Comparative study of the adsorption of *n*-aliphatic alcohols on metal-doped alumina samples

A. K. Khattak[a]; K. Mahmood[a]; M. Afzal[b]; M. Saleem[b]; G. Yasmeen[b]
[a] Department of Chemistry, Gomal University, Pakistan [b] Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

To cite this Article Khattak, A. K. , Mahmood, K. , Afzal, M. , Saleem, M. and Yasmeen, G.(2002) 'Comparative study of the adsorption of *n*-aliphatic alcohols on metal-doped alumina samples', Separation Science and Technology, 37: 6, 1431 — 1451

To link to this Article: DOI: 10.1081/SS-120002620

URL: http://dx.doi.org/10.1081/SS-120002620

SEPARATION SCIENCE AND TECHNOLOGY, 37(6), 1431–1451 (2002)

COMPARATIVE STUDY OF THE ADSORPTION OF *n*-ALIPHATIC ALCOHOLS ON METAL-DOPED ALUMINA SAMPLES

A. K. Khattak,[1,*] K. Mahmood,[1] M. Afzal,[2]
M. Saleem,[2] and G. Yasmeen[2]

[1]Department of Chemistry, Gomal University, D.I. Khan,
Pakistan
[2]Department of Chemistry, Quaid-i-Azam University,
Islamabad, Pakistan

ABSTRACT

A study has been made of the adsorption isotherms of *n*-aliphatic alcohols (methanol, ethanol, 1-propanol, and *n*-butanol designated C_1, C_2, C_3, and C_4, respectively) on parent and metal-doped γ-alumina samples in the temperature range 273–313K as a function of temperature and coverage, using CAHN 1000 electrobalance. It is noted from the data that at a given relative pressure, the adsorbed amount for the sample treated at the same temperature decreases in the order $C_4 < C_3 < C_2 < C_1$. From the adsorption data, thermodynamic parameters such as isosteric heat of adsorption (q_{st}), free energy (ΔG^0), differential enthalpy (ΔH), and molar entropy (ΔS^0) of adsorption have been calculated as a function of temperature and coverage. The values of q_{st} are found

---

*Corresponding author.

www.dekker.com

to be higher for metal-doped alumina which may be due to the coordination of *n*-aliphatic alcohols to metal vacancies present on the surface of alumina. It has been observed that at a given relative pressure, the enthalpy of adsorption for *n*-aliphatic alcohols (C_1–C_4) treated at the same temperature decreases in the order $C_1 < C_2 < C_3 < C_4$. The values of ΔH are higher for metal-doped alumina than parent alumina, which indicate that strong adsorbate–adsorbent interaction is found after impregnation. It has also been noted that the values of ΔG^0 for (C_1–C_4) are negative showing that the adsorption processes are spontaneous. These values decrease with increase in temperature indicating that alumina samples have higher adsorption affinity for (C_1–C_4) at low temperature. The low values of entropy (ΔS^0) indicate more constraint on the mobility of adsorbate molecules.

INTRODUCTION

The adsorption of organic molecules (*n*-aliphatic alcohols) on metal oxide surfaces is a basic phenomenon in the catalytic reactions occurring on the surface, and hence much research has been done in this area. A study on the adsorption of alcohols on metal oxide is of special interest in connection with catalytic decomposition of alcohols such as dehydration and dehydrogenation (1–6) and surface modification of solids for practical purposes (7,8).

Alumina is used commonly as a catalyst or catalyst support. A step toward understanding its catalytic properties is to understand the adsorption mechanism of the reactants (adsorbates) with which it comes in contact (9). Alumina has a large surface area and adsorption capacity and is employed extensively to remove toxic and health hazardous particles and ions from gases and solutions. The importance of alumina as a support catalyst or adsorbent has been recognized widely. As an adsorbent or co-catalyst, it is used in many catalytic processes of industrial importance (10,11). Alumina is a porous material and thus its porous structure plays an important role in adsorption processes. It is used commercially in adsorption chromatography. In physical adsorption, especially at high relative pressure, the behavior and amount of adsorbate to be adsorbed depends upon the pore structure. Hence adsorption is related directly to the size and shape of the pores in addition to other factors (12).

The efficiency (13) of alumina as an adsorbent is based on its physical adsorption capacity, which in turn depends on its porosity, on the intrinsic properties of the parent material, on its structure, and on the surface properties of the adsorbent itself. In order to improve the efficiency of alumina as an adsorbent, different types of impregnates/dopants are often added to it. These impregnated/doped metal oxides act as catalysts and are used widely in various catalytic processes. These impregnates also change the nature, surface, and adsorbing properties of the γ-alumina and are found to be effective adsorbents generally (14,15) on which not only adsorption, but also chemical reactions and the catalytic decomposition of different gases can take place.

Pore structure, apparent surface area, average pore diameter, and total micropore volume for metal-doped alumina samples containing different concentration of metals (Cr, Mn, Fe, and Co) have been investigated (16) previously by mercury penetration (using Mercury Porosimeter) and low temperature nitrogen adsorption (using Quantasorb Sorption System). Whilst surface areas of the powdered alumina samples (A_L and A_{BET}) were determined by the two most common methods i.e., the Langmuir method and the BET method elsewhere (17) through the adsorption of *n*-aliphatic alcohols on metal-doped alumina samples.

However, the objectives of the present work were to study the adsorption of *n*-aliphatic alcohols (C_1-C_4) on parent γ-alumina and metal-doped alumina with different metal chlorides loading. Adsorption isotherms of (C_1-C_4) were determined on the samples of γ-alumina at temperatures between 273 and 313K. From the adsorption data, thermodynamic parameters such as isosteric heat of adsorption (q_{st}), free energy (ΔG^0),differential enthalpy (ΔH) and molar entropy (ΔS^0) of adsorption of (C_1-C_4) were determined at different temperatures and coverages and were interpreted.

