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that the second virial coefficient of a gas is directly related to the two-body intermolecular potential¹⁸

$$B_{2}(T) = -\left(\frac{N_{\rm av}}{16\pi^{2}}\right) \int_{0}^{\infty} dr \ r^{2} \int d\Omega \ [\exp(-E_{12}t(r,\Omega)/kT) - 1]$$
(9)

where N_{av} is Avogadro's number, r is the distance between the origins of the references frames of molecules 1 and 2, and Ω stands for the five Eulerian angles defining the relative orientation of 1 and 2. The supersript t on E_{12} indicates the true pair potential rather than some effective pairwise additive potential fitted to liquid or solid data.

The six-dimensional integrals were evaluated by using the same algorithm as for the internal energy computations. The program was tested on monoatomic gases and on CS_2 , and our calculated values were in perfect agreement with those calculated inde-pendently in the literature,^{7,18} and this serves to assess the reliability of our integration scheme. We then calculated the second virial coefficient of o-, m-, and p-xylene and toluene. The results obtained for o-xylene with three different potentials (see Table V) are displayed in Figure 3.

When comparing experimental and calculated second virial coefficients, one must keep in mind that the pairwise additivity of intermolecular potential is not strictly valid: in condensed phases, many-body forces obviously contribute to total interaction energy. However, in a first approximation, their relatively smaller

contribution to the energy can be incorporated in a effective way in the pair potential. The dominant contribution to these forces is thought to be the repulsive Axilrod-Teller term.^{7,33} We therefore expected our effective pair potentials to give slightly overpositive second virial coefficients, especially at low temperatures.¹⁸ It was therefore clear that model 3 was not suitable. However, it was impossible to apply this criteria to discriminate between models 1 and 2. We chose to use model 2 for self-consistency with ref 2 but it must be noted that both models give internal energies which are indistinguishable within their confidence limits. The results obtained for toluene and *m*- and *p*-xylene were in all respects comparable to the results obtained for o-xylene, and we therefore used model 2 in all cases. Unfortunately, the experimental values of $B_2(T)$ for organic molecules > C_{10} are rather scarce, and we were therefore unable to test the potentials used for naphthalene, mesitylene, and the decalins. If one is primarily concerned with energy results, second virial coefficients calculations provide a first test of pair potentials which is undoubtedly useful in the case of organic molecules when one must rely on rather crude assumptions to build pair potentials, and it can only be hoped that such experimental values will become available.

Sorption and Diffusion of Alcohols in Heteropoly Oxometalates and ZSM-5 Zeolite

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The sorption and diffusion of a series of alcohols have been measured on various microporous ammonium heteropoly oxometalates and on ZSM-5 zeolite. The sorption capacities, heats of sorption, and diffusivities have been compared and contrasted, and the factors responsible for such differences have been delineated. While in ZSM-5 the pore size restriction may be dominant, it is apparent that in the larger pore heteropoly oxometalates the electric field potential plays an important role.

Introduction

The world's oil crisis in the 1970s has led to the search for fuels from alternative sources. As coal is available in huge quantity in many parts of the world, the conversion of syngas, derived from coal, to gasoline via the formation of methanol appears to offer an attractive alternative. To this date, no single catalyst has been bound that is effective for the conversion of syngas to methanol and the conversion of methanol to gasoline. Although no efficient catalyst has been developed for the syngas to methanol process, ZSM-5 zeolite first developed in 1972 by Mobil Oil Corp.^{1,2} has been shown to be an efficient catalyst for the methanol to gasoline/hydrocarbon process. As a consequence of its shape-selective behavior, high stability, high activity, and very high resistance to deactivation due to coking, the ZSM-5 zeolite has been gaining importance in a variety of industrially important processes such as alcohols to olefins, isomerization of xylenes, disproportionation of toluene, and alkylation of benzene and toluene.

Earlier work from this laboratory has shown that 12-tungstophosphoric acid (H₃PW₁₂O₄₀), 12-tungstosilicic acid (H₄SiW₁₂- O_{40}), and their ammonium salts are active and selective in the conversion of methanol to C_2-C_6 hydrocarbons³⁻⁶ and 12molybdophosphoric acid $(H_3PMo_{12}O_{40})$ and its salts are active in the oxidation reactions.⁶ However, the ammnoium salt of 12-tungstophosphoric acid (HPW) produced larger quantities of hydrocarbons from methanol than the parent solid acid.^{5,6} Furthermore, the hydrocarbons obtained with this salt consisted of substantially larger proportions of saturates, in contrast to the olefinic products with the parent acid. These results are similar to those observed with certain zeolites.

