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Letter

Promoting Aromatic C−H Activation through Reactive Brønsted Acid−Base Pairs on Penta-Coordinated Al-Enriched Amorphous Silica−Alumina

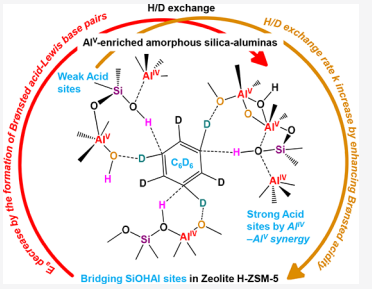
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ABSTRACT: The surface acidity and local coordination environment of zeolites and amorphous silica−aluminas (ASAs) can promote acid-catalyzed C−H activation in many important hydrocarbon conversion reactions. Acid sites generated by penta-coordinated Al species (Al^V) can lead to enhanced acidity and changes in the surface coordination. We evaluated the potential of flame-derived ASAs with enriched Al^V for C−H activation using hydrogen/deuterium (H/D) exchange with benzene-d_6. With increasing Al content of ASAs, the exchange rate increased, whereas the activation energy (E_a) slightly decreased due to the enhanced Brønsted acidity. The ASAs exhibited significantly higher exchange rates and lower E_a values than the sol−gel-derived ASAs and zeolite H-ZSM-5. The superior activity is attributed to the fact that more oxygen coordinated with Al^V species on flame-made ASAs, which can act as acceptors for D^+, enhancing the deuterium displacement. These findings could offer a valuable alternative strategy for tailoring high-performance solid acids to promote hydrocarbon conversion reactions.



The activation of C−H bonds is a key step in driving versatile industrially important hydrocarbon conversion reactions, such as hydrocracking, alkylation, isomerization, and dehydrogenation.[1,2] Zeolites and amorphous silica−aluminas (ASAs) are extensively applied to promote these reactions through hydrocarbon protonation at surface Brønsted acid sites (BASs), forming carbon cation intermediates. In general, BASs with high acid strength promote C−H activation at a high rate[3,4] and exhibit a lower activation energy (E_a) in H/D exchange with deuterated hydrocarbons, in line with the high activity of aluminosilicates.[5−7] Therefore, C−H bond activation in hydrocarbons often requires strong BASs, and the lower performance of ASAs is attributed to their weaker Brønsted acidity compared with that of zeolites.

Hydrogen-deuteron (H/D) exchange of benzene, the simplest aromatic compound, is a suitable model reaction for studying C−H bond activation and is thus of fundamental importance in synthesizing key chemicals via aromatics alkylation reactions.[7−11] The H/D exchange between C_6D_6 and BASs is described as an electrophilic substitution.[12] Initially, C_6D_6 can be adsorbed or protonated at BASs, which then transfer to σ-bonded complexes to release a deuteron to the surface oxygen as a proton acceptor, such as the negatively charged oxygen on the zeolite framework generated after BAS deprotonation (Figure 1).[8] Therefore, it has been suggested that H/D exchange of benzene is selective on strong BASs.[3,7,8,13,14] Because BASs in zeolites are generated by protons compensating for the negative charge from the tetra-coordinated Al (Al^{IV})-substituting framework Si atoms, increasing the Si/Al ratio of zeolites can enhance the strength of BASs but decreases the number of BASs for C−H activation.

In addition to increasing the BAS strength to promote σ-bonded complex formation, nearby surface oxygen atoms as deuteron acceptors facilitate the H/D exchange as well. Using zeolites, mainly one negatively charged framework oxygen formed upon BAS deprotonation acts as a deuteron acceptor. The formation of moderate BASs in ASAs is widely accepted as Al^{IV} sites interacting with neighboring SiOH groups in the silica networks. Surrounding oxygen atoms at BASs in silica networks are less basic than those in the alumina phase and are considered to be less effective at promoting the H/D exchange of C_6D_6. Recently, flame-derived ASAs with highly dispersed and populated penta-coordinated Al (Al^V) species were prepared, which could promote the density and strength of BASs in ASAs.[15−24] At high Al/Si ratios, populating Al atoms in the local structure of BASs in the Al matrix are reported to enhance the local ionicity in these ASAs. Electron-rich oxygen atoms from the Al matrix of Al^V species are expected to provide more effective deuteron acceptors than conventional ASAs, which promotes the H/D exchange of C_6D_6.

In this work, we demonstrate a novel strategy for promoting the C−H activation of benzene via the cooperativity of

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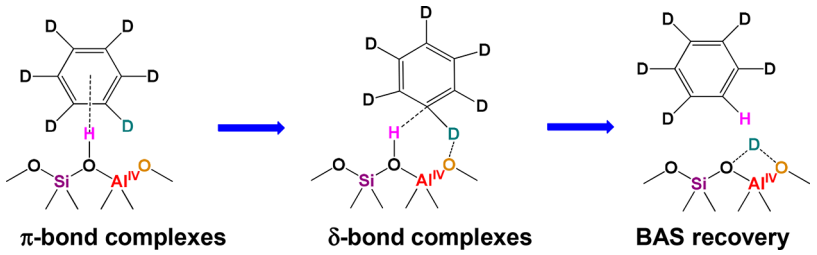


Figure 1. Proposed scheme for the H/D exchange of C_6D_6 at strong BASs in zeolites.[8]

Table 1. H/D Exchange Degree, Exchange Rate k at Different Temperatures, and Activation Energy E_a for the H/D Exchange of C_6D_6 over ASAs and Zeolite H-ZSM-5

	H/D exchange degree (%)				k ($\times 10^{-3}$ min^{-1})				
	313 K	333 K	353 K	373 K	313 K	333 K	353 K	373 K	E_a (kJ/mol)
SA/10	2.1	4.8	9.4	19	4.5	7.8	11.3	17.1	22.5
SA/30	8	17	22	33	7.1	9.9	13.5	20.5	17.5
SA/70	10	20	28	38	9.5	11.9	16.2	27.1	15.9
H-ZSM-5	41	62	71		7.0	27	105		61.2
ASA, Si/Al = 15[30]		4.5	9.2	17		2.3	4.1	8.6	33.8

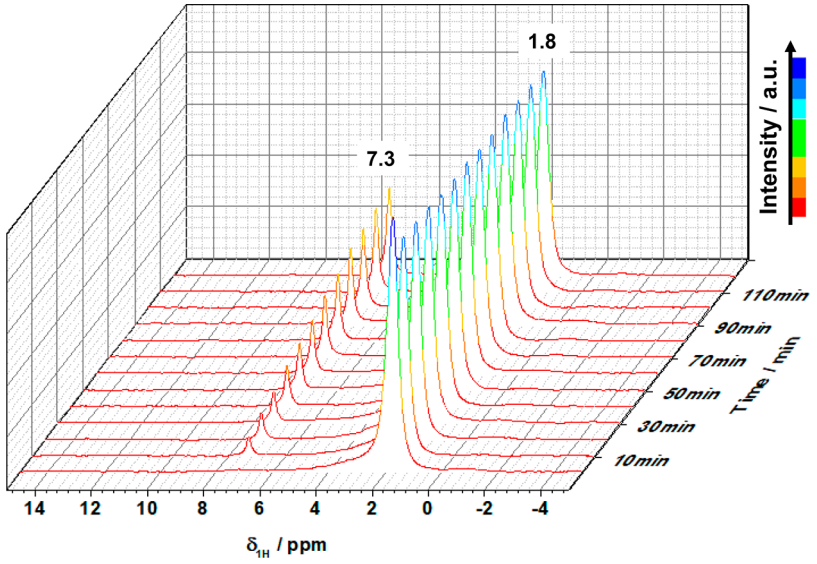


Figure 2. Stacked plot of the ^{1}H MAS NMR spectra recorded at 373 K during H/D exchange of benzene-d_6 loaded on SA/70.

Brønsted acid and base pairs on Al^V-enriched ASAs, as studied by the H/D exchange of adsorbed benzene-d_6. *In situ* ^{1}H NMR investigations show that H/D exchange occurs selectively between BASs and benzene-d_6. The H/D exchange of ASAs is found to correlate with the strength of the BASs and the existence of Brønsted acid−base pairs. Finally, we propose a model for promoting the H/D exchange of benzene-d_6 on Al^V-enriched ASAs.

ASAs prepared by the flame spray pyrolysis (FSP) technique[22] and H-ZSM-5 prepared by hydrothermal synthesis[25] are described in detail in the Supporting Information. The FSP ASAs are designated as SA/x, where x is equal to 10, 50, and 70, indicating the molar ratio of Al/(Si + Al) of the as-prepared samples. Benzene-d_6 with a deuteration degree of 99.6% was purchase from Cambridge Isotope Laboratories. The ^{27}Al MAS NMR spectra of ASAs are presented in Figure S1, demonstrating that Al^V and Al^{IV} are the dominant Al species in the dehydrated ASAs.

The ^{1}H MAS NMR spectroscopy was carried out on a Bruker Avance III 400 WB spectrometer at resonance frequencies of 400.1 MHz with 4 mm MAS rotors spinning at 8 kHz. Spectra were recorded after single-pulse $\pi/2$ excitation with repetition times of 20 and 8 scans. Before measurements, all samples were dehydrated at 723 K in vacuum (pressure $<10^{-2}$ bar) for 12 h in glass tubes. The density of BASs on all dehydrated samples was determined by quantitative ^{1}H MAS NMR experiments using NH_3 as probe molecules. The total number of BASs was calculated based on the BAS density and weight of the sample. A known amount of dehydrated samples was transferred into the MAS rotors under dry nitrogen gas inside a glovebox. Then, the open sample rotor was put into a glass tube, which was sealed by connecting it to a closed valve via a quick fit, followed by transferring the closed glass tube from the nitrogen-filled glovebox onto the vacuum line for the *in situ* loading of benzene-d_6. The loading pressure of benzene-d_6 was calculated and controlled according to the total number of BASs and the known volume of the

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vacuum line to ensure one molecule of benzene-d_6 per BAS. Then, the sample was cooled by liquid nitrogen until nearly no pressure could be detected. Subsequently, the glass tube with the loaded sample was closed and transferred to the glovebox; then, the MAS rotor was closed by the cap. The H/D experiments were performed by heating the MAS rotor to 313, 333, 353, and 373 K in a variable-temperature probe for the *in situ* ^{1}H MAS NMR investigations. The concentration of protons bound to the aromatic rings was calculated as the ratio between the integrated intensity of the aromatic ^{1}H signal and the number of Brønsted acid sites.

The rate k of the H/D exchange between the deuterated benzene and the BASs is described by an exponential relationship[26]

$$I(t) = I(\infty)\cdot[1 - b\cdot\exp\{-kt\}] \quad (1)$$

where $I(t)$ and $I(\infty)$ denote the intensity of the ^{1}H MAS NMR signal of the aromatic rings at the observation time t and the time $t \rightarrow +\infty$ in the equilibrium state, respectively. The value b describes the concentration of protons bound to the aromatic rings in the first measurement of the H/D exchange experiment, which is defined as $t = 0$.

The activation energy (E_a) of the different samples for H/D exchange was determined from the slopes of the curves, described by

$$k = k_0\cdot\exp\{-E_a/RT\} \quad (2)$$

where k_0, R, and T are the rate constant, gas constant, and reaction temperature, respectively. The as-determined E_a values are summarized in Table 1.

The stacked plot and the kinetics of the H/D exchange in the temperature range from 313 to 353 K for H-ZSM-5 zeolite are shown in the Supporting Information, Figure S2. The activation energy E_a determined for H-ZSM-5 is ~61 kJ/mol, in good agreement with the values reported in the literature,[6,7] demonstrating the feasibility of the used system for H/D exchange investigations.

A stacked plot of the ^{1}H MAS NMR spectra recorded at 373 K for the H/D exchange of C_6D_6 over SA/70 under the same conditions is shown in Figure 2. The ^{1}H MAS NMR spectrum recorded in the initial state is dominated by the signal of SiOH groups, which is typical for dehydrated ASAs. The increase in the reaction time was accompanied by a decrease in the signal intensity at 1.8 ppm, compensating for the rising signal at 7.3 ppm attributed to hydrogen bonding to aromatic rings. It has been accepted that nonacidic SiOH groups on either zeolites or silica are unable to initialize the H/D exchange reaction.[27,28] In ASAs, the signal of acidic SiOH groups (BASs) often overlaps with the one of the nonacidic SiOH groups, which have been identified using ^{1}H MAS NMR of the dehydrated sample upon ammonia loading.[22] Therefore, the decrease in the signal intensity at 1.8 ppm with concomitant increasing intensity of the signal at 7.3 ppm indicates that the H/D exchange occurs between surface BASs and C_6D_6.

H/D exchange has been widely accepted as an electrophilic aromatic substitution reaction.[12] It often requires the formation of a π complex as the initial step, which is a donor−acceptor -type complex formed after the protonation of benzene on BASs. For a substitution reaction, for example, in the case of H/D exchange, the π complex must be converted into a σ complex, described as a cationic intermediate, in which the carbon at the site of substitution is bonded to the electrophile (e.g., proton) and the deuteron at the aromatic ring that is being displaced. It is well known that only BASs of solid acids can contribute to the protonation of the aromatic rings to form the cationic intermediate, whereas Lewis acid sites (LASs), such as those in alumina, cannot protonate aromatic rings. Lewis acid−base pairs (Al cations with AlOH groups) on alumina may be active in the H/D exchange[29] but normally require a very high temperature (650 K) compared with the low temperature used here (≤373 K). As shown in Figure S3, no signal assigned to hydrogen bonded to aromatic rings at 7.3 ppm could be observed after 90 min of reaction time with loading an excess amount of C_6D_6 at 373 K, clearly demonstrating that H/D exchange cannot be promoted by LASs and AlOH groups on dehydrated Al_2O_3 and the alumina-rich phase in ASAs at the low temperatures used here. Therefore, in FSP-made ASAs, only the hydroxyl atoms of the Brønsted-acidic OH groups attack the aromatic rings, which are protonated to yield σ complexes. After protonation, the σ complexes are decomposed by transferring deuterons to the negatively charged oxygen atoms in the local structure of the former Brønsted-acidic OH groups.

The kinetic studies of H/D exchange of C_6D_6 over ASAs were performed at various temperatures (Figure 3 and Figures S4−S6), and the H/D exchange degree and exchange rate k were determined by fitting the corresponding experimental data and are summarized in Table 1. On all SA/x catalysts, H/D exchange occurred already at low temperature (313 K). The H/D exchange degrees and k values were all remarkably increased at elevated temperatures up to 373 K from 1.9 to 10% to 19 to 38% and from 0.0082 to 0.0095 min^{-1} to 0.0171 to 0.0271 min^{-1}, respectively. At the same temperature, the exchange degree and the rate k were enhanced at higher Al loading, in line with the increasing Brønsted acidity in SA/x catalysts.[22]

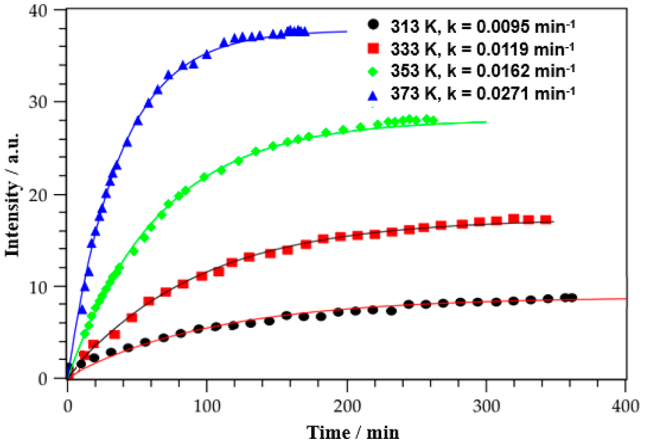


Figure 3. H/D exchange rates of benzene-d_6 (99.6%) at Brønsted acid sites in SA/70 at 313, 333, 353, and 373 K, respectively.

The measured H/D exchange degrees and rates k of SA/x are much higher than those of the sol−gel-prepared ASAs. As characterized by ^{13}C MAS NMR using 2-^{13}C-acetone, ASAs (Si/Al = 15) exhibited similar moderate BAS strength as SA/10 and SA/30.[22,30] Because the H/D exchange of C_6D_6 is selective for strong BASs on solid acids,[31−33] the sol−gel-prepared ASA was nearly inactive compared with H-ZSM-5 and SA/70 with strong BASs; in particular, no reaction occurred at 313 K. Consequently, SA/10 and SA/30 with mainly moderate BASs should be inactive, similar to the sol−

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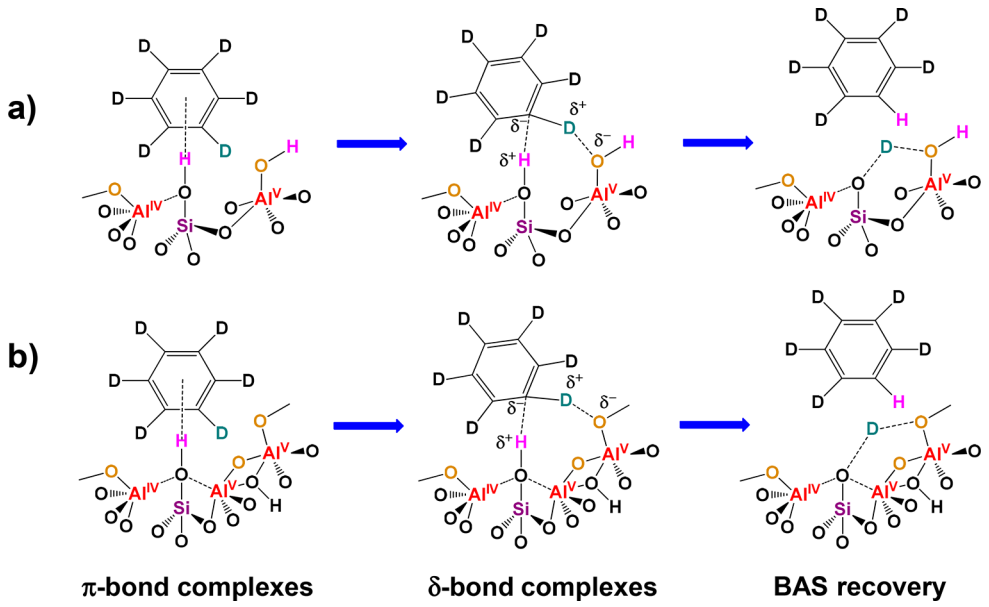


Figure 4. Proposed scheme for the H/D exchange of C_6D_6 at Brønsted acid−Lewis base pairs on ASAs. In panels a) and b), the SiOH group with neighboring Al species acts as a BAS, whereas AlOH groups in Si-rich ASAs and electron-rich oxygen atoms (yellow) at the Al-rich ASAs are deuteron acceptors as basic sites, respectively. The dotted line does not denote a covalent bond but only the proximity between O and Al atoms.

gel-prepared ASAs. However, even with a similar H/D exchange degree, the rate k of SA/10 with a lower BAS density was two to three times higher than that of the sol−gel-prepared ASAs. SA/30 and the sol−gel-prepared ASAs have similar BAS densities and strengths, but the exchange degree and rate k determined for SA/30 are two to four times higher than those for sol−gel-prepared ASAs.

Because mainly Al^{IV} but nearly no Al^{V} species could be detected in sol−gel-prepared ASAs,[30] the higher activity of SA/10 and SA/30 is attributed to the dominant presence of Al^{V} species. Al^{V} species could either act as LASs or be involved in BASs in ASAs, which are often balanced with neighboring OH groups (Al^{V}−OH).[19] Because Lewis acid−base pairs, such as those on alumina (Figure S3), are inactive under the current conditions, H/D exchange through Lewis-acidic Al^{V} species with AlOH groups was considered unfavorable here. Instead, promoting the H/D exchange via a BAS and basic AlOH (or basic O site on the network) pair is proposed (Figure 4a), driven by the presence of a large content of basic AlOH groups in SA/10 and SA/30. Thus it seems likely that C_6D_6 is protonated at a BAS to form a cation intermediate, whereas AlOH groups act as effective deuteron acceptors that are similar to those proposed for alumina. The presence of basic sites in proximity to moderate BASs is proposed to facilitate the deuteron replacement compared with the H/D exchange at BASs solely in sol−gel-prepared ASAs.

In addition to AlOH groups, the formation of strong BASs together with the enhancement of the basicity of local oxygen in SA/50 and SA/70[21] provides excellent H/D exchange activity, with higher exchange rates than those observed for SA/10, SA/30, and sol−gel-derived ASAs at all temperatures. At high Al/Si ratios, the synergy between Al^{V} and Al^{IV} or Al^{V} at the same SiOH groups in ASAs (e.g., SA/50 and SA/70) could generate BASs of zeolitic strength, which are comparable to those of strong BASs on H-ZSM-5 due to the homogeneous dispersion of Si throughout the Al matrix in ASAs. The Al matrix could introduce high local ionicity to enhance the basicity of the local oxygen, similar to that reported for ASAs prepared by the chemical liquid deposition of SiO_2 on Al_2O_3 and aluminosilicate glasses.[34,35] Therefore, stronger basic oxygen atoms could be located at the local structure of BASs, which promote the donor−acceptor-type H/D exchange reaction (Figure 4b). The synergy of these strong BASs with neighboring basic oxygen atoms is proposed to promote the H/D exchange reaction at a higher rate (k values) compared with other ASAs, even higher than that of H-ZSM-5 (0.0083 and 0.0095 min^{-1} vs 0.7 min^{-1}) at 313 K. However, the exchange rates k of H-ZSM-5 increased dramatically by 15 times compared with ca. 2 times for SA/70 at a higher temperature. In H-ZSM-5, some BASs could be disturbed by the electrostatic interaction with the zeolite framework but have similar strengths as the others.[36,37] A higher temperature could promote the interaction between C_6D_6 and the disturbed strong BASs (δ_{1H} 5.2), as shown in Figure S7, accelerating the H/D exchange reaction. In SA/70, after the H/D exchange with the pairs of strong BASs and the basic oxygen or AlOH groups (such as those active at 313 K), the reaction could occur at other sites, for example, moderate BASs with AlOH groups, such as those observed with SA/10 and SA/30 at rising temperature. However, these sites are less active, leading to extremely low k values, and thus lower the average rate k with SA/70 compared with that of H-ZSM-5, which is supported by the two to four times higher exchange degree of H-ZSM-5 compared with that of SA/70 at 333−353 K. Therefore, it can be concluded that the strong BASs or active sites in ASAs can provide similar activities as zeolites; however, the large number of weak BASs involved in the reaction lowers the overall catalytic performance of ASAs compared with zeolites.

Activation energies (E_a) are compared in Figure 5 and Table 1. In general, a lower E_a of the proton transfer should correspond to a higher acid strength and *vice versa*.[7] For example, the activation energies increased (15.9 kJ/mol for SA/70 and 22.5 kJ/mol for SA/10) with a decrease in the BAS strength. The E_a values determined for the SA/x catalysts are 30−50% lower than those obtained for the sol−gel-prepared ASAs. The sol−gel prepared ASA has a similar BAS density

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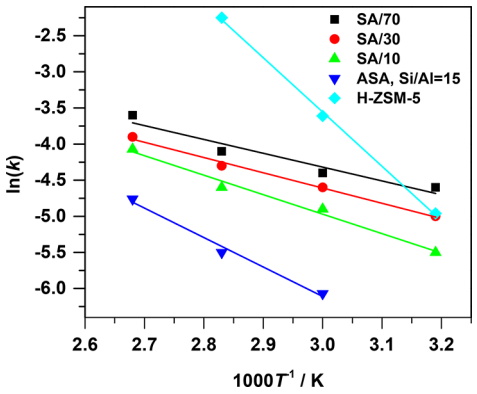


Figure 5. Arrhenius plots of the H/D exchange of benzene-d_6 over SA/70, SA/30, SA/10, ASA (Si/Al = 15), and H-ZSM-5.

and strength as SA/10 and SA/30. The lower E_a values of SA/10 and SA/30 support the notion that the presence of more neighboring basic O/OH sites promotes the H/D exchange reaction compared with the sol−gel-made ASAs with mainly moderate BASs. With a similar BAS strength, the E_a determined for H-ZSM-5 is four times higher than that for SA/70. In the transition state of the H/D exchange with zeolite H-ZSM-5, the deuteron can be displaced at only one local negatively charged oxygen generated after BAS deprotonation. However, SA/70 could provide stronger basic oxygen atoms at the local structure of SiOAl, facilitating the deuteron transfer from C_6D_6 to surface oxygen. Therefore, elevating the reaction temperature could enhance the molecule rotation for deuteron displacement at the negatively charged framework oxygen,[9,38] which is less sensitive compared with that on ASAs due to more basic oxygen sites acting as deuteron acceptors, resulting in lower E_a values.

In situ ^{1}H NMR investigations of the selective H/D exchange of C_6D_6 with Al^V-enriched ASAs were carried out to evaluate their activity in aromatic C−H bond activation. Nonacidic SiOH groups, AlOH groups, and Lewis acid−base pairs of Al cations and AlOH groups in the aluminum-rich phase in ASAs were all inactive in the H/D exchange reaction under the conditions applied. The ^{1}H NMR intensity increase at δ_{1H} 7.3 was compensated by a decrease in the signal at δ_{1H} 1.8 (Figure 2), indicating that acidic SiOH groups (BASs) act as hydrogen donors to the aromatic rings in the H/D exchange of C_6D_6. At low Al/Si ratios (≤3/7), the dominant Al^V species promoted the formation of AlOH groups on ASAs, whereas basic oxygen atoms were generated due to the increasing local ionicity in ASAs at high Al/Si ratios (≥5/5). The cooperativity of BASs and AlOH or oxygen atoms, denoted as acid−base pairs, could facilitate deuteron replacement at basic sites, and they thus exhibit significantly higher exchange rates and lower activation energies compared with the sol−gel-prepared ASAs. These findings may disclose a new possibility for the C−H bond activation of benzene through tailoring Brønsted acid−base pairs and provide an alternative strategy for the rational design of high-performance solid acids for efficient C−H activation in various hydrocarbon conversion reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c03489.

Catalyst preparation and *in situ* ^{1}H MAS NMR spectra of the H/D exchange of C_6D_6 on dehydrated zeolite H-ZSM-5, Al_2O_3, SA/10, SA/30 and the sol−gel prepared ASA (Si/Al = 15) at various temperatures (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Jianzhong Chen on the occasion of his 70th birthday.

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