

Zeolite Based Adsorbents and Catalysts for Environmental Applications Utilizing a Function of Hydrocarbon-adsorption

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Hydrothermal stability and hydrophobicity of FAU, MOR, FER, MFI and BEA type zeolites with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios have been examined under a variety of conditions. Some of them were found to exhibit high structural stability at 1000 °C in air containing water vapor and higher hydrophobicity. Adsorption-desorption properties of toluene, ethene, and n-decane of these siliceous zeolites were studied, and suitable zeolites with modification were proposed for hydrocarbon trap materials. A combination of the Pt-loaded zeolite with high activity of NOx conversion and another zeolite with higher adsorption capacity of hydrocarbons for reductant has been proposed as the effective lean NOx catalyst.

1 . Introduction

Increasing emission of hazardous compounds has become an important problem for environmental protection, especially in highly industrialized countries. Zeolite adsorbents and catalysts are recognized as useful and hopeful materials for the removal of harmful substances.

It has been reported that siliceous zeolites are effective for adsorption of organic compounds from paints, inks and solvents in air [1], and for removal of organic contaminants in water [2]. Higher hydrophobicity of zeolite adsorbents is required for these applications, since organic contaminants are extremely dilute in wet gas streams and in aqueous solutions. The use of hydrocarbon traps to reduce cold-start emissions is

one of the numerous methods that have been suggested to meet ULEV hydrocarbon emission requirements. It has been reported that the hydrocarbon traps are generally effective for trapping aromatics, C_4^+ alkanes and alkenes, but ineffective for methane, ethane, and ethene. Therefore, further improvements in trapping performance for $\text{C}_2\text{-C}_3$ hydrocarbons are required to achieve the Super ULEV emission performance [3-5].

Since Cu-MFI had been reported to be effective for the selective catalytic reduction of NOx even in oxygen excess conditions [6], several reports were published on the lean-NOx catalysts with hydrocarbons [7-9]. A new diesel catalyst using zeolite has been reported to reduce SOF (soluble organic fraction) and hydrocarbon emissions at low exhaust temperature [10]. Higher performance of

NO_x conversion may be expected by enhancing the function of zeolites in adsorption and cracking of hydrocarbon.

In this paper, we report useful hydrocarbon trap materials and lean-NO_x catalysts based on some siliceous zeolites which have high hydrophobicity, hydrothermal stability and excellent adsorption-desorption properties for organic molecules even in the presence of water.

2. Experimental

Commercially available zeolites (Tosoh Corp.) and some zeolites prepared in a laboratory scale were used in this study. "Fresh samples" were calcined in dry air at 500 °C for 1h, and "aged samples" were treated in air containing 10% water at a prescribed temperature for 5h. Hydrothermal stability was evaluated by the measurement of surface area and XRD crystallinity before and after the hydrothermal treatment. The surface area was measured by BET one-point method of N₂. Hydrophobicity was indicated by the adsorbed amounts of H₂O and benzene. The adsorbed amount of H₂O was measured by TG analysis using each fresh sample hydrated in relative humidity of 80% at 25 °C. The adsorbed amount of benzene was obtained from the adsorption isotherm at 25 °C by gravimetric method.

Adsorption-desorption properties of hydrocarbons were measured by temperature programmed desorption (TPD) method. Samples were pretreated at 500 °C for 1h under the stream of dry air. Hydrocarbon adsorption was carried out at room temperature by flowing a model gas containing a prescribed amount of hydrocarbon and 3% water, then, the hydrocarbon in gas phase was removed by flowing air containing 3% water. TPD measurements were carried out from room temperature up to 700 °C at the rate of 10 °C/min under the stream of air containing 3% water, and effluent gas was monitored by FID and TCD in gas chromatography.

Catalytic activities were evaluated in a fixed-bed flow reactor. The gas mixture composed of NO (200ppm), hydrocarbon (1000ppmC), SO₂ (25ppm), O₂ (10%), H₂O (7%), and N₂ as a balancing gas was passed through the catalyst at 120,000h⁻¹ of GHSV. C₃H₆ or n-C₁₀H₂₂ was used as a reactant hydrocarbon. The reactants and products were analyzed by an on-line gas chromatograph and a chemiluminescence NO_x meter.

