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Adsorption of Hydrocarbons on Sodium and Demetallated Synthetic Faujasites

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Adsorption of *n*-hexane and benzene on sodium and demetallated synthetic faujasites at elevated temperatures was measured gravimetrically. Hexane was adsorbed with nearly equal heats of adsorption on sodium and demetallated Y zeolites; no preferential adsorption sites were detected. Heats of adsorption on NaY were less than on NaX because of reduced negative charge on the zeolite lattice. Benzene was also adsorbed on NaY nonspecifically but more strongly than was hexane. Both Bronsted acid sites in hydrogen Y and Lewis sites in decationized Y apparently serve as preferential sites for adsorption of benzene.

INTRODUCTION

Synthetic X and Y zeolites, analogs of the mineral faujasite, as synthesized in the sodium forms are relatively inactive as catalysts for carbonium ion type reactions compared to the forms in which sodium is replaced by ammonium (a process which may be called demetallation) or polyvalent cations. Many published investigations have been concerned with determining the nature of this difference in catalytic activity. A requirement for catalytic activity appears to be the presence of Bronsted acid sites (*1, 2*) although not all Bronsted sites are equally active (*3*).

Adsorption studies over a wide range of surface coverages at elevated temperatures should yield detailed information on surface–adsorbate interactions. Such information could conceivably reveal something of the nature of catalytically active sites.

Many studies of physical adsorption of hydrocarbons on synthetic faujasite have been reported since the pioneering work of Barrer and Sutherland (*4*) and Barrer, Bultitude, and Sutherland (*5*), but many of them have been limited by being either at low temperature–high surface coverage or on catalytically less active species. Exceptions have been some gas chromatographic studies on polyvalent cationic forms (*6–10*) and on demetallated forms (*11, 12*); this technique has the disadvantage of measuring adsorption only at extremely low (near zero) surface coverages and therefore reveals nothing about site heterogeneity (*13*). Adsorption isotherms have been obtained on demetallated forms at 20°C (*14*), and adsorption was studied by ultraviolet spectroscopy (*15*).

The faujasite structure (*16, 17*) is such that two interconnected pore systems, one large and one small, exist within it. The only one accessible to hydrocarbon molecules is the large pore system, which is a three-dimensional network of nearly spherical cavities commonly referred to as supercages. A supercage has a diameter of about 14 Å, but the diameter of the entrances to it are about 8–9 Å. The small pore system is inaccessible to hydrocarbons, but is accessible to cations and small molecules such as water. There are eight supercages in each crystallographic unit cell. Because each silicon or aluminum ion is surrounded tetrahedrally by four larger oxygens, the internal surfaces consist only of oxygen, the only other elements exposed to adsorbates being the exchangeable cations.

Replacement of the sodium ions in catalytically inactive sodium Y (NaY) by ion exchange with ammonium ions (demetallation) yields a material which, when properly activated by heat treatment, is an excellent catalyst. Mild heating, up to about 400°C, drives off occluded water and ammonia, leaving protons to supply the necessary cationic charge (*18*). This material is generally referred to as hydrogen Y (HY). More severe heating yields either of two other forms, depending on the manner of heating (*19, 20*). If the material is heated so that the water formed by dehydroxylation escapes quickly, ordinary decationized Y (DcY) is formed; if the heating is done in bulk so that the zeolite is steamed in its own escaping water, an ultrastable form (UsY) is formed, so-called because of its greater thermal stability (*20*). Dehydroxylation creates Lewis acid sites, probably aluminum ions exposed by removal of lattice oxygen (*18*).

Work done to determine cation positions in X and Y zeolites has been summarized recently (*21*), but the actual occupancy of positions, particularly at elevated temperatures, is not completely certain. Some of the sodium cations in dehydrated NaY occupy sites in supercages (*22*). Some of the hydroxyl groups of HY are also in the supercages (*23*); the Lewis acid sites of DcY must face supercages because all framework oxygens face supercages.

To determine whether these rather drastic changes in the accessible internal surface might affect the adsorption of hydrocarbons in a manner relatable to catalytic activity, gravimetric adsorption studies were conducted on sodium and demetallated faujasites, using *n*-hexane and benzene as probes representing two different types of molecules of catalytic interest. Adsorption was studied at the highest possible temperatures to simulate catalytic conditions. The primary object was to determine if there were any preferential adsorption sites within the faujasite lattice. If there were, a decrease in the heat of adsorption with increasing surface coverage would be observed as the filling up of the preferred sites was followed by adsorption on weaker sites.