In this light, our major focus was to characterize a number of alumina/doped metal systems as adsorbents for various *n*-aliphatic alcohols, looking for synergistic interactions in catalytic processes, however, further work was required to study the catalytic properties of metal-doped γ-alumina samples and to draw more definite conclusions. In the present work, therefore, alumina was loaded with Cr, Mn, Fe, and Co, but here, the data (Tables 2–7) for parent γ-alumina and Cr-doped alumina samples were tabulated. Whilst other metal-doped alumina samples (Mn, Fe, and Co) behaved more or less like Cr, hence were not tabulated. The choice of metal was based on the fact that these metals are used as catalysts on silica, carbon, and alumina. Normal aliphatic alcohols have been chosen as adsorptive, because these substances are used extensively as reactants in the chemical industry (13).

EXPERIMENTAL

Material

The aluminium oxide used for doping purposes in the present work was a sample of commercially available γ-alumina. It was supplied by Fluka Chemie AG (Buchs, Switzerland) (item #06290) with density 920 g/L and surface area

(150 ± 10% m^2/g), chromium chloride (item #2487) and iron chloride (item #3943) were supplied by Merck (Germany) whilst manganese chloride (item #63543) and cobalt chloride (item #60820) were supplied by Fluka with purities better than 99%. The adsorbates (methanol, ethanol, 1-propanol, and *n*-butanol) used for thermodynamic investigation were of HPLC grade which were supplied by Merck and were used as such.

Preparation of Adsorbents

A series of metal-doped γ-alumina samples was prepared by impregnation technique of the host oxide (γ-Al_2O_3) with different additives i.e., Cr, Mn, Fe, and Co. For preparation of such metal-impregnated alumina samples (18–20), a pre-determined amount of metal chloride was stirred magnetically in 200 mL of double distilled water and 20 g of alumina was added to the mixture for impregnation. The mixture was stirred for 8 hr at 373K till a slurry was formed. The excess solution was then driven off through vacuum desccicator connected with suction pump. The samples were then dried at 373K for 3 hr. A blank alumina sample was also prepared by giving the same treatment except that distilled water was used in place of metal chloride solution. Two samples of different concentrations for every metal were prepared.

The metal-impregnated alumina samples were designated by the formulae "M_x–Al_2O_3" where M stands for Cr, Mn, Fe, and Co and x represents the number of the moles per 100 g of alumina.

Determination of the Amount of Metal in the Alumina-Supported Metal Adsorbents

For the measurement of metal concentration, 1 g of the sample was stirred thoroughly with nitric acid solution for 4 hr at room temperature. The total amount of the metal in the solution was then determined by atomic absorption spectrophotometer (Model Shimadu AA-670) (Kyota, Japan). The results of samples whose preparation was tried out and composition of the doped alumina samples is collected in Table 1.

Adsorption Isotherm Measurement

Adsorption data for *n*-aliphatic alcohols were obtained using CAHN electrobalance attached to a vacuum line. Prior to the adsorption measurement, all the physisorbed species were removed from the surface of the sample by heating at 563K under a vacuum of 10^{-5} mbar. Then 0.15 g of the sample

Table 1. Results of Preparation and Analysis of Metal-Doped Alumina

Sample Tried to Prepare	Period of Stirring (hr)	Ratio of Doped to Charged Metal	Composition of Doped Alumina
Al_2O_3	8	—	—
$Cr_{0.01}-Al_2O_3$	8	0.865	$Cr_{0.0086}-Al_2O_3$
$Cr_{0.05}-Al_2O_3$	8	0.833	$Cr_{0.0417}-Al_2O_3$
$Mn_{0.01}-Al_2O_3$	8	0.900	$Mn_{0.009}-Al_2O_3$
$Mn_{0.05}-Al_2O_3$	8	0.877	$Mn_{0.0439}-Al_2O_3$
$Fe_{0.01}-Al_2O_3$	8	0.900	$Fe_{0.009}-Al_2O_3$
$Fe_{0.05}-Al_2O_3$	8	0.870	$Fe_{0.0435}-Al_2O_3$
$Co_{0.01}-Al_2O_3$	8	0.893	$Co_{0.0089}-Al_2O_3$
$Co_{0.05}-Al_2O_3$	8	0.872	$Co_{0.0436}-Al_2O_3$

(adsorbent) was taken in a glazed silica crucible and the crucible was placed in the weighing unit. Prior to pumping, the hang down tube was maintained at a fixed temperature using a constant temperature, water-circulating thermostat (accuracy ± 0.1°C).The entire system was then evacuated at 10^{-5} mbar for at least 4 hr before taking adsorption data. Vapors of the adsorptive were admitted and equilibrium pressure was read from a mercury manometer with the aid of a cathetometer. Dissolved gases were removed from the adsorptive liquid by several cycles of freeze–pump–thaw technique.

RESULTS AND DISCUSSION

Adsorption isotherms of *n*-aliphatic alcohols on parent and metal-doped γ-alumina samples were taken in the temperature range 273–313K. All the adsorption isotherms (Figs. 1–4) were of type I, which indicates the microporosity of alumina samples. Adsorption isosteres for the system investigated in the present work were calculated from a series of adsorption isotherms at different temperatures by reading pressure and temperature at a constant coverage. From these adsorption isosteres, the values of q_{st} were calculated by the Clausius–Clapeyron equation applied in the appropriate form. This equation is applicable if isotherms at several temperatures are available (21,22).

$$(\ln p)_{n_a} = -\frac{q_{st}}{RT} + \text{constant} \tag{1}$$

where R is the gas constant, p the pressure calculated from isotherm at given temperature and at a constant coverage, n_a the amount adsorbed