The unique catalytic properties of ZSM-5 zeolite are attributed to both its strong acid sites and its unique channel structure of two intersecting tunnel systems with cross sections of 5-6 Å. The crystal structure of ZSM-5 has as its characteristic feature a chain formed by fusing five-membered rings of corner-shared tetrahedra.7,8

Heteropoly oxometalates are ionic solids with discrete anions and cations, the former being high molecular weight cagelike structures. Of special interest in the present work are those with Keggin structure. In such structures the anion has a central atom such as, for example, phosphorus or silicon, surrounded by four oxygen atoms arranged tetrahedrally (Figure 1). Twelve oc-

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Figure 1. Structure of SiW₁₂O₄₀⁻⁴.

tahedra, with oxygen atoms at their vertices and a peripheral metal atom, for example, tungsten or molybdenum, at their centers, envelop the central tetrahedron and share their oxygen atoms with the latter and each other. Three types of oxygen atoms are found in the Keggin anion, one bridging the central atom and the peripheral metal atoms, the second connecting each pair of peripheral metal atoms while the third is attached only to the peripheral metal atoms and protrudes from the anion. The results of photoacoustic FTIR studies from this laboratory have shown that, while the heteropoly acids are essentially nonporous and have small surface areas of approximately 10 m^2/g , molecules such as ammonia, pyridine, and various alcohols are able to penetrate into the bulk structure and interact with the protons present.9-13 In addition, spectroscopic evidence for the existence of protonated methanol at room temperature and methylated anions at higher temperatures have provided information on the nature of the methanol conversion process on heteropoly oxometalates.14

As noted above the ammonium salt of 12-tungstophosphoric acid showed both higher activity as well as significantly different selectivity in the conversion of methanol than that observed with the parent acid.^{5,6} Subsequent work demonstrated that not only ammonium 12-tungstophosphate but also a number of additional monovalent salts of this acid were microporous.^{11,15} More recent work has shown that such microporosity is not confined to the tungstophosphate anion but occurs with the molybdophosphate, tungstosilicate, and tungstoarsenate anions.^{16,17} The low surface area parent solid acids of these salts possess interstitial voids apparently separated from one another by the terminal oxygen atoms. The pore structures that exist in certain of the salts of these acids appear to result from a translation and rotation of the anions to permit an interconnection of the void spaces to produce channels of sizes ranging from 6 to 13 Å.¹⁵⁻¹⁷

The present work is concerned with the sorption and diffusion of alcohols on various microporous ammonium salts of the heteropoly oxometalates and ZSM-5 zeolite. While these catalysts are all acidic and microporous, it is important to note that not

only do the acid strength distributions differ but also the former show relatively broad distributions of pore sizes as compared to those of the latter. Differences in the catalytic properties of these catalysts may be due, at least in part, to the differences in micropore structures and consequently to their sorption and diffusion properties. It is therefore important to have some insight into the sorption and diffusion of alcohols into these heteropoly compounds and to compare the results with those of ZSM-5 zeolites. Little or no information is currently available on this subject.

Experimental Section

The ammonium salts of 12-tungstophosphoric acid (NHPW), 12-tungstosilicic acid (NHSiW), and 12-molybdophosphoric acid (NHPMo) were prepared by adding stoichiometric amounts of an aqueous solution of ammonium carbonate to an aqueous solution of the heteropoly acid with constant stirring and evaporating to dryness over a water bath followed by drying at 383 K in an air oven for 4 h. ZSM-5 zeolite with a Si/Al ratio of 990 was prepared by a procedure described elsewhere.¹⁸ The morphology of the crystals of ammonium salts of heteropoly acids and ZSM-5 zeolite was evaluated by use of a scanning electron microscope (JEOL-JSM-840). High-purity alcohols methanol (BDH), ethanol (BDH), 1-propanol (Baker Analyzed), 1-butanol (Baker Analyzed), 2-methyl-2-butanol (Baker Analyzed), 2-methyl-1butanol (MCB), and 1-hexanol (J. T. Baker) were used without further purification.