3. Results and discussion

3.1. Hydrothermal stability and hydrophobicity of siliceous zeolites

Measured values of surface area before and after

Table 1 Surface areas and adsorbed amounts of water and benzene of various H⁺ form zeolites

Structure Code	SiO ₂ /Al ₂ O ₃ ratio	BET Fresh	surface area[m ² /g] ^{a)}			Adsorbed amount[wt%]		Note ^{b)}
			After aging			Fresh		
			850	900	1000	H ₂ O ^{c)}	Benzene ^{d)}	
FAU	14	540	540	500	350	5.9	17.6	D
	108	640	590	570	420	4.3	18.9	D
	260	670	630	630	580	3.6	19.2	D
MOR	26	440	360	330	20	14.4	9.5	D
	220	450	390	380	330	8.8	9.6	D
FER	17	300	280	270	160	10.6	1.5	S
	67	330	320	310	290	6.9	1.5	S*
	93	290	300	300	290	4.2	1.5	S*
MFI	40	350	330	320	320	9.9	9.1	S
	390	360	360	360	350	4.0	8.3	S
	1900	360	360	350	350	3.2	9.0	S
BEA	26	590	390	250	20	23.7	18.8	S
	37	510	400	330	10	18.5	18.8	S
	500	470	450	400	310	16.0	17.5	D*
	1700	460	480	470	390	10.1	19.0	D*

a) Fresh; calcined in dry air at 500 °C for 1h.

Aging; treated in air containing 10% of water at a given temperature for 5h.

b) at 20torr, 25 °C.

c) at 10torr, 25 °C.

d) preparation method; D: dealuminated, S: synthesized, *: laboratory scale.

the aging, and adsorbed amounts of water and benzene of each sample are summarized in Table 1, and illustrated in Fig. 1 and Fig.2. Although the decrease of surface areas after the aging was observed with the increase of aging temperature, those of siliceous FER and MFI were almost maintained even after the treatment at 1000 . The adsorbed amount of benzene was dependent on the structure of zeolites, but independent of the

$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. On the other hand, the amount of water apparently decreased with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in each zeolite. These results show that hydrothermal stability and hydrophobicity increase with the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

It is generally understood that the degradation of zeolitic structure by hydrothermal treatment is attributed to dealumination from the framework, and that structural defects (hydroxyl nests) are

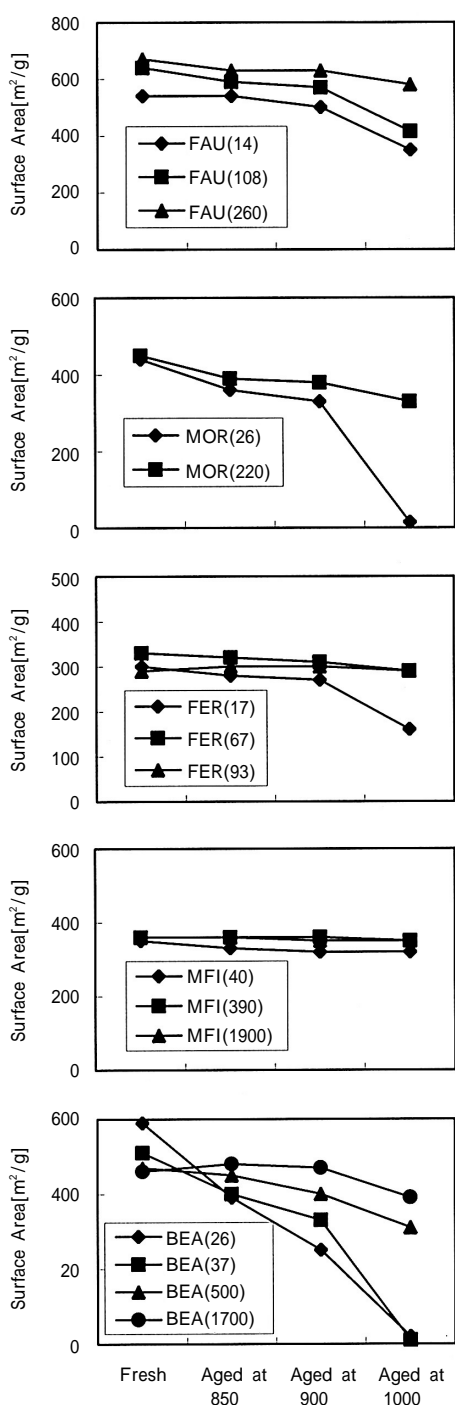


Fig. 1 Hydrothermal stability of various zeolites.