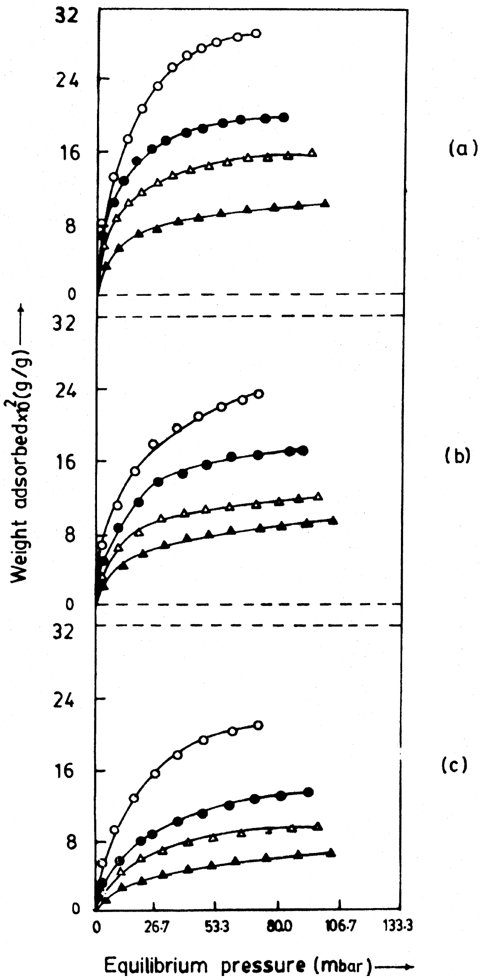


Figure 1. Adsorption isotherms for methanol on (a) alumina; (b) $Cr_{0.0086}$–Al_2O_3; (c) $Cr_{0.0417}$–Al_2O_3, ○, 273; ●, 293; △, 303; ▲, 313K.

(surface coverage), and q_{st} the isosteric heat of adsorption at constant coverage.

The values of q_{st} calculated from the above equation, are the same as the enthalpy change (ΔH) for the adsorption process, except that since this q_{st} is positive when adsorption occurs, heat is therefore evolved. Thus, the values of q_{st} calculated in kJ/mol from the experimental data at different coverages and

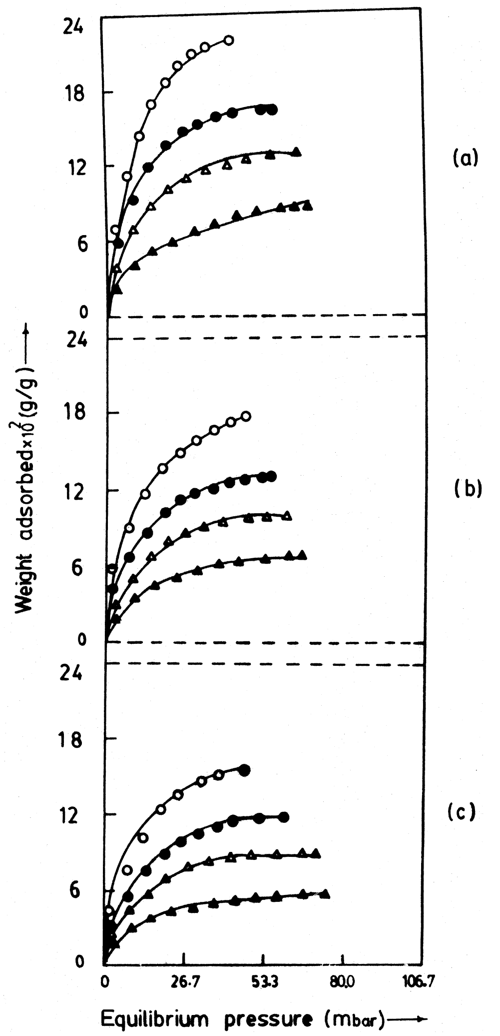


Figure 2. Adsorption isotherms for ethanol on (a) alumina; (b) $Cr_{0.0086}$–Al_2O_3; (c) $Cr_{0.0417}$ –Al_2O_3, ○, 273; ●, 293; △, 303; ▲, 313K.

temperatures for different alumina samples are not tabulated. The Clausius–Clapeyron equation, which represents an adsorption isostere—the relation between p and T for a given amount adsorbed—can be plotted from the isotherms for a series of temperatures. The value of q_{st} is then immediately calculable from the slope of the isosteric plot, the Clausius–Clapeyron plot ($\ln p$ vs. $1/T$) at a

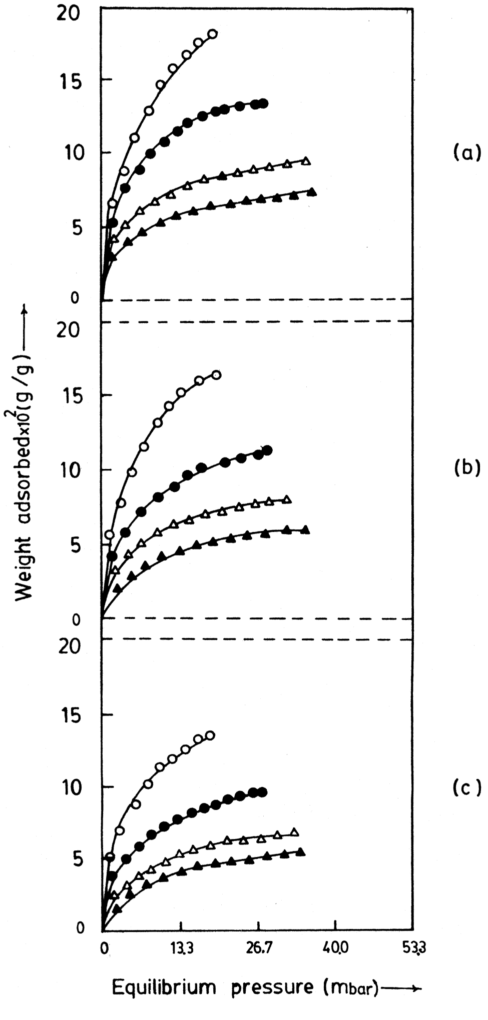


Figure 3. Adsorption isotherms for propanol on (a) alumina; (b) $Cr_{0.0086}–Al_2O_3$; (c) $Cr_{0.0417}–Al_2O_3$, ○, 273; ●, 293; △, 303; ▲, 313K.

constant surface coverage. The isosteric plots of $\ln p$ vs. $1/T$, (Fig. 5) for the adsorption of C_1 on pure and Cr-doped alumina at a surface coverage of 0.02 g/g are linear according to Eq. (1). The isosteric heat of adsorption q_{st} so calculated from a series of adsorption isotherms can provide information on the energetics of the gas–solid interface as well as the distribution of energetic sites on the solid