Sorption equilibria and kinetics were studied gravimetrically with a Cahn RG electrobalance fitted to a high-vacuum system $(<10^{-4} \text{ mbar})$. The detailed procedure has been described elsewhere.¹⁹ The recorder response time and the buoyancy effect were determined from measurements in the absence of catalyst at different initial pressures of the sorbates. To reduce the resistance to the external mass transfer and to minimize the resistance to the transfer of heat liberated upon sorption from the solid to its surroundings, we used only small quantities (<20 mg) of heteropoly compounds or ZSM-5 zeolite spread in the form of single layers of crystals over a wide surface of the aluminum pan. Measurements with decreasing quantities of solid showed that the rates of sorption became constant when the mass of sorbent was less than 25 mg, indicating that intercrystalline diffusion resistance was negligible under such conditions. The pretreatment consisted of heating the ammonium salts of heteropoly acids and ZSM-5 zeolite at 523 and 623 K, respectively, under vacuum. The temperature of the sample could be kept constant with a variation of ± 0.1 K by immersing the sample leg of the balance in a constant-temperature bath. The pressure in the system could be increased or decreased by opening to the storage bulb or to the vacuum bulb, respectively. As the volume of the storage bulb was greater than that of the balance system, the change in pressure necessary to attain equilibrium was relatively small. Consequently the equilibrium pressure could be reached within a fraction of a second. Blank runs were employed to allow for buoyancy effects. Sorption equilibrium data were collected at 293, 308, and 323 K with both increasing and decreasing pressure. All data in the present work are reproducible to within $\pm 5\%$.

Results

In the present work sorption capacity will be defined as the amount of sorbate taken up at a pressure beyond which sorption is almost independent of pressure change. The shape of the sorption isotherm and the rate of attainment of sorption equilibrium of the C_1 - C_6 alcohols are found to be dependent upon the type of sorbent used.

Table I shows the sorption capacities of the ammonium salts of the three heteropoly acids and ZSM-5 zeolite at 293, 308, and 323 K. In general, the sorption capacities of the ammonium salts of the heteropoly acids are much lower than those of the ZSM-5 zeolite. Sorption isotherms of methanol at 293 K on the three

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TABLE I: Sorption Capacity $(mmol^{-1} g)$ of Heteropoly Compounds for Different Aliphatic Alcohols

	pressb	temp.		sorbent ^a	pent ^a		
sorbate	mbar	K K	NHPW	NHSiW	NHPMo	ZSM-5	
		293	0.90	1.70	1.00	3.25	
methanol	40	308	0.81	1.60	0.91	2.50	
		323	0.71	1.50	0.81	1.75	
		293	0.695	1.20	0.75	2.70	
ethanol	20	308	0.605	1.125	0.66	2.30	
		323	0.530	1.055	0.58	1.90	
		293	0.660	1.08	0.69	2.40	
1-propanol	20	308	0.570	0.995	0.60	2.15	
		323	0.485	0.930	0.515	1.80	
		293	0.600	0.83	0.575	1.80	
1-butanol	5	308	0.505	0.74	0.485	1.55	
		323	0.400	0.67	0.415	1.30	
		293	0.40	0.645	0.445	1.00	
2-methyl-2-	5	308	0.34	0.580	0.385	0.80	
butanol		323	0.275	0.510	0.320	0.62	
		293	0.460	0.655	0.470	1.65	
1-hexanol	1	308	0.380	0.580	0.405	1.40	
		323	0.315	0.505	0.335	1.15	

^aSorbents are labeled with abbreviated formula (see text). ^bPoint beyond which sorption is essentially independent of sorbate pressure.



Figure 2. Sorption isotherms of methanol (a) on ammonium salts of heteropoly acids at 293 K and (b) on ZSM-5 zeolite (Si/Al = 990) at 293, 308, and 323 K; \bullet , \blacktriangle , and \blacksquare represent data collected for increasing pressure and O, \triangle , and \square represent data collected for decreasing pressure.

ammonium salts and those at 293, 308, and 323 K on ZSM-5 are shown in Figure 2, parts a and b, respectively. Among the ammonium salts, NHSiW shows much higher sorption capacity for all the alcohols than NHPW or NHPMo. There is relatively little difference between the sorption capacities of NHPW and NHP-Mo, even though the former shows somewhat lower sorption capacity for all the alcohols studied. For a particular alcohol the sorption capacity of ZSM-5 (Si/Al = 990) is about twice the sorption capacity of NHSiW. For comparison, examples of the sorption capacity defined in terms of the mass of sorbate per unit volume of sorbent are shown in Table II.