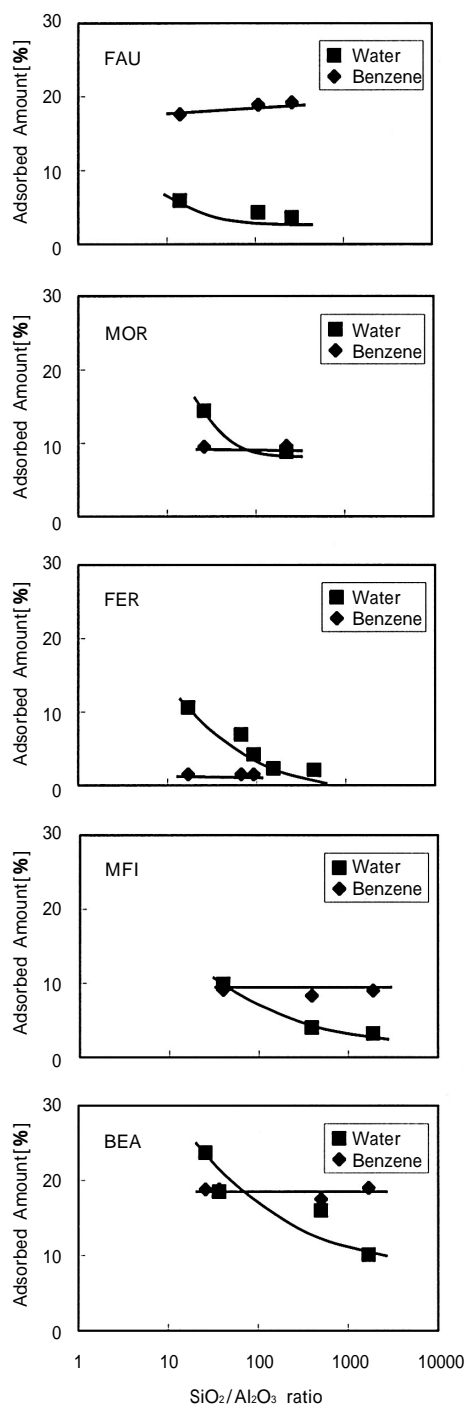


Fig. 2 Adsorbed amounts of water and benzene of various zeolites.

generated. The defects causes structural instability and lowers hydrophobicity. Consequently, the key points of the base materials are to synthesize siliceous zeolites without structural defects and to effectively remove Al atoms from the framework preventing the generation of silanols.

3.2. Adsorption-desorption properties of hydrocarbons

There are many kinds of hydrocarbons with different molecular dimensions and properties in automobile exhaust. It is basically important to select a preferred zeolite for each hydrocarbon. In this study, the adsorption-desorption properties of toluene, ethene, and n-decane on various zeolites were investigated by TPD method.

3.2.1 Toluene

TPD profiles of toluene on H-MFI(40) and H-MFI(1900) are illustrated in Fig. 3 A and B. On the fresh sample of H-MFI(40), double peaks of desorbed toluene were detected in the absence of water (Fig. 3 A, b). The higher temperature desorption peak was attributed to the adsorbed species at acid sites. However, the corresponding peak was hardly detected in the presence of water (Fig. 3 A, a). The aged samples of H-MFI(40) showed a single desorption peak of toluene in the presence and absence of water (Fig. 3 A, c and d). These results indicate that the hydrophobicity is enhanced by the extraction of Al atoms from the framework through the hydrothermal treatment. On the other hand, H-MFI(1900) showed enough adsorption capacity of toluene in all conditions as

shown in Fig. 3 B. Similar results were obtained in H-FAU(260), H-MOR(220), and H-BEA(1700). The maximum temperature of the desorption of these siliceous zeolites was near the boiling point of toluene, 110.6 . It is easily understood that hydrocarbons with a higher boiling point are adsorbed in channels of siliceous zeolites, and so the acid sites due to framework Al atoms are not necessary. Siliceous zeolites with high hydrophobicity and hydrothermal stability are effective for adsorption of toluene.