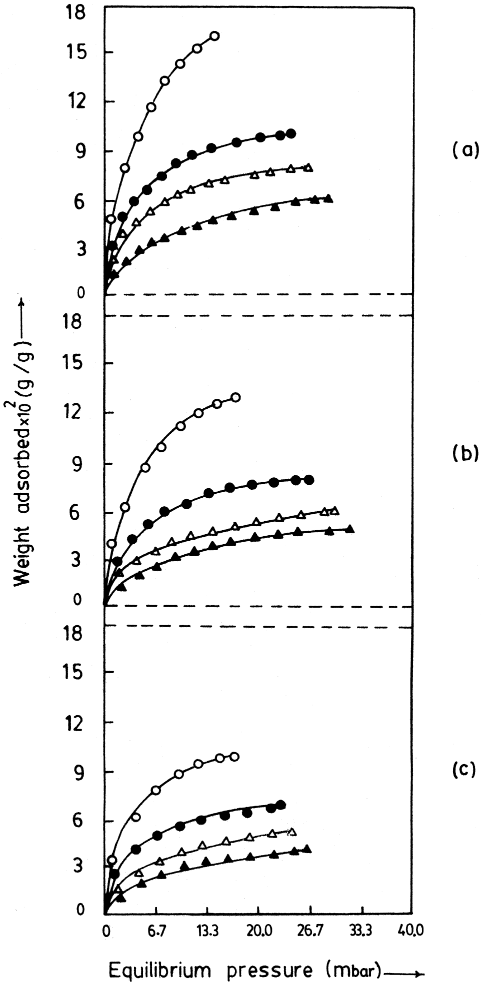


Figure 4. Adsorption isotherms for *n*-butanol on (a) alumina; (b) $Cr_{0.0086}–Al_2O_3$; (c) $Cr_{0.0417}$ $–Al_2O_3$, ○, 273; ●, 293; △, 303; ▲, 313K.

surface. The values of other isosteric thermodynamic parameters so called standard free energies (ΔG^0) and entropies (ΔS^0) of adsorption were calculated for a standard gaseous state of one atmosphere from the equations (23).

$$\Delta H = -q_{st} \tag{2}$$

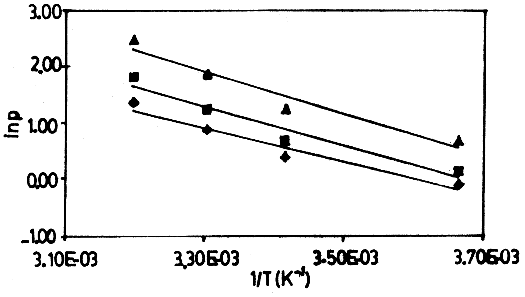


Figure 5. Plots of ln p vs. 1/T calculated from Clausius–Clapeyron expression, ▲, Alumina; ■, $Cr_{0.0086}–Al_2O_3$; ◆, $Cr_{0.0417}–Al_2O_3$.

where ΔH is the differential enthalpy (heat) of adsorption

$$\Delta G^0 = -RT \ln\left(\frac{760}{p}\right), \tag{3}$$

where p = pressure in Torr, and,

$$\Delta S^0 = \frac{(\Delta H - \Delta G^0)}{T} \tag{4}$$

$$\Delta G^0 = \Delta H - T\Delta S^0 \tag{5}$$

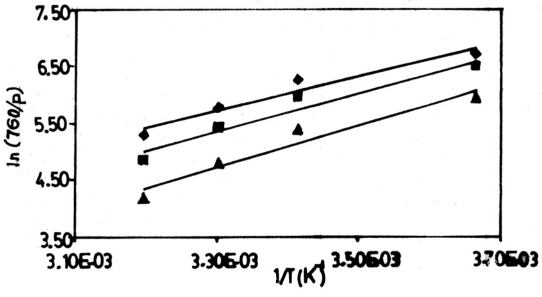


Figure 6. Plots of ln(760/p) vs. 1/T calculated from ln (760/p) = $-\Delta H/RT + \Delta S/R$ expression, ◆, Alumina; ■, $Cr_{0.0086}–Al_2O_3$; ▲, $Cr_{0.0417}–Al_2O_3$.

equating Eqs. (3) and (5), we get

$$\ln\left(\frac{760}{p}\right) = -\frac{\Delta H^0}{RT} + \frac{\Delta S}{R} \tag{6}$$

When $\ln(760/p)$ is plotted against $1/T$, a straight line is obtained with slope $= -\Delta H/R$ and intercept $= \Delta S^0/R$, from the slope the value of ΔH is calculated while ΔS^0 is calculated from Eq. (4). The plots of $\ln(760/p)$ vs. $1/T$ (Fig. 6) for the adsorption of C_1 on pure and Cr-doped alumina at a surface coverage of 0.02 g/g are linear according to Eq. (6). The negative values of ΔG^0 for all the systems indicate that these adsorption processes are spontaneous in nature.From the data of q_{st}, it has been noted that there are variations in the observed q_{st} values for *n*-aliphatic alcohols adsorption on metal-doped alumina samples. It has been suggested by various authors (24,25) that two factors contribute mainly to the experimentally observed variation in the heats of adsorption. These are (i) physical heterogeneity of the surface and (ii) lateral interactions between the molecules adsorbed. According to Beebe et al. (26) and Qadeer and Hanif (27), if the adsorbent is porous, the interpretation of q_{st} behavior is further complicated.

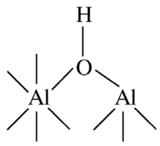
If all the pores are large in diameter in comparison to adsorbate molecule, then we may expect effects, which are essentially the same as in the case of nonporous powders. On the other hand, if the pore diameters are not greater than a few adsorbate molecule diameters, then it is to be expected that the adsorbate molecules will be attracted by more than one wall with a corresponding high heat of adsorption. Barrer (28) has calculated that such effects may give rise to heat values several times higher than those obtained on plain surfaces.