EXPERIMENTAL METHODS

Equipment

Adsorption was measured using a Cahn RG electrobalance attached to a standard vacuum system capable of 10^{-6} Torr. Samples and counterweights were suspended by quartz fibers and buckets. Heating was by an aluminum tube furnace controllable to ±0.5°C. Temperatures were measured by a thermocouple suspended adjacent to the sample (within ca. 0.5 in.). Pressures of hydrocarbons were limited to below about 40 Torr, because above that limit heat conduction throughout the balance housing made temperature control difficult.

Materials

NaY was lot No. 1280-133 obtained from Linde Division, Union Carbide. Analysis gave a unit cell composition of $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]$ for the anhydrous material. NH_4Y was prepared from this by exchange three times with 10% ammonium nitrate solution; a 74% reduction in sodium content was obtained. NaX was Linde lot No. 1340080 with the composition $Na_{83.5}[(AlO_2)_{83.5}(SiO_2)_{108.5}]$. UsY was obtained from Davison Division, W. R. Grace and Co. and had a Si/Al ratio of 140/52 and a sodium content of 2.15% (77% removal). This sodium content corresponds to the intermediate form in the preparation of UsY (*20*), but the sample was determined to be ultrastable by its retention of surface area after heating above 700°C.

Hexane (99.99%) and benzene (99.91%) were Phillips Research Grade, used without further purification.

Procedure

Adsorption runs were made on 200 to 250 mg samples of fragmented pellets or pressed discs. Blank runs with low surface area silica established that no corrections to the raw data were required because of bouyancy effects, etc.

Sodium forms were precalcined at 500°C in 360 Torr of oxygen for 2 to 4 hr and evacuated 16 hr at 500°C prior to use. The NH_4Y was evacuated at 280°C for 14 hr to produce HY, and at 500°C for 14 hr to produce DcY; these temperatures were picked to coincide with zero and maximum cracking activities for this material (*3*). Figure 1 shows the weight of a single sample of NH_4Y evacuated 16 hr at successively higher temperatures. It demonstrates that the two temperatures produced different species, 280°C coming well before the discontinuity near 450°C caused by dehydroxylation. The difference in weight between 280 and 500°C is about equal to the theoretical weight loss expected for dehydroxylation. However, the nonzero slope of the low temperature part shows that dehydroxylation occurs over a wide temperature range and the species investigated probably do not represent either HY or DcY stoichiometrically. The existence and size of the discontinuity does suggest that they represent reasonable approximations to the "pure" materials. Figure 2 shows typical isotherms obtained for *n*-hexane on decationized Y.

One sample of NaY or UsY was used to obtain isotherms at all temperatures; samples were evacuated at 500°C for 16 hr between each experiment; this treatment returned them to their original weight. Experiments on similar systems showed that reproducible isotherms could be obtained in this manner and that calcination between experiments did not affect the results. For HY and DcY a sample of NH_4Y was first evacuated at 280°C, an isotherm for HY was obtained, and then evacuated at 500°C and an isotherm for DcY was obtained; a new sample was used for each pair of isotherms. 500°C is below the temperature at which structural collapse of NH_4Y begins as shown by a DTA endotherm at about 650°C (*3*). Other work is in agreement with this (*20*).

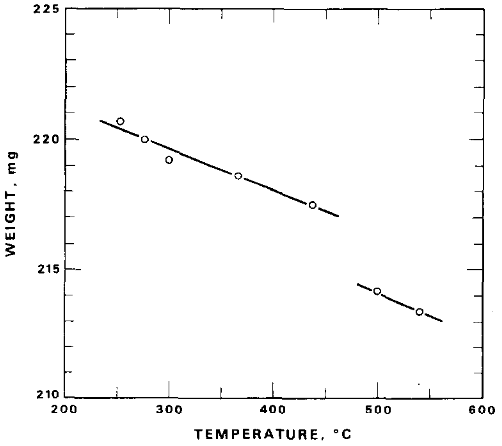

FIG. 1. Weight loss of NH_4Y as a function of evacuation temperature.