3.2.2. Ethene

The adsorbed amounts of ethene of various H-zeolites were smaller about three orders of magnitude than those of toluene. It is necessary to promote chemical interaction between hydrocarbon molecules and the surface of zeolites to increase ethene adsorption. The metal loading effect on adsorption of ethene was examined with various metal loaded zeolites, prepared by impregnation with metal nitrate solution and subsequent thermal treatments. The loading amount of impregnated metal component on each zeolite was adjusted to 2wt%. Ag was found to be most effective in various metal loaded FER(17) as shown in Fig. 4 [11]. The loading effect of Ag on various zeolites was tested, and siliceous FER showed large adsorption-desorption capacity as shown in Fig. 5. The effect of hydrophobicity of FER is clearly shown in TPD profiles as illustrated in Fig. 6. The desorbed amount of H₂O decreased while that of C₂H₄ increased with increasing SiO₂/Al₂O₃ ratio of

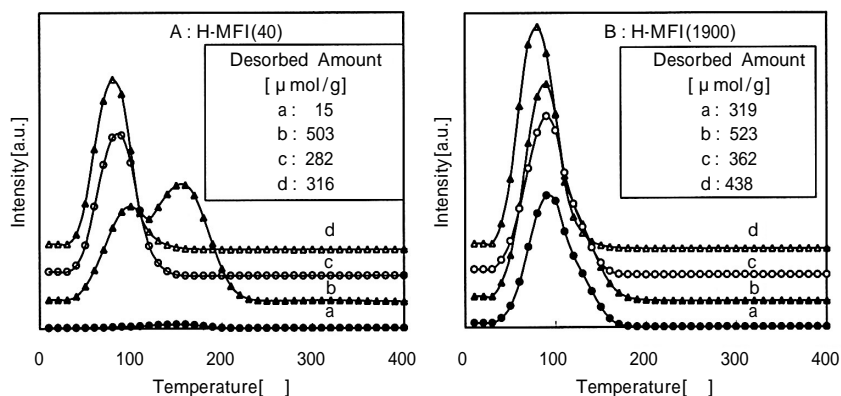


Fig. 3 TPD profiles of toluene on (A) H-MFI(40) and (B) H-MFI(1900). a : fresh sample with H₂O, b ; fresh sample without H₂O, c ; aged sample with H₂O, d ; aged sample without H₂O.

FER. It was confirmed that the hydrophobic zeolite was preferable to adsorb light-hydrocarbons in coexistence of water even in the case of metal loaded zeolites. It is estimated that small pore size of FER is effective to accommodate small hydrocarbon molecules.

3.2.3. *n*-Decane

BEA zeolite showed the largest adsorption

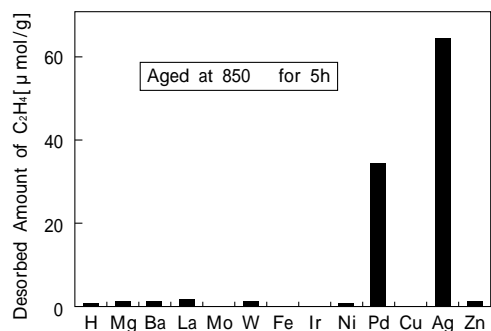


Fig. 4 Effect of metal loading on the adsorption property of ethene based, on FER(17).

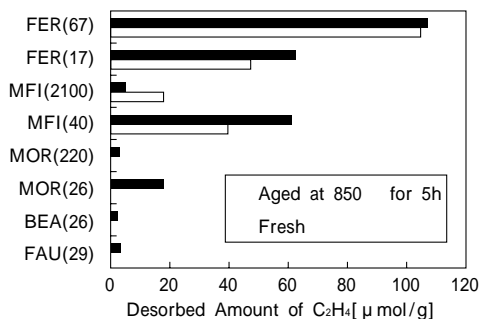


Fig. 5 Ag-loading effect of various zeolites.