In addition to the factors mentioned previously, the q_{st} values are also complicated by other factors such as cross-sectional area of the molecules, polarity of the adsorbate molecule, symmetry of the molecules, vertical and horizontal interactions between adsorbate–adsorbate molecules and many others (24). In the same way, the q_{st} values are also influenced by the nature of the adsorbent, impurities incorporated in the surface, the porous nature of the adsorbent, pore size distribution of the adsorbent, geometric arrangement of the molecule of the solid and so on.

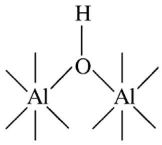
The structure of the pores of the adsorbent (Al_2O_3) play an important role in adsorption processes. However, when it is doped with metals like Cr, Mn, Fe, and Co, new surface is created. The thermodynamic and kinetic properties of the new surface are changed and are quite different from the parent γ-Al_2O_3 (13). In its normal state, the surface of alumina is covered with an adsorbed film, which may contain oxygen, water, and other impurities both chemically and physically adsorbed. In the present work, by heating alumina to about 563K, it is expected that all the physically adsorbed impurities will be removed leaving on the surface sites some chemisorbed species. However, according to Peri and Hannan (29) various chemically distinct types of hydroxyl groups also persist on the surface of alumina. At higher temperatures these hydroxyl groups, condense gradually to eliminate water. Surface hydroxyl groups are not eliminated completely, however, even by dragging under vacuum at 800–1000°C (30,31). These hydroxyl groups have been assumed to supply protons, either directly (32) or indirectly (33) in certain catalytic reactions on alumina. Removal of the hydroxyl groups have been postulated as creating on the surface-strained sites that are catalytically active (34) as strained oxide linkages (35).

Aluminas are used extensively as adsorbents, active catalysts, and catalyst supports and despite the widespread interest in catalytic aluminas, there is still only a limited understanding about the real nature of the surface of alumina. The alumina surface (36) as an adsorbent is certainly an extremely complicated surface. Among the surface models and site configuration reported in the literature, Knozinger and Ratnasamy (37) proposed five possible OH configurations.

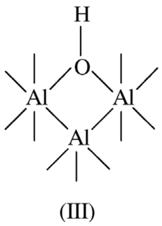
(Ia)



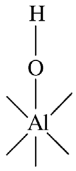
(IIa)



(IIb)



(III)



(Ib)

(Ia) a terminal OH group is coordinated to a single tetrahedral Al^{3+} cations; (IIa) a bridging OH group links a tetrahedral and octahedral cation (thrice as frequent as type Ia); (IIb) the OH group links two cations in octahedral positions (thrice as frequent as type III); (III) the OH group is coordinated to three cations in octahedral interstices; (Ib) the OH group is coordinated to a single cation in octahedral interstices, if possible vacant cation positions exist. On the basis of the above discussion, we may, therefore assume that the surface used in this work is heterogeneous containing sites of different activities as the characterization of alumina surfaces have revealed already. Adsorption on alumina under such conditions may occur physically or chemically, initially involving the most active sites and then, as the pressure of the adsorbate is increased, on the sites of decreasing activity (10). To a first approximation, therefore, one would expect the heat of

Table 2. Thermodynamic Parameters for the Adsorption of Methanol and Ethanol on Al_2O_3 at Different Temperatures and Different Coverages

Adsorbate	Surface Coverage (10^2 g/g)	Temperature (K)	$-\Delta G^\circ$ (kJ/mol)	$-\Delta H$ (kJ/mol)	$-\Delta S^\circ$ (kJ/molK)
Methanol	3.00	273	16.01	26.36	0.03791
		293	15.97	26.36	0.03546
		303	15.23	26.36	0.03673
		313	14.40	26.36	0.03821
	4.00	273	15.25	25.12	0.03615
		293	15.20	25.12	0.03386
		303	14.50	25.12	0.03505
		313	13.71	25.12	0.03645
	6.00	273	14.65	32.14	0.06410
		293	14.24	32.14	0.06109
		303	13.17	32.14	0.06261
		313	11.96	32.14	0.06447
Ethanol	3.00	273	16.21	29.33	0.04806
		293	16.03	29.33	0.04539
		303	15.15	29.33	0.04678
		313	14.18	29.33	0.04840
	3.75	273	15.27	28.55	0.04862
		293	15.06	28.55	0.04601
		303	14.22	28.55	0.04728
		313	13.21	28.55	0.04898
	6.00	273	14.55	40.35	0.09450
		293	13.75	40.35	0.09078
		303	12.27	40.35	0.09267
		313	10.63	40.35	0.09495

adsorption to decrease steadily with coverage, if no new processes are brought into play at a particular coverage (38). This is true in general. However, in the present work, exceptional results with some discrepancies and anomalies appear.

For (C_1–C_4) alumina systems (Tables 2–7), heats of adsorption as a function of coverage and temperature change very little. The behavior with regard to heats of adsorption of all *n*-aliphatic alcohols used as an adsorbate on metal-doped alumina is not quite different to that of the parent alumina. In general, it is concluded that the values of heats of adsorption for all the *n*-aliphatic alcohols are higher on metal-doped alumina than they are on the parent alumina. The results for all the systems (C_1–C_4) will now be considered collectively and attempts will be made to explain anomalies at places where they occur.

Table 3. Thermodynamic Parameters for the Adsorption of 1-Propanol and *n*-Butanol on Al_2O_3 at Different Temperatures and Different Coverages

Adsorbate	Surface Coverage (10^2 g/g)	Temperature (K)	$-\Delta G^\circ$ (kJ/mol)	$-\Delta H$ (kJ/mol)	$-\Delta S^\circ$ (kJ/mol K)
1-Propanol	3.00	273	17.53	35.14	0.06451
		293	17.19	35.14	0.06126
		303	16.09	35.14	0.06287
		313	14.82	35.14	0.06492
	3.50	273	16.51	31.55	0.05509
		293	16.26	31.55	0.05222
		303	15.29	31.55	0.05370
		313	14.18	31.55	0.05553
	4.50	273	15.39	32.89	0.06410
		293	14.99	32.89	0.06109
		303	13.91	32.89	0.06264
		313	12.71	32.89	0.06447
n-Butanol	2.00	273	18.41	39.87	0.07857
		293	18.01	39.87	0.07457
		303	16.75	39.87	0.07627
		313	15.26	39.87	0.07862
	3.00	273	17.23	38.70	0.07864
		293	16.69	38.70	0.07511
		303	15.42	38.70	0.07683
		313	13.93	38.70	0.07913
	3.50	273	16.84	39.75	0.08391
		293	16.26	39.75	0.08017
		303	14.91	39.75	0.08198
		313	13.31	39.75	0.08447

The results of isosteric heat of adsorption q_{st} for *n*-aliphatic alcohols (C_1–C_4) obtained on metal-doped alumina samples indicate that the heat of adsorption is constant as a function of temperature but show relatively small and slight variation with coverage on the majority of sites. The results reported in the present work are consistent with those described by Afzal (38) who has studied the adsorption of C_1 at porous carbon and has presented that heats at lower coverages are very approximately constant with temperature.