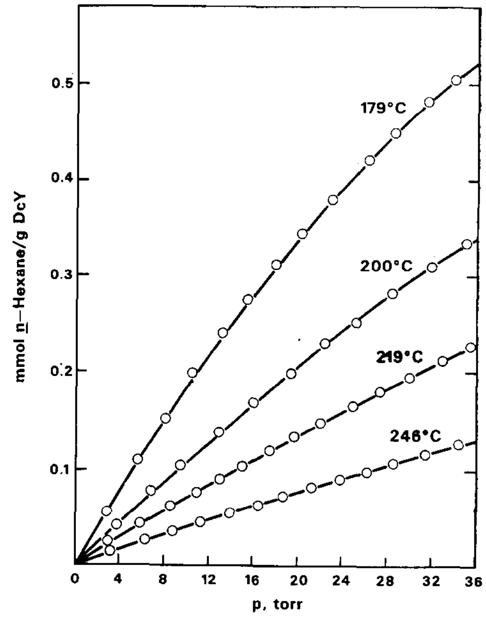

FIG. 2. Adsorption isotherms of *n*-hexane on DcY.

Isotherms were obtained at the highest temperatures possible in order to approach surface coverages typical of those existing during catalytic reactions. For catalytically active species a practical upper temperature limit was found in the 250–300°C region, because reactions began to occur and equilibrium could not be attained. Also, at higher temperatures adsorption in the available pressure range became too low in many systems. At least four isotherms at temperatures between about 170°C and the upper limit were obtained for each system.

Isosteric heats of adsorption, q_{st}, were calculated using the Clausius-Clapeyron equation:

$$q_{st} = -R\left(\frac{d \ln p}{d 1/T}\right)_X,$$

where X = surface coverage. All Clausius-Clapeyron plots were essentially straight lines; estimated maximum error in ΔH was less than 0.5 kcal/mol in all cases. No ΔH from less than three valid data points is reported.

Following previous work on zeolites (*4*, *24*) so-called standard free energies, ΔG^0, and entropies, ΔS^0, of adsorption were calculated in some cases for a standard gaseous state of one atmosphere from the equations:

$$\Delta H = -q_{st},$$

where ΔH is the differential enthalpy of adsorption

$$\Delta G^0 = -RT \ln(760/p),$$

where p = pressure in Torr, and,

$$\Delta S^0 = \frac{\Delta H - \Delta G^0}{T}.$$

Since ΔH and therefore the activity of the condensed phase varied with the amount adsorbed, neither ΔG^0 or ΔS^0 are true standard state thermodynamic properties. For *n*-hexane adsorption, which appeared to be largely nonspecific, use of such data for comparison at the low surface coverages reported is probably valid.

RESULTS AND DISCUSSION

n-Hexane Adsorption

Isosteric heats of adsorption for *n*-hexane on NaX (178–248°C) and NaY (163–220°C) are plotted in Fig. 3. The heats of adsorption for NaX of 13.8–14.7 kcal/mol are in excellent agreement with the 14.5–15.0 kcal/mol determined calorimetrically at 20°C (*25*) in the same adsorption range. Both NaX and NaY adsorb hexane more strongly with increasing coverages, implying that adsorbate–adsorbate interactions are occurring. Evidently, the tendency for such interactions is strong because the coverage interval in Fig. 2 represents adsorption of less than 1 molecule/supercage (1 molecule/supercage = 0.63 mmol/g for NaY and 0.60 mmol/g for NaX). The heats of adsorption in this region are several kcal/mol greater than those determined gas chromatographically for very low adsorption (*10*, *26*), further indication that adsorbate–adsorbate interactions begin at low coverages. Similar evidence for adsorbate–adsorbate interactions at low coverages has been found for the systems *n*-hexane–NaX (*25*) and *n*-hexane–sodium mordenite (*24*).

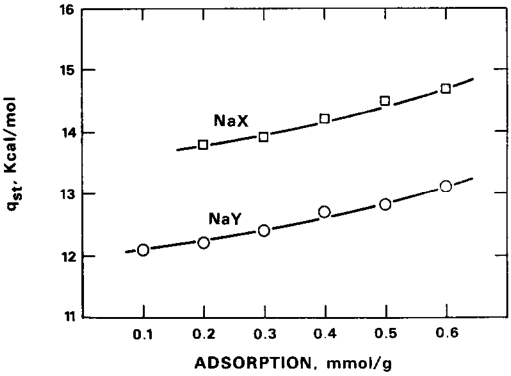

FIG. 3. Heats of adsorption of *n*-hexane on sodium faujasites.