TABLE II: Sorption Capacity (g/cm³) of Heteropoly Compounds for Different Aliphatic Alcohols

	sorption capacity, (g/cm ³) at 293 K			
sorbent ^a	methanol	1-propanol	1-hexanol	
NHPW	0.038	0.058	0.069	
NHPMo	0.034	0.050	0.058	
ZSM-5	0.094	0.144	0.168	

"Sorbents are labeled with abbreviated formula (see text).

TABLE III: Heats of Adsorption^a (kcal mol⁻¹) of Aliphatic Alcohols on Heteropoly Compounds

		sort	ent ^b				
sorbate	NHPW	NHSiW	NHPMo	ZSM-5			
methanol	9.4	8.4	8.6	10.6			
ethanol	10.2	9.9	9.4	11.1			
l-propanol	10.8	10.5	10.2	12.3			
1-butanol	11.5	11.5	11.0	14.3			
2-methyl-2-butanol	10.5	10.6	10.3	13.2			
1-hexanol	13.5	с	13.0	15.2			

^aAt fractional coverage, $\theta = 0.6 \oplus 0.1$. ^bSorbents are labeled with abbreviated formula (see text). ^cIrreversible.



Figure 3. Sorption isotherms of methanol (1), ethanol (2), 1-propanol (3), 1-butanol (4), 2-methyl-2-butanol (5), and 1-hexanol (6) at 293 K on (a) $(NH_4)_3PW_{12}O_{40}$ and (b) ZSM-5 zeolite (Si/Al = 990) P_0 is the saturated vapor pressure of the sorbate at the adsorption temperature.

While the mass of sorbate taken up by a given sorbent *increases*, the sorption capacities (mmol g^{-1}) of the ammonium salts and ZSM-5 decrease with boiling point and molecular size of the alcohol. With the four sorbents the order of sorption capacities for the alcohols is

methanol > ethanol > 1-propanol > 1-butanol > 1-hexanol > 2-methyl-2-butanol

For illustrative purposes the sorption isotherms of the six alcohols at 293 K on NHPW and ZSM-5 are shown in Figure 3, parts a and b, respectively. These orders show that for ZSM-5 zeolite the sorption capacity for the alcohols depends very much on the molecular size (kinetic diameter) of the alcohol.

The heats of sorption calculated from the equation

$$\Delta H^{s} = -R[\partial \ln P/\partial(1/T)]_{\theta}$$
(1)

		diffusivity, $10^{11}D$, cm ² s ⁻¹			
diffusing species	temp, K	$\overline{\mathbf{NHPW}}$ $L^a = 0.117$	$\frac{\text{NHSiW}}{L = 0.583}$	$\frac{\text{NHPMo}}{L = 0.208}$	ZSM-5 (Si/Al = 990) L = 0.541
methanol	293	1.0	24.1	4.2	57.5
	308	1.6	34.6	6.3	82.8
	323	2.2	47.1	8.5	113
ethanol	293	0.7	15.4	2.7	13.2
	308	1.0	22.5	3.7	23.5
	323	1.3	30.9	5.2	40.6
l-propanol	293	0.5	12.9	2.1	5.9
	308	0.8	16.7	3.1	13.2
	323	1.2	22.5	4.4	23.5
1-butanol	293	0.4	9.6	1.6	4.5
	308	0.6	12.9	2.3	7.4
	323	0.8	16.7	3.1	11.1
2-methyl-2-butanol	293	2.2	54.1	10.3	1.5
	308	3.0	72.3	13.5	2.8
	323	4.0	96.2	17.1	5.2
l-hexanol	293	0.05	b	0.5	0.8
	308	0.09	b	0.8	1.9
	323	0.13	Ь	1.1	3.3

^aL is characteristic length (micrometer). ^bSorption is irreversible.

where R is the gas constant, P is the pressure, T is the temperature, and θ is the fraction of the surface covered, are listed in Table III. The data show that in general the heats of sorption increase with the increase in molecular weight of the alcohol.