In the case of (C_1–C_4) metal-doped alumina, the q_{st} values are high at low coverages and then decrease slightly with the increase in the surface coverage while finally q_{st} again increases. This behavior is nearly true at all temperatures for all the metal-doped alumina samples. This sort of behavior can be interpreted in terms of

Table 4. Thermodynamic Parameters for the Adsorption of Methanol and Ethanol $Cr_{0.0086}-Al_2O_3$ at Different Temperatures and Different Coverages

Adsorbate	Surface Coverage (10^2 g/g)	Temperature (K)	$-\Delta G^\circ$ (kJ/mol)	$-\Delta H$ (kJ/mol)	$-\Delta S^\circ$ (kJ/molK)
Methanol	3.00	273	15.45	30.79	0.05619
		293	15.20	30.79	0.05321
		303	14.19	30.79	0.05479
		313	13.09	30.79	0.05655
	4.00	273	14.72	28.65	0.05103
		293	14.47	28.65	0.04840
		303	13.60	28.65	0.04967
		313	12.56	28.65	0.05141
	6.00	273	13.62	36.97	0.08533
		293	12.96	36.97	0.08195
		303	11.61	36.97	0.08369
		313	10.05	36.97	0.08601
Ethanol	3.00	273	15.96	33.59	0.06457
		293	15.56	33.59	0.06153
		303	14.41	33.59	0.06330
		313	13.29	33.59	0.06485
	3.75	273	14.86	31.61	0.06169
		293	14.45	31.61	0.05856
		303	13.43	31.61	0.06000
		313	12.30	31.61	0.06169
	6.00	273	13.65	41.08	0.1005
		293	12.72	41.08	0.0968
		303	11.19	41.08	0.0986
		313	9.487	41.08	0.1009

nonuniformity and the site variation in affinity for a given adsorbate is therefore said to be heterogeneous. When the adsorbate molecules are adsorbed on a clean catalyst surface, the highest energy sites tend to be covered first, the lower energy sites last. Consequently, the heat of interaction released generally falls off as successive doses of adsorbate (gas) are adsorbed. However, the later increase in q_{st} probably represents adsorbate–adsorbate interaction. When the final heats are higher than the heats of liquefaction, it could be due to the formation of surface coordination complex. These complexes would result in coulombic forces, which are much stronger than the relatively weak van der Waals interaction forces (36).

Figures 1–4 show the adsorption isotherms of C_1, C_2, C_3, and C_4, respectively, on the metal-doped alumina samples. It is noted that at a given

Table 5. Thermodynamic Parameters for the Adsorption of 1-Propanol and *n*-Butanol on $Cr_{0.0086}-Al_2O_3$ at Different Temperatures and Different Coverages

Adsorbate	Surface Coverage (10^2 g/g)	Temperature (K)	$-\Delta G°$ (kJ/mol)	$-\Delta H$ (kJ/mol)	$-\Delta S°$ (kJ/molK)
1-Propanol	3.00	273	16.19	35.17	0.06952
		293	15.75	35.17	0.06628
		303	14.56	35.17	0.06802
		313	13.29	35.17	0.06990
	3.50	273	15.43	33.40	0.06582
		293	15.01	33.40	0.06276
		303	13.91	33.40	0.06432
		313	12.68	33.40	0.06620
	4.50	273	14.83	36.01	0.07758
		293	14.26	36.01	0.07423
		303	13.01	36.01	0.07591
		313	11.59	36.01	0.0802
n-Butanol	2.00	273	17.53	41.64	0.08831
		293	16.80	41.64	0.08477
		303	15.37	41.64	0.08669
		313	13.88	41.64	0.08869
	3.00	273	15.73	38.11	0.08197
		293	15.15	38.11	0.07836
		303	13.79	38.11	0.08026
		313	12.31	38.11	0.08242
	3.50	273	15.15	39.47	0.08391
		293	14.48	39.47	0.08017
		303	13.02	39.47	0.08198
		313	11.44	39.47	0.08447

relative pressure, the adsorbed amount for the samples treated at the same temperature and hence covered with the same number of hydroxyls groups, decreases in the order, $C_1 > C_2 > C_3 > C_4$. It is also noted from these figures that shapes of all the isotherms belong to the Langmuir type than to the BET type. A similar tendency has been reported by Barto et al. (39) for the adsorption of *n*-aliphatic alcohols (C_1-C_4) on alumina.

The values of other isosteric thermodynamic parameters (ΔG^0, ΔH and ΔS^0) for (C_1-C_4) calculated from the thermodynamic constants are given in Tables 2–7. Results indicate that the values of free energy of adsorption are negative for all the systems as expected for spontaneous adsorption process. These values decrease with increase in temperature indicating that alumina

Table 6. Thermodynamic Parameters for the Adsorption of Methanol and Ethanol on $Cr_{0.0417}$–Al_2O_3 at Different Temperatures and Different Coverages