NaX and NaY differ primarily in sodium and aluminum contents so any difference in adsorption is probably related to one or both of those factors. Previous studies have shown the importance of exchangeable cations in adsorption. Cations with large polarizing power, such as Li^+ and Ca^+, in X zeolite act as specific adsorption sites for argon and nitrogen; Na^+ specifically adsorbs nitrogen but not argon (*27*). Water adsorbs on alkali metal cations (*28*). Li^+ and possibly Na^+ in X zeolites are specific adsorption sites for ethylene but not for ethane (*29*). It is difficult to picture a saturated alkane, which may be thought of as a bundle of dipoles with positive (H) ends on the outside and the negative (C) ends buried in the center, as being preferentially attracted to a cation. Nor does the inaccessibility of the negative carbons favor a cation–oxygen pair as an adsorption site. It seems preferable to picture adsorption through attraction of the positive hydrogens to the negatively charged zeolite framework. All of the present data can be rationalized on this basis.

Heats of adsorption on NaX are more exothermic by about 1.5 kcal/mol than on NaY. Under the above assumption this would be because the higher aluminum content of NaX gives the internal surface a higher negative charge density. If the negative charge on the lattice is assigned equally to each oxygen, the charge per oxygen, above that which arises from the polarity of the (Si,Al)-O bonds, is 0.217 on NaX and only 0.146 on NaY. The actual difference on oxygens at adsorption sites is probably smaller than this, because the charge will be greater on oxygens which are located near sodium ions and which are less likely adsorption sites. The absence of larger heats of adsorption at low coverages indicates that there are at most very few preferential adsorption sites which adsorb *n*-hexane strongly; *n*-hexane, therefore, is adsorbed through interaction with the anionic oxide surface with no strong site preference. Such nonspecific adsorption is what one would expect of alkanes which are nonpolar and without double bonds. The entire internal surface of the large pore system in faujasite should be available to the hexane molecule, subject to geometric considerations and the avoidance of regions occupied by sodium ions.

Thermodynamic properties for adsorption of *n*-hexane on NaY and its demetallated derivatives are summarized in Table 1. Less *n*-hexane was adsorbed on the demetallated Y samples than on NaY at the same conditions; thermodynamics could not be reliably calculated at coverages greater than 0.2 mmol/g because of the pressure limitations noted above. The thermodynamic properties in the region measured are not much different from those measured on NaY. The heats of adsorption on all three demetallated species are slightly less than on NaY, but the differences are so small that it is reasonable to postulate similar adsorption sites on all four species. The constancy of the entropies of adsorption supports this view. Certainly the small differences in heats of adsorption do not account for differences in catalytic activity of the zeolites.

TABLE 1

ISOSTERIC THERMODYNAMIC PROPERTIES FOR ADSORPTION OF *n*-HEXANE

		Thermodynamics of adsorption					
		X[a] = 0.1			X = 0.2		
Substrate	Adsorption temp (°C)	$-\Delta G^0$[b]	$-\Delta H$	$-\Delta S^0$	$-\Delta G^0$	$-\Delta H$	$-\Delta S^0$
NaY	163	5.66	12.1	14.8	4.99	12.2	16.5
	180	5.47		14.6	4.74		16.5
	199.5	5.16		14.7	4.40		16.5
	220	4.86		14.7	4.04		16.5
HY	179	5.08	11.7	14.6	4.37	11.9	16.7
	197	4.85		14.6	4.10		16.6
	219	4.50		14.6	3.69		16.7
	248	4.03		14.7	3.12		16.8
DcY	179	4.44	11.0	14.5	3.81	11.0	15.9
	200	4.13		14.5	3.45		16.0
	219	3.86		14.5	3.13		16.0
	246	3.45		14.5	—		—
UsY	181	4.62	11.3	14.7	3.93	11.7	17.1
	201.5	4.34		14.7	3.67		16.9
	226	3.94		14.7	3.22		17.0
	250	3.59		14.7	—		—

[a] X = surface coverage (mmol *n*-hexane/g catalyst).