Rates of Sorption. The solution of the Fickian diffusion equation for a system of uniform spherical particles with a step change in surface concentration at time zero is

$$\frac{n}{n_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{k} \frac{1}{k^2} \exp \frac{-k^2 \pi^2 Dt}{r^2}$$
(2)

where n/n_{∞} is the fractional uptake at time t, D is the diffusivity (cm² s⁻¹), and r is the radius (centimeter) of the sorbent crystal.

The kinetics of sorption of alcohols may be described by n/n_{∞} versus $t^{1/2}$ plots. Since the n/n_{∞} versus $t^{1/2}$ plots are linear up to a n/n_{∞} value of about 0.5, the rates of sorption may be assumed to be controlled by intracrystalline diffusion of the alcohol molecules into the solid crystals. Diffusivity may then be calculated from the initial slopes of n/n_{∞} vs $t^{1/2}$ plots by using the equation

$$\lim_{t \to 0} \frac{\mathrm{d}(n/n_{\infty})}{\mathrm{d}t^{1/2}} = \frac{2}{\pi^{1/2}} \left(\frac{D}{L^2}\right)^{1/2} \tag{3}$$

where L is the characteristic length (centimeter) which is the ratio of volume (v) to external surface area (a) of the solid crystal.

The rates of sorption of methanol, ethanol, 1-propanol, 1-butanol, 2-methyl-2-butanol, and 1-hexanol at 293 K are shown in Figure 4 with NHPW and NHSiW and in Figure 5 with NHPMo and ZSM-5 zeolite. The n/n_{∞} vs $t^{1/2}$ plots are linear at least up to a value of about 0.5 for n/n_{∞} in all cases except in the sorption of 1-hexanol onto NHSiW. Sorption of 1-hexanol on NHSiW shows an induction period during which the sorption rate is low and subsequent to which the sorption rate increases sharply and finally decreases as the sorption capacity is approached. The diffusivities calculated from the initial slopes of n/n_{∞} vs $t^{1/2}$ plots at 293, 308, and 323 K are listed in Table IV. The diffusivities of alcohols in heteropoly compounds are evidently different from those in ZSM-5.

With both ZSM-5 and the heteropoly oxometalates the diffusivity, in general, decreases with increase in molecular weight of the alcohol, for a given temperature. However, with the heteropoly oxometalates, in contrast to ZSM-5, 2-methyl-2-butanol diffuses much more rapidly than any of the remaining alcohols. The diffusivity of a given alcohol in NHSiW is found to be approximately 20 and 6 times larger than in NHPW and NHPMo, respectively. All alcohols, with the exception of methanol, diffuse as rapidly if not more rapidly in NHSiW than in ZSM-5 zeolites. However, in ZSM-5 methanol diffuses approximately twice as



Figure 4. Kinetics of sorptions of (1) methanol (O), (2) ethanol (Δ), (3) 1-propanol (\Box), (4) 1-butanol (\bullet), (5) 2-methyl-2-butanol (Δ), and (6) 1-hexanol (\blacksquare) on (a) (NH₄)₃PW₁₂O₄₀ and (b) (NH₄)₄SiW₁₂O₄₀ at 293 K.

rapidly as in NHSiW. The order of diffusivity of alcohols in heteropoly compounds is

2-methyl-2-butanol > methanol > ethanol > 1-propanol > 1-butanol > 1-hexanol

and the order in ZSM-5 zeolite is

methanol > ethanol > 1-propanol > 1-butanol > 2-methyl-2-butanol > 1-hexanol

Discussion

While the sorption capacities of the ammonium heteropoly oxometalates decrease with increasing molecular weight of the sorbate alcohols, the values of the former parameter for these solids are considerably smaller than those observed with ZSM-5 (Figure



Figure 5. Kinetics of sorptions of (1) methanol (O), (2) ethanol (Δ), (3) 1-propanol (\square), (4) 1-butanol (\bullet), (5) 2-methyl-2-butanol (Δ), and (6) 1-hexanol (\blacksquare) on (NH₄)₃PMo₁₂O₄₀ and ZSM-5 (Si/Al = 990) zeolite at 293 K.



Figure 6. Sorption capacities of ammonium salts of heteropoly acids and ZSM-5 zeolite (Si/Al = 990) for different alcohols at 293 K.