Adsorbate	Surface Coverage (10^2 g/g)	Temperature (K)	$-\Delta G^\circ$ (kJ/mol)	$-\Delta H$ (kJ/mol)	$-\Delta S^\circ$ (kJ/molK)
Methanol	3.00	273	14.50	32.07	0.06436
		293	14.03	32.07	0.06157
		303	13.00	32.07	0.06294
		313	11.80	32.07	0.06476
	4.00	273	13.48	30.92	0.06388
		293	13.09	30.92	0.06085
		303	12.00	30.92	0.06244
		313	10.81	30.92	0.06425
	6.00	273	12.39	38.42	0.06410
		293	11.50	38.42	0.06109
		303	10.02	38.42	0.06264
		313	8.45	38.42	0.06447
Ethanol	3.00	273	14.93	34.32	0.07102
		293	14.41	34.32	0.06795
		303	13.24	34.32	0.06957
		313	11.98	34.32	0.07137
	3.75	273	13.90	32.52	0.06821
		293	13.90	32.52	0.06525
		303	12.90	32.52	0.06673
		313	11.05	32.52	0.06860
	6.00	273	12.51	42.11	0.1084
		293	11.50	42.11	0.1045
		303	9.88	42.11	0.1064
		313	7.99	42.11	0.1090

samples have higher adsorption affinity for *n*-aliphatic alcohols (C_1–C_4) at low temperature. The results also show that the values of free energy of adsorption are less negative for metal-doped alumina than that found on parent alumina, however, the difference is not significant.

The isosteric enthalpy of adsorption (which is related closely to the strength of the bond between the adsorbed species and surface) usually falls with the increase in surface coverage, either linearly or logarithmically. The reasons for this effect have been much discussed and the most common explanations seem to be, that surface in general are not atomically smooth, and an adsorbing molecule will react first and most energetically with atoms or ions having low coordination numbers, molecules arriving later cannot then adsorb so strongly. However, in the present work, the

Table 7. Thermodynamic Parameters for the Adsorption of 1-Propanol and *n*-Butanol on $Cr_{0.0417}-Al_2O_3$ at Different Temperatures and Different Coverages

Adsorbate	Surface Coverage (10^2 g/g)	Temperature (K)	$-\Delta G^\circ$ (kJ/mol)	$-\Delta H$ (kJ/mol)	$-\Delta S^\circ$ (kJ/molK)
1-Propanol	3.00	273	15.65	37.61	0.08044
		293	15.09	37.61	0.07686
		303	13.75	37.61	0.07875
		313	12.30	37.61	0.08086
	3.50	273	15.07	36.86	0.07982
		293	14.47	36.86	0.07686
		303	13.16	36.86	0.07822
		313	11.75	36.86	0.08022
	4.50	273	14.18	41.05	0.09842
		293	13.33	41.05	0.09461
		303	11.77	41.05	0.09663
		313	10.01	41.05	0.09817
n-Butanol	2.00	273	16.90	42.47	0.09366
		293	16.14	42.47	0.08986
		303	14.62	42.47	0.09191
		313	13.02	42.47	0.09408
	3.00	273	15.29	40.42	0.09205
		293	14.55	40.42	0.08829
		303	13.06	40.42	0.09026
		313	11.48	40.42	0.09246
	3.50	273	14.88	41.46	0.09736
		293	14.03	41.46	0.09361
		303	12.50	41.46	0.09557
		313	10.85	41.46	0.09779

results agree with this statement to some extent, but are in close agreement with those suggested by Gervasini and Auroux (36). The present study reveals that differential enthalpy is maximum at low coverage, but as the coverage increases, the enthalpy is either approximately constant or decreases slightly. But this decrease is insignificant, however, finally it increases again. Therefore, it can be argued that high initial heats are due to adsorbate–adsorbent interaction and the initial doses are adsorbed on the strongest available sites forming strong bond with the surface and liberating large heats. However, the dropping off of the enthalpy in the intermediate region may be attributed to the neutralization of all sites. But in the third region, the increase in enthalpy with the increase in surface coverage may be due to adsorbate–adsorbate lateral interactions.

The negative values of ΔH show that the adsorption of (C_1–C_4) on metal-doped alumina is exothermic in nature. The values of ΔH are higher for metal-doped alumina than parent alumina, which indicates that strong adsorbate–adsorbent interaction is found after impregnation. It may be that doping of alumina results in the increase in the contribution of the specific interactions to the total adsorption energy. It is also noted from the results that isosteric enthalpy of adsorption of (C_1–C_4) on metal-doped alumina are not the same, although the concentration of the metal used in the alumina lattice is nearly the same. It means that nature of the metal used for doping plays its role in the adsorption mechanism. It might be assumed that (C_1–C_4) act as Lewis base and coordinate with metal vacancies (40–42).

Summarizing the discussion on enthalpy of adsorption of *n*-aliphatic alcohols, we conclude that at given relative pressure, the enthalpy of adsorption for *n*-aliphatic alcohols (C_1–C_4) treated at the same temperature decreases in the order $C_1 < C_2 < C_3 < C_4$. The results reported here are consistent with those described by Nagao and Morimoto (1) and Morimoto et al. (2) who studied the adsorption of *n*-aliphatic alcohol on zinc oxide surfaces. This is because an alkyl group in organic molecule has an inductive effect. The inductive effect of the alkyl group, i.e., the tendency of thrusting its electrons at the neighboring atoms in the molecule, (43) is greater for alcohols with more carbon atoms; $C_1 < C_2 < C_3 < C_4$. Consequently, the oxygen atom in the butoxyl group becomes more negative than that in the propoxyl, ethoxyl, and methoxyl groups, which results in the enhancement of the bonding force of the butoxyl group to surface aluminum atoms, in comparison with that of methoxyl group. In addition to this effect, hydrogen bonding and mutual van der Waals interaction between hydrocarbon chains themselves may contribute to the heats of adsorption (44). The order of these effects is $C_4 > C_3 > C_2 > C_1$.

The values of entropies (Tables 2–7) show that these values are negative for all the adsorption systems investigated. The comparison of these values indicates that they are more negative for metal-doped systems. These low values indicate more constraint on the mobility of adsorbate molecules by metal-doped alumina.

According to ΔH and ΔS^0 values, one could classify these systems into two types of adsorption. The high values of ΔH and ΔS^0 for metal-doped alumina suggest the localized adsorption of (C_1–C_4) *n*-aliphatic alcohol. For parent alumina these values are lower than those of the metal adsorbents which means nearly localized adsorption.