[b] ΔG^0 and ΔH in kcal/mol, ΔS^0 in cal/degree mol.

The differences in heats of adsorption between NaY and HY, although not much greater than experimental error, are consistent with greater localization of the negative lattice charge in hydroxyl oxygens and away from the adsorption sites in HY. The slightly smaller heats of adsorption on DcY and UsY are also consistent with reduced negative charge on the lattice oxygens because of fewer cations. The charge on the oxygens at adsorption sites may be further decreased by the greater polarizing power of the aluminum Lewis acid sites compared to sodium ions.

An interesting difference between DcY on one hand and NaY and HY was determined from *n*-hexane isotherms obtained at ambient temperature. These isotherms had sufficiently flat plateaus that apparent monolayer capacities could be determined by the point B method (*30*). These "monolayer capacities" were determined as 21.6 molecules/unit cell for DcY (23.5°C), 24.4 for NaY (25.5°C), and 25.2 for HY (23.5°C). When corrected for temperature differences the capacities of NaY and HY are essentially equal. These adsorption levels are equivalent to about 3 molecules/supercage, in essential agreement with Barrer and Sutherland (*4*) who determined a capacity of 3.8 molecules/supercage in NaY from the adsorption at a reduced pressure of 0.5.

Reduced adsorption capacity can best be accounted for by assuming that it results from the avoidance by the adsorbate of positive cationic or Lewis acid sites. There appear to be three possible explanations for the reduced capacity of DcY; either (a) there are more Lewis acid sites in the supercages of DcY than sodium ions in NaY or protons in HY, or (b) Lewis acid sites affect a larger area than protons or sodium ions, or (c) Lewis acid sites occupy more of that portion of the internal surface which otherwise would be most favorable for adsorption. The correctness and relative importance of these possibilities cannot be determined from the data at hand. Data on cation positions (*21*) do, however, show that more than one-half the sodium ions in NaY may be in the supercages so there may be more Na^+ in supercages in NaY than Lewis acid sites in DcY. Recent work on dehydrated KY supports this (*31*). Therefore, possibility (a) appears to be incorrect.

Benzene Adsorption

Heats of adsorption of benzene on the various faujasites are shown in Fig. 4. Benzene was adsorbed more strongly than hexane; consequently data were obtained up to higher coverages, particularly on the demetallated substrates; however, since the pressures were smaller there was greater scatter in the measurements.

In contrast to hexane, the heats of adsorption of benzene on the three forms of Y follow quite different paths. On NaY the heat of adsorption of benzene, like that of hexane, increased with increasing surface coverage; the rate of increase was greater for benzene than for hexane, indicating a greater tendency towards adsorbate–adsorbate interactions. The increase in the heat of adsorption of benzene on NaY in this coverage region is in disagreement with work on NaX by Avgul *et al.* (*25*), who found constant or slightly falling heats with increasing adsorption at ambient temperature after evacuation of the sample at 400°C for 50 hr. Factors which differed in the two systems are the temperatures of adsorption, a difference in the numbers of sodium ions in the large cavity system, and

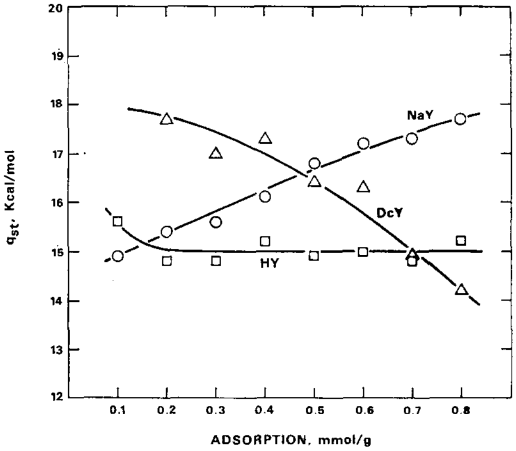

FIG. 4. Heats of adsorption of benzene on Y faujasites.