6). It is evident that NHSiW possesses a significantly higher sorption capacity for all of the alcohols than that found for the remaining two heteropoly oxometalates, in spite of the earlier observations, from nitrogen adsorption, that the former solid contained the smallest micropore volume.¹⁵⁻¹⁷ The difference in the sorption capacities for the linear alcohols is mainly attributable to the difference in the surface areas of the solid sorbents. In general, sorption capacities of heteropoly compounds and ZSM-5 zeolite decrease with the increase in boiling point and kinetic diameter of alcohols. The effect of the kinetic diameter of the alcohol molecule on the sorption capacity is more pronounced in ZSM-5 than in the ammonium salts of heteropoly compounds. This observation is in agreement with data obtained earlier on the average pore radius in heteropoly compounds relative to that in ZSM-5.¹⁵⁻¹⁷

In the case of heteropoly compounds the diffusivity of a particular alcohol in NHSiW is significantly larger than that observed

with NHPW and NHPMo. The order of magnitude of diffusivity of a particular alcohol except methanol and 2-methyl-2-butanol (Table III) is the same in NHSiW and ZSM-5 zeolite. Methanol diffuses about 2.4 times faster in ZSM-5 than in NHSiW, at least between 293 and 323 K, whereas 2-methyl-2-butanol diffuses about 36 and 18 times faster in NHSiW than in ZSM-5 at 293 and 323 K, respectively. The diffusivity of normal alcohols increases with decrease in molecular weight in both the heteropoly compounds and ZSM-5 zeolite, but the increase in diffusivity with decrease in molecular weight is more pronounced in ZSM-5 than in heteropoly compounds. It should be noted that the values for the diffusivities obtained through the use of eq 3 are subject to error resulting from the inaccuracies in the determination of volume/surface area from scanning electron microscopy. It should also be noted that the diffusion equation can be fitted to the entire range of uptake data if there is no degree of disordering in the sorbent crystal (which is very rare). In the case of ZSM-5 zeolite it has been observed by Fyfe et al.²⁰ that the structure of the solid is altered upon sorption of some sorbents. The observed intersections of the sorption curves of methanol with ethanol and of ethanol with 1-propanol on ZSM-5 at relatively large values of $t^{1/2}$ may be due to changes in the solid structure during alcohol sorption.

It is interesting to note that the diffusivities of 2-methyl-2butanol (2M2B), while of the expected order with ZSM-5, are considerably higher than those of the remaining alcohols with all of the heteropoly oxometalates. A priori, this would appear to be attributable to one or more of the following and related factors: (1) the size of the sorbate molecule, particularly in comparison with the pore radii of the sorbent; (2) the distribution of charge on the sorbate molecule; (3) the nature of the surface of the solid sorbent. Since the average micropore radii are 0.95, 1.03, and 1.30 nm for NHSiW, NHPW, and NHPMo, respectively, $^{15-17}$ while that for ZSM-5 is approximately half these values, it appears that the observations with 2M2B and the heteropoly oxometalates cannot be attributed to a purely geometric effect, although the participation of such a factor cannot be completely neglected.

For purposes of assessing the importance of the molecular charge distribution it may be useful to compare the diffusivities measured for 1-hexanol and *n*-heptane,¹⁹ which are of similar kinetic diameter and molecular weight. With the heteropoly oxometalates the diffusivity of the former is considerably lower than that of the latter (e.g., by a factor of approximately 40 in NHPMo). Evidently the substitution of an hydroxyl for a methyl group results in a substantial decrease in the diffusivity. Since such a substitution leaves the kinetic diameter essentially unchanged, the observed differences in the diffusivity of 1-hexanol and *n*-heptane must be attributed to the contrasting natures of the methyl and hydroxyl groups.

A number of factors may be considered in explaining the apparently anomalous results for the diffusivity of 2-methyl-2-butanol in the heteropoly oxometalates. A semiquantitative comparison of the polar natures of 1-butanol, 2-methyl-2-butanol, and 2methyl-1-butanol (2M1B) suggests that the magnitude of the negative charge on the oxygen atom of 2M1B should be greater than that on 1-butanol itself while that on 2M2B is expected to be larger than that found with 2M1B. The order of charge magnitude on oxygen is thus predicted to be

2-methyl-2-butanol > 2-methyl-1-butanol > 1-butanol

which is seen to be identical with that measured for the diffusivity (e.g., the diffusivities of 2-methyl-2-butanol, 2-methyl-1-butanol, and 1-butanol in NHPW at 298 K are 2.2×10^{-11} , 1.1×10^{-11} , and 0.4×10^{-11} cm² s⁻¹, respectively) with the heteropoly oxometalates.