CONCLUSIONS

The results indicate that impregnation of alumina with metal particles provide new adsorption surfaces and hence produce new adsorption sites with high activity, which increase the adsorption affinity of alumina for *n*-aliphatic alcohols (polar adsoptives) and make the adsorption more spontaneous. The results also show that the increase in the spontaneity of organic vapor adsorption is not an entropy effect, but is related to the increase in the values of enthalpy of adsorption. These high values of enthalpy of adsorption indicate that the adsorptives (C_1-C_4) act as a Lewis base and coordinate with metal vacancies present on the surface of alumina samples.

ACKNOWLEDGMENTS

One of the authors (A. K. Khattak) wishes to thank the University Grants Commission Islamabad, Pakistan for financial support.

REFERENCES

1. Nagao, M.; Morimoto, T.; J. Phys. Chem. **1980**, *84*, 2054.
2. Morimoto, T.; Kiriki, M.; Nagau, M.; J. Phys. Chem. **1980**, *84*, 2058.
3. Knozinger, H.; Stubner, B.; J. Phys. Chem. **1978**, *82*, 1526.
4. Kagel, R.O.; J. Phys. Chem. **1967**, *71*, 844.
5. Deo, A.V.; Dalla Lana, I.G.; J. Phys. Chem. **1969**, *73*, 716.
6. Schiffino, R.S.; Merrill, R.P.; J. Phys. Chem. **1993**, *97*, 6425.
7. Chahal, R.S.; Pierre, L.E.St.; Macromolecules **1968**, *1*, 152.
8. Hodgkin, J.H.; Solomon, D.H.; J. Macromol. Sci. Chem. **1974**, *3*, 621.
9. Greenler, R.G.; J. Chem. Phys. **1962**, *37*, 2094.
10. Afzal, M.; Khan, M.; Ahmad, H.; Colloid Polym. Sci. **1991**, *269*, 483.
11. Saleem, M.; Afzal, M.; Mahmood, F.; Ali, A.; Adsorp. Sci. Technol. **1992**, *9*, 17.
12. Afzal, M.; Khan, M.; J. Chem. Soc. Pak. **1987**, *9*, 337.
13. Afzal, M.; Mahmood, F.; Saleem, M.; Carbon **1993**, *31*, 01.
14. Gervasini, A.; Bellussi, G.; Fenyvesi, J.; Auroux, A.; J. Phys. Chem. **1995**, *99*, 5117.
15. Chiou, C.T.; Reucroft, P.J.; Carbon **1977**, *15*, 49.
16. Khattak, A.K.; Afzal, M.; Saleem, M.; Yasmeen, G.; Ahmad, R.; Colloid Surf. A: Physicochem. Eng. Aspects **2000**, *162*, 99.
17. Khattak, A.K.; Afzal, M.; Saleem, M.; Yasmeen, G.; Afzal, J.; Adsorp. Sci. Technol. **1999**, *17*, 181.
18. Afzal, M.; Mahmood, F.; Saleem, M.; Colloid Polym. Sci. **1992**, *270*, 917.
19. Afzal, M.; Mahmood, F.; Ahmad, H.; Colloids Surf. **1992**, *66*, 287.
20. Afzal, M.; Mahmood, F.; Saleem, M.; Ber. Bunsen-Ges. Phys. Chem. **1992**, *96*, 693.

21. Gregg, S.J.; Sing, K.S.W. *Adsorption Surface Area and Porosity*, 2nd Ed.; Academic Press: London, 1882; 17.
22. Afzal, M.; Jaffar, M.; Ahmad, J.; Perveen, N.; Colloid Polym. Sci. **1978**, *256*, 356.
23. Hopkins, P.D.; J. Catal. **1973**, *29*, 112.
24. Rhodin, T.N.J.R.; J. Am. Chem. **1950**, *72*, 5691.
25. Graham, D.; J. Phys. Chem. **1953**, *57*, 665.
26. Beebe, R.A.; Millard, B.; Cynarski, J.; J. Am. Chem. Soc. **1953**, *75*, 839.
27. Qadeer, R.; Hanif, J.; Adsorp. Sci. Technol. **1994**, *11*, 201.
28. Barrer, R.M.; Proc. R. Soc., Lond. **1937**, *161A*, 476.
29. Peri, J.B.; Hannan, R.B.; J. Phys. Chem. **1960**, *64*, 1526.
30. Peri, J.B.; J. Phys. Chem. **1965**, *69*, 211.
31. Peri, J.B.; J. Phys. Chem. **1965**, *69*, 220.
32. Oblad, A.G.; Messenger, J.U.; Brown, H.T.; Ind. Eng. Chem. **1947**, *39*, 1462.
33. Dowden, D.A.; J. Chem. Soc. **1950**, 242.
34. Hindin, S.G.; Weller, S.W.; Adv. Catal. **1957**, *9*, 70.
35. Cornelins, E.B.; Milliken, T.H.; Mills, G.A.; Oblad, A.G.; J. Phys. Chem. **1955**, *59*, 809.
36. Gervasini, A.; Auroux, A.; J. Phys. Chem. **1993**, *97*, 2628.
37. Knozinger, H.; Ratnasamy, P.; Catal. Rev. Sci. Eng. **1978**, *17*, 31.
38. Afzal, M.; Kolloid-Z. U.Z. Polym. **1971**, *248*, 1026.
39. Barto, J.; Durham, J.L.; Baston, V.F.; Wade, W.H.; J. Colloid Interface Sci. **1966**, *22*, 491.
40. Johnso, N.S.; Madix, R.J.; Surf. Sci. **1981**, *103*, 361.
41. Kojima, I.; Miyazak, H.S.; Yasumoi, I.; J. Chem. Soc. Faraday Trans., 1 **1981**, *77*, 1315.
42. Sexton, B.A.; Surf. Sci. **1979**, *88*, 299.
43. Fieser, E.G.; Fieser, M.L.F. *Textbook of Organic Chemistry*; Maruzen: Tokyo, 1952.
44. Pimentel, G.C.; Meclellan, A.L. *The Hydrogen Bond*; Freeman: San Francisco, CA, 1960; Chap. 6.

Received February 2000
Revised January 2001