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ADSORPTION ACTIVITY OF PILLARED CLAYS WITH RESPECT TO VAPORS OF ORGANIC ADSORBATES

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ABSTRACT

Cr and Cr + Al intercalated montmorillonites and their adsorption activity with respect to various adsorbates have been studied. The results of X-ray phase analysis showed that for the Logon bentonite sample, the value of the basal reflection d_{001} is about 12.3 Å. For Cr and Cr + Al intercalated materials, a shift of the d_{001} reflection towards a smaller angle is observed, which indicates an increase in the basal distance and intercalation efficiency and its values are 17.5 and 19.8 Å, respectively. A structural change in montmorillonite as a result of pillaring leads to an increase in its textural characteristics and adsorption activity with respect to polar and nonpolar molecules. The textural characteristics of mixed chromium-aluminum intercalated montmorillonite, calculated from the adsorption of nitrogen, hexane and toluene, are much higher compared to the characteristics of a sample of chromium intercalated bentonite.

Keywords: intercalation, pillar materials, polyoxocations, adsorption, hexane, toluene, ethanol.

INTRODUCTION

Intercalated smectites containing active ions between the layers are used as an effective adsorbent, active photocatalyst in various processes of transformation of organic substances. In particular, chromium pillar clays have shown high efficiency as catalysts for the destruction of hydrocarbons, the dehydration of alcohols, and the synthesis of esters [1]. Clay minerals, especially montmorillonite, are also widely used as adsorbents and acid catalysts [2, 3]. Recently, significant efforts have been made to investigate the role of modified clays as supports for many catalysts in various organic syntheses [4 - 7]. Suitable polynuclear metal hydroxy cations after intercalation with smectite clays produce so-called columnar clays with a larger pore size compared to zeolite, which can act as effective adsorbents and catalysts for fluid catalytic cracking and for other organic syntheses [8, 9].

Research work is being carried out to create new highly porous materials based on montmorillonite clays and oligomeric polycations. In this regard, special attention is paid to optimizing the conditions for the synthesis of oligomeric varieties of chromium and other metals, intercalating them into layered minerals, increasing thermal stability, adsorption and catalytic properties during the oxidation of organic substances from gaseous and aqueous media [10].

The microporosity and catalytic properties of smectite clays modified by intercalation and acid treatment have made them the subject of intense research [11, 12]. Supported inorganic reagents are rapidly becoming new and environmentally acceptable materials to improve process efficiency or to replace environmentally hazardous reagents and catalysts [13].

Montmorillonite mainly exhibits sorption activity due to exchangeable cations and anions. It is the availability of interplanar cations that is probably the decisive factor in adsorption processes. They also determine the porosity of the surface. It is known that pillared materials are characterized by low values of exchangeable cations, since the embedded polyoxocations lose their lability after heat treatment. Instead, they have an increase in the number of anion exchange centers due to the inserted columns, as well as the total negative charge of the surface, as evidenced by the value of the ζ potential [14].

Pillar clays have been identified as the porous materials of the current century and have attracted much attention from both science and industry [15 - 17]. Their high specific surface area, large volume of micropores, concentration of surface acid sites, increased hydrophobicity and density of sorption sites make them excellent adsorbents and catalysts for the extraction of pollutants from wastewater [18 - 20].

To establish the productivity of intercalation processes, the specific surface area is usually used. A change in the method of modification of the same bentonite demonstrates the difference in the values of the specific surface area and thermal stability [21]. However, there is currently no sufficient scientific justification for these phenomena. It has been established that due to the formed columnar structure between the layers of montmorillonite, during modification, the thermal stability increases and the surface area increases. Establishing patterns in the sorption of organic and inorganic substances, surfactants from aqueous solutions, proved an increase in adsorption capacity due to an increase in the volume of anion exchange centers and the specific surface area [22].