possibly differences in the residual water content in the supercages. Carter, Lucchesi, and Yates (*32*) found detectable amounts of residual molecular water in NaX after extensive evacuation up to 450°C but none was detected above that temperature. The amount of hydroxyl water retained at 450°C was much larger than at 600°C. Uytterhoeven, Christner, and Hall (*18*) found that NaX retained more hydroxyl than NaY after pretreating at 500°C. Thus the present sample of NaY, evacuated at 500°C, undoubtedly contained less hydroxyl and molecular water than the NaX of Avgul *et al.* Specific adsorption of benzene on the hydroxyl groups of NaX would give the adsorption trends found (see below). The differences in adsorption temperatures should not lead to the observed differences in adsorption behavior at the low surface coverages involved. The effect of the difference in sodium contents on benzene adsorption is difficult to evaluate. It is possible to envision an interaction between Na^+ and the π electron cloud of benzene but the lack of evidence for specific adsorption on NaY indicates that such interaction does not occur.

The heats of adsorption of benzene on HY remained essentially constant at 15 kcal/mol up to a coverage of 0.8 mmol/g. The heat of adsorption at 0.1 mmol/g was slightly higher; if true, this might indicate stronger adsorption at low coverage because of a few Lewis acid sites formed at 280°C (see discussion of DcY below). Since the curve for NaY (Fig. 3) indicates a relatively strong tendency for adsorbate–adsorbate interaction, the flatness of the HY curve suggests a set of specific adsorption sites widely spaced within the lattice. The similarity of the remainder of the NaY and HY structures suggests the hydroxyl groups in HY might be the specific adsorption sites.

The heat of adsorption of benzene on DcY was high at low coverages and then dropped with increasing adsorption. This behavior indicates that there are a small number of preferred high energy adsorption sites. Again, because of the similarity of the rest of the lattice to NaY or HY the Lewis acid sites are the most likely adsorption sites. Lewis acid sites have been recently proposed by others as preferential adsorption sites for aromatics in decationized faujasite (*12*). The Al or Si cations which are exposed in the Lewis acid sites should tend to form ferrocene-like structures with benzene; this would seem to be a preferred geometry for benzene to approach the Lewis acid site; approach to chemical bond distance is prevented by neighboring oxygen atoms so the heat of adsorption is much lower than expected for chemical bond formation. Complete dehydroxylation of HY would yield 20–21 Lewis acid sites/unit cell or about 2.5 sites/supercage. Although all oxygens in Y are part of the large pore system, not all Lewis acid sites seem to be equally accessible to benzene, since the heat of adsorption is decreasing in the coverage region of 1 molecule/supercage. The drop in q_{st} below the values measured on NaY indicates that insufficient amounts of undisturbed oxide surface remain to allow benzene adsorption of the type found on NaY.

If the postulates about adsorption sites are correct, it follows that adsorption on Lewis acid sites is stronger than on hydroxyl groups, as shown by the larger heats of adsorption on DcY than on HY at low coverages and by the larger heat at very low coverage on HY (assumed to be due to traces of Lewis acid sites).

Previous gas chromatographic studies of demetallated Y zeolites found the heat of adsorption of benzene at essentially zero coverage to be 14.1 kcal/mol after pretreating 3 hr at 555°C (*11*), and 14.9 kcal/mol after pretreating 2 hr at 600°C (*12*). These values are in better agreement with those found here for HY than for DcY. However, those pretreatment conditions should have produced primarily DcY, because loss of most chemically bound water is rapid at the temperatures used as shown by DTA (*3*, *33*) (see also discussion above). In order to reconcile these differences, it is necessary to assume that the Lewis acid sites which are the most preferred sites for benzene are the ones formed most slowly on dehydroxylation, or that structural rearrangements occur on prolonged evacuation at elevated temperatures.

CONCLUSIONS

Adsorption of *n*-hexane on sodium and demetallated faujasites, which probably occurs through interaction of the polar carbon–hydrogen bonds with the anionic oxygen framework, shows no strong preference for specific sites within the faujasite structure; adsorbate–adsorbate interactions become important at low concentrations on the sodium forms and probably on the demetallated form, as well, although data could not be obtained at high enough adsorptions on the demetallated forms to show this. Adsorption of benzene on NaY follows a pattern similar to hexane, but on HY and DcY benzene adsorption is more specific; preferred sites are probably the hydroxyl groups and Lewis acid sites, respectively; these sites are separated sufficiently to suppress adsorbate–adsorbate interactions at low to moderate adsorption levels.

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