As the negative charge on the oxygen atom increases, it is expected that the influence of intramolecular hydrogen bonding will surpass that of intermolecular hydrogen bonding. Any decrease in the extent of intermolecular hydrogen bonding should

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result in a decrease in the boiling point of that liquid. Accordingly the order of intermolecular hydrogen bonding in the butanols is predicted to be 2-methyl-2-butanol < 2-methyl-1-butanol < 1butanol. In spite of its relatively lower molecular weight 1-butanol boils much above the boiling point of 2-methyl-2-butanol and 2-methyl-1-butanol because of its high intermolecular hydrogen-bonding effect. From the order of diffusivity and the order of intermolecular hydrogen bonding, it can be concluded that hydrogen bonding has a substantial influence on the diffusivity.

A decrease in the intermolecular hydrogen bonding is presumably accompanied by an increase in the energies associated with the various degrees of freedom. This would be expected to be reflected in an increased diffusivity. It is well-known that molecules containing one or more hydroxyl functionalities are susceptible to both intermolecular and intramolecular hydrogen bonding. Such effects could produce an enhanced concentration gradient that would alter the diffusivity but in the latter case may also introduce a geometric factor. However, the electric field that undoubtedly exists within the pores of the catalyst could presumably produce an attractive interaction with the sorbate molecules containing the hydroxyl group and provide an attractive potential gradient. It has previously been shown through the application of photoacoustic FTIR that the interaction between methanol and heteropoly oxometalates results in the protonation of the methanolic oxygen atom.^{13,14} While a similar phenomenon is possible with the ZSM-5 catalysts, the smaller pore sizes in these catalysts introduce a geometric factor that evidently takes precedence over such electric field effects.

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Registry No. NHPW, 12026-93-6; NHSiW, 77981-80-7; NHPMo, 12026-66-3; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 1-butanol, 71-36-3; 2-methyl-2-butanol, 75-85-4; 2-methyl-1-butanol, 137-32-6; 1-hexanol, 111-27-3.

Interaction Chemistry between Molybdena and Alumina: Infrared Studies of Surface Hydroxyl Groups and Adsorbed Carbon Dioxide on Aluminas Modified with Molybdate, Sulfate, or Fluorine Anions

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The surface OH groups on γ -Al₂O₃ modified with various concentrations of F⁻, SO₄²⁻, or molybdate anions were studied by use of IR techniques as well as by the adsorption of CO_2 in order to reveal the interaction chemistry between Al_2O_3 and molybdate species. Physicochemical characterizations of the modified Al₂O₃ were also conducted by means of LRS, XPS, and TPR techniques. It was revealed that the chemical reactivities and surface concentrations of hydroxyl groups determined the interaction modes between the anion and Al₂O₃, that is, the dispersion and distribution of the anion and its configuration. The molybdate anions were found to react with basic OH groups in a stoichiometry of $OH^-/Mo = 1$ at a concentration of $<10 \times 10^{13}$ Mo cm⁻². It was shown that nonbasic OH groups were simultaneously consumed for anchoring molybdate species in tetrahedral configurations. In this concentration range, the OH/anion ratio was almost identical for SO_4^{2-} and molybdate anions. With increasing molybdenum content, the OH/Mo ratio decreased markedly, resulting in the formation of polymolybdate species. With SO₄²⁻/Al₂O₃ and F⁻/Al₂O₃, similar correlations were established between the formation of surface or subsurface species and the concentrations of reactive OH groups. On reduction or sulfurization of the MoO₃/Al₂O₃ catalysts, a part of the consumed OH groups was restored and the extent of recovery increased as the wavenumber decreased.

Introduction

Surface chemistry of supported molybdena catalysts has received much attention.¹⁻⁴ Several molybdena-alumina interaction species and their dependencies on the loading level of molybdenum have been proposed.⁴⁻¹² With MoO₃/ γ -Al₂O₃ catalyst systems,

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the molybdenum species and their surface concentrations are summarized in Table I as a function of surface molybdenum content.2,9-21

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