The adsorption of adsorbates is related to the conditions of the adsorption process, the nature of the adsorbent and adsorbates. Hexane and toluene differ from ethanol molecules in their low polarity, due to which these molecules can be adsorbed through physical adsorption due to van der Waals forces. Physical adsorption is possible in the presence of pores of suitable size. Such pores can be mainly micropores, between the basal surfaces, and minor mesopores between the contacting particles of montmorillonite, because the molecular sizes of hexane are $x = 10.344$ Å, $y = 4.536$ Å, $z = 4.014$ Å, and of toluene $x = 6.625$ Å, $y = 4.012$ Å, $z = 8.252$ Å [23]. On the contrary, the adsorption of ethanol is carried out not only due to the physical interactions of charged particles, but also the formation of chemical bonds. It is due to the greater number of contacts between the particles of the adsorbate and the charged active centers of the adsorbent that the adsorption of polar molecules proceeds, regardless of their size. Therefore, one should expect underestimated values of the limiting adsorption of these hydrophobic adsorbates and the textural indices calculated on their basis in comparison with the data based on the adsorption of ethanol. Similar results were presented in [24, 25].

The aim of the research was to establish the adsorption activity of synthesized pillared clays with respect to polar and non-polar organic molecules. The data obtained can be used to substantiate the mechanism of interaction of various adsorbates with the surface of sorbents and the ongoing structural changes during the intercalation of chromium and other pillars.

EXPERIMENTAL

Montmorillonite (MM) containing clay of the Logon deposit (Republic of Uzbekistan, Fergana region) was chosen as the starting material. Before use, bentonite went through a preparatory stage - enrichment, which was carried out by elutriation and isolation of a fraction with a particle size of not more than 10 microns. The establishment of the chemical and mineralogical composition of bentonite (LB) samples and its pillar forms was carried out by X-ray phase analysis using XRD Empyrean PANanalytical X-ray diffractometer with the possibility of a minimum scanning step of 0.0001° and reproducibility of setting the angle < 0.0002°. CuKα radiation was used (β-filter, Ni, 1.54178 current mode and tube voltage 30 mA, kV) and the detector rotation speed was 4 deg min^{-1} in 0.02 deg increments, and the scanning angle varied from 4 to 80º.

In the early works of the authors, the results of studying the processes of synthesis of polyoxocations, their intercalation into the interlayer space of the enriched form of the selected bentonite are presented [26]. According to the obtained experimental data, the synthesis of polyoxocations was carried out using a solution of a hydrolyzing agent, which was chosen as sodium hydroxide. The initial concentration of chromium salts was no more than 0.5 M, and the ratio OH^-/Cr^{3+} was about 2 - 2.2. Under such synthesis conditions, the greatest stability values of pillaring cations are achieved.

For mixed chromium-aluminum pillars, the ratio $OH^-/(Cr^{3+} + Al^{3+})$ is about 2.4 - 2.5. As established, the process temperature also differs for these polyoxocations and is 70°C - 72°C and 53°C - 55°C, respectively.

Enriched clay was added to the synthesized pillaring solutions containing polyoxocations of chromium and aluminum with constant stirring at a temperature of 50ºC, so that 5 mmol of the cation per 1 g of montmorillonite clay. After stirring for 2 hours, the resulting suspensions were kept at a temperature of 20°C - 25°C for a day. The suspension was stirred from time to time. Then the upper part of the suspension (the formation of a precipitate and partial clarification of the upper part was observed) was removed by decantation. The lower part was centrifuged and the precipitate was washed with distilled water. The washing water was examined for the presence of Cl^- ions and then only the precipitate was dried at room temperature or in an oven. The obtained samples were stored in a desiccator.

The textural characteristics of the samples were determined based on low-temperature nitrogen adsorption data (autosorb iQ-MP/XR).

Adsorption isotherms of vapors of organic adsorbates at a temperature of 20ºC were taken by the gravimetric method on a vacuum adsorption unit with McBain-Bakr balances. Data on the facility designed in the Laboratory of Colloid Chemistry (IGIC AS RUz) are given in [27]. Before measuring adsorption, clay samples were evacuated at 200°C and 500ºC (up to a residual pressure in the system of 10^{-3} mmHg).

RESULTS AND DISCUSSION

The effectiveness of the use of pillar materials, generally known layered systems, as an adsorption or catalytically active substance for various processes, both in industry and for environmental protection, primarily depends on the availability of their adsorption centers. It is precisely because of the nature of adsorption sites and their availability that the adsorbent and catalysts perform their functions. Therefore, the surface indices of layered systems and pillar materials based on them must be studied in a wide range, including composition, structure, surface area, adsorption volume, etc.

The mineralogical composition of Logon natural bentonite is represented by montmorillonite (40 % - 55 %), kaolinite (5 % - 8 %), hydromica (13 % - 22 %), soluble salts (< 7 %), etc. Enrichment led to an increase in the content of montmorillonite to 93.6 % while reducing soluble salts and kaolinite to 0.11 % and 1.1 %, respectively. At the same time, the cation-exchange capacity increased noticeably: from 63.3 to 96.3 meq 100^{-1} g^{-1}. This change is primarily associated with a decrease in the amount of non-clay substances, as well as kaolinous and hydromica clay, and an increase in the content of the main component, montmorillonite.

It is known that the intercalation of polyoxocations of various metals or organic molecules (ions) occurs with an increase in the interplanar distance, and as a result, an increase in microporosity [15, 28]. The results of X-ray phase analysis showed (Fig. 1) that for the LB

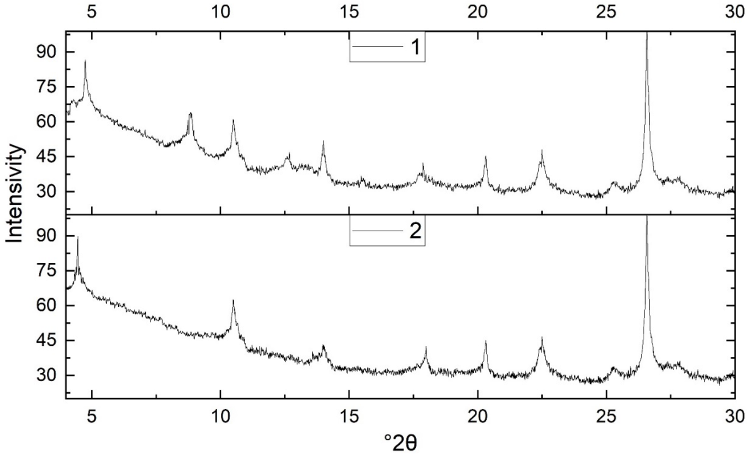

Fig. 1. X-ray pattern of enriched LB.

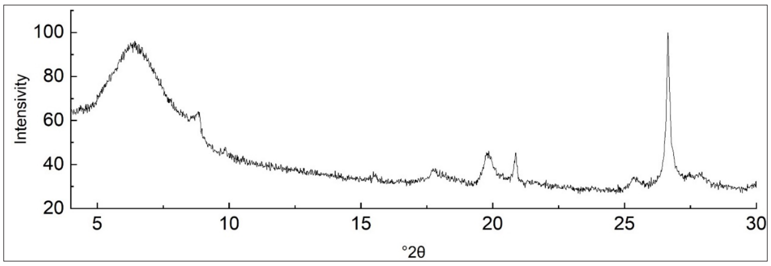

Fig. 2. X-ray pattern of pillar materials: 1) Cr-LB; 2) Cr/Al-LB.

sample the value of the basal reflection d_{001} is about 12.3 Å. For Cr (Cr-LB) and Cr + Al (Cr/Al-LB) intercalated materials, a shift of the d_{001} reflection towards a smaller angle is observed, which indicates an increase in the basal distance and intercalation efficiency [28]. Its values are 17.5 Å and 19.8 Å, respectively (Fig. 2).

The calcination of intercalated materials (pillaring) is considered the main technique for retaining embedded pillars and large interplanar distances. Therefore, the obtained samples were subjected to calcination at a temperature of at least 550°C. Thermal treatment of LB reduces the interplanar spacing to 9.1 Å, and for pillar specimens, the value of the basal reflection d_{001} upon calcination decreases only to 15.8 Å and 18.6 Å, and the intensity d_{001} decreases from 83 % and 91 % to 75 % and 81 %, respectively, which indicates the preservation of a significant part of the microporous structure. Probably, the increased values of these indicators for the mixed polyoxocation are associated with its greater stability. Similar changes are also given in [1, 21, 28, 29]. The relatively high intensity of the peak's characteristic of Cr_2O_3 indicates that some part of the Cr^{3+} ions is located outside the clay interlayers [28, 30].

Thus, the intercalation of Cr and Cr/Al polycations into the interlayer space of montmorillonite leads to noticeable changes in the structure and porosity of these systems, which will primarily affect their adsorption activity. The specific surface area of an adsorbent is a significant parameter affecting its adsorption activity. The larger the specific surface area, the larger the space for contact in adsorption and other chemical processes [31].

Fig. 3 shows N_2 adsorption isotherms on the samples under study.

The textural characteristics calculated on the basis of the results of low-temperature nitrogen adsorption are given in Table 1.

The resulting isotherms (Fig. 3) are characterized by a similar shape and can be defined as type IV isotherms according to the IUPAC classification, which is typical for mesoporous materials. A hysteresis loop of the H3 type shows that the material belongs to layered systems with slit-like gaps-pores between the plates [32].

As the data in Table 1, the adsorption activity of LB is significantly lower than that of intercalated clays, as indicated by the values of the pore volume and specific surface area. This indicates that the intercalation process increases the porosity of the clay. Comparison of the values of the specific surface of pillar materials shows a significant increase in porosity during the intercalation

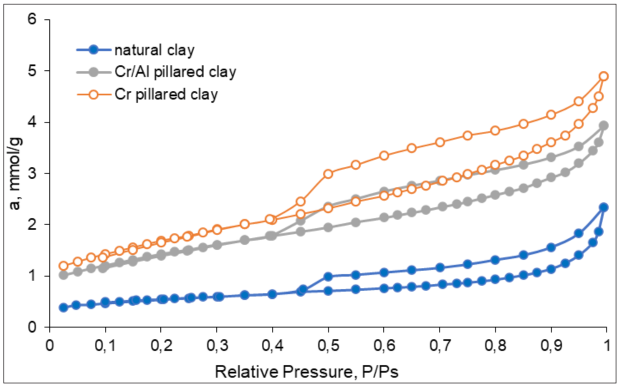

Fig. 3. Nitrogen adsorption isotherms of natural and pillared clays.

Table 1. Textural characteristics of samples calculated from nitrogen adsorption data.

Sample	S_{BET}, m^2 g^{-1}	Pore Volume, cm^3 g^{-1}	D_{pore}, Å
LB	40.81	0.054	30.36
Cr-LB	130.39	0.144	28.51
Cr/Al-LB	110.18	0.115	29.54

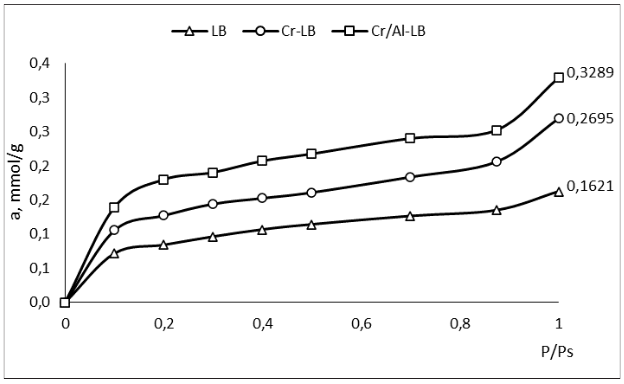

Fig. 4. Adsorption isotherms of toluene vapor on natural and pillared clays.

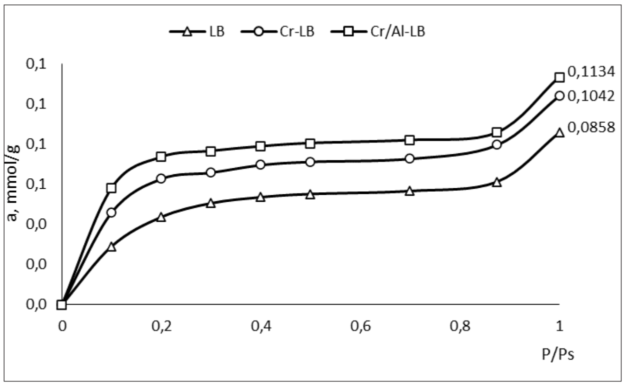

Fig. 5. Adsorption isotherms of hexane vapors on natural and pillared clays.

of mixed polyoxocations, showing the presence of a correlation of these indicators on the size and stability of polyoxocations.

Fig. 4 shows adsorption isotherms of toluene at 20°C on enriched LB and intercalated materials.

A steeper rise in the adsorption isotherm of toluene on pillar adsorbents is observed at low relative pressure, and a significant difference in the adsorption capacity of the studied samples at high relative pressure is also visible. The adsorption values at the corresponding values of relative pressure ($P/P_s \leq 0.2$) for two pillars of montmorillonites are higher than for the enriched sample, which demonstrates an increase in the proportion of micropores after pillaring.

At the same time, the sorption capacity for hexane on the objects under study is somewhat lower than that for toluene (Fig. 5). Thus, the sorption capacity for hexane at atmospheric pressure is 0.1621 mmol g^{-1} for the LB sample, and 0.2695 and 0.3289 mmol g^{-1} for mono- and heteronuclear pillar samples, respectively. The hexane molecule exhibits an interaction of the CH-π type, due to the Al=O bond. If we take into account the dimensions of the hexane molecule, then it can be oriented between the layers of intercalated materials, both parallel and perpendicular to the surface.

A more significant adsorption of toluene is explained by the presence of π-π interaction due to the aromatic ring and Al=O bonds and CH_3-π in the adsorbate-adsorbent system [33].

It should be noted that the sorption capacity of Al/Cr-LB for ethanol is greater than for nonpolar hexane and toluene molecules at high relative pressures ($P/P_0 > 0.25$). However, the reverse effect is clearly visible when the adsorption values of toluene are higher compared to ethanol at low relative pressures ($P/P_0 < 0.1$). This is probably due to the different structures of the adsorbate molecules. Low adsorption values were also established for hexane. It is known that adsorption affinity depends on the structure of micropores at low relative pressures. Toluene with a disk-like structure can more easily pass-through narrow constrictions at the pore entrances and reach adsorption sites [34]. Meanwhile, for non-polar compounds such as benzene, physical properties play a more important role than surface properties at low relative pressures [35].

According to the above experimental results, the factors affecting the adsorption mechanism of gaseous organic adsorbates are related to the properties of both the adsorbent and the adsorbate. The developed microporous structure of montmorillonite pillars plays a key role in the adsorption process. The efficiency of adsorption of polar adsorbates can be obviously influenced by surface functional groups and the structure of adsorbents, as well as the polarity of adsorbates [36].

All displayed isotherms show an increase in values in the region of saturated vapor pressure close to $P/P_0 = 1$. The distinctively high adsorption activity with respect to ethanol of the initial LB can be described by the tendency to expand the interlayer distance due to the penetration of polar ethanol molecules into the interlayer space. An increase in the sorption capacity for ethanol pillared clay is associated with an increase in the volume of micropores and a negative charge on the surface. These sites that accept an electron pair appear in the absence of water and OH groups with complete dehydration of polycation columns, for which pillared interlayer cations

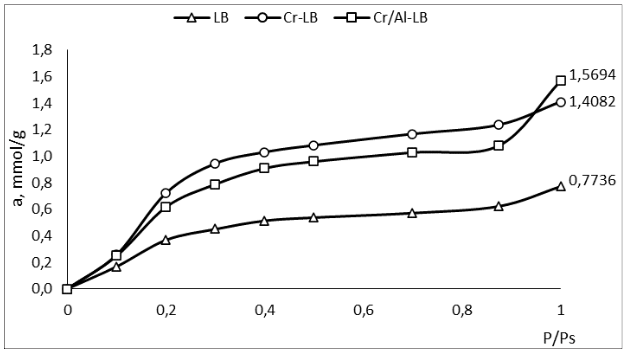

Fig. 6. Adsorption isotherms of ethanol vapors on natural and pillared clays.

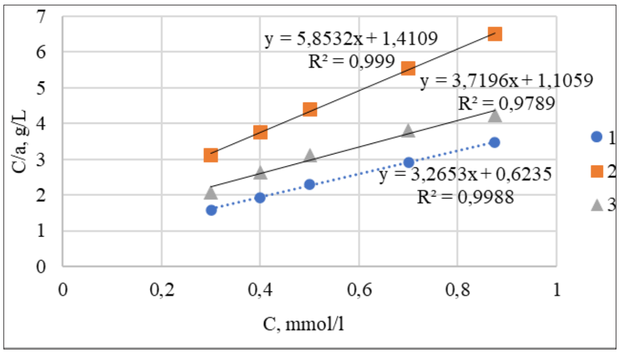

Fig. 7. Adsorption isotherms of toluene vapors in the coordinates of the linear form of the Langmuir equation: 1) Cr/Al-LB; 2) Cr-LB; 3) LB.

Table 2. Textural characteristics of samples calculated from hexane vapor adsorption data.

Sample	S_{BET}, m^2 g^{-1}	Pore Volume, cm^3 g^{-1}	R, nm
LB	20.937	0.011	10.765
Cr-LB	27.034	0.014	10.124
Cr/Al-LB	28.131	0.015	10.589

Table 3. Textural characteristics of samples calculated from toluene vapor adsorption data.

Sample	S_{BET}, m^2 g^{-1}	Pore Volume, cm^3 g^{-1}	R, nm
LB	48.751	0.017	7.057
Cr-LB	76.715	0.029	7.456
Cr/Al-LB	87.388	0.065	7.987

Table 4. Textural characteristics of samples calculated from ethanol vapor adsorption data.

Sample	S_{BET}, m^2 g^{-1}	Pore Volume, cm^3 g^{-1}	R, nm
LB	118.540	0.045	7.524
Cr-LB	229.501	0.081	7.074
Cr/Al-LB	205.731	0.090	8.735

are responsible. Therefore, the adsorption of ethanol vapor increases, and the more, the greater the number of these adsorption centers [37].

It was found that the Langmuir model satisfactorily describes the adsorption of these adsorbates at low values of relative pressure, as evidenced by the value of R^2 (Fig. 7).

The calculated values of the textural parameters of the studied samples are given in Tables 1 - 3.

As can be seen from the data in Table 2, the original montmorillonite and its pillar forms are characterized by practically similar values of the specific surface area and pore size calculated from the adsorption of hexane vapor. The total pore volume increases from 0.011 to 0.014 - 0.015 cm^3 g^{-1}. Probably, the main fraction of adsorbed hexane molecules are in the pores between the contacting particles and the side faces of montmorillonite (MM), which, after annealing at 550°C, largely lost their hydrophilic groups, and only an insignificant part is adsorbed in the interplanar space [38].

Despite the similarity of the nature of the adsorbates, the surface characteristics of toluene adsorption are much higher, especially for the Cr/Al sample. The calculated values of the total pore volume of pillar bentonites increase from 0.017 to 0.029 and 0.065 cm^3 g^{-1}, respectively, for Cr-LB and Cr/Al-LB samples.

The adsorption activity of both the initial calcined and pillared montmorillonites is much higher with respect to polar molecules, which can be seen from the data in Table 4. Higher values of the specific surface area of Cr-LB compared to Cr/Al-LB, despite the larger pore volume of the latter, is associated with the number of surface-active ethanol adsorption sites.

CONCLUSIONS

Thus, the conducted studies have shown that the adsorption activity of the initial montmorillonite and pillared clays with respect to adsorbates of different nature differ from each other. The surface activity of pillared clays depends mainly on the nature of the intercalating cation, its stability and size. Thermal treatment of natural bentonite reduces the volume of micropores, which is also evidenced by a decrease in the interplanar distance from 12.3 Å to 9.1 Å. For pillar specimens, the value of the basal reflection d_{001} during calcination decreases only to 15.8 Å and 18.6 Å, and the intensity d_{001} decreases from 83 % and 91 % to 75 % and 81 %, respectively, which indicates the preservation of a significant part of the microporous structure. The adsorption activity of LB is significantly lower than that of intercalated clays, which is indicated by the values of the pore volume and specific surface area calculated from the results of low-temperature nitrogen adsorption.

As it turned out, the initial MM and its pillar forms are characterized by similar values of the specific surface area and pore size calculated from the adsorption of hexane vapor. However, despite the similarity of the nature of the adsorbates, the surface characteristics of toluene adsorption are much higher, especially for the Cr/Al sample. The calculated values of the total pore volume of pillar bentonites increase from 0.017 to 0.029 and 0.065 $cm^3 g^{-1}$, respectively, for Cr-LB and Cr/Al-LB samples. The adsorption activity of both the initial calcined and pillar montmorillonites is much higher in relation to polar ethanol. The higher values of the specific surface area of Cr-LB compared to Cr/Al-LB, despite the larger pore volume of the latter, are related to the number of surface-active ethanol adsorption sites.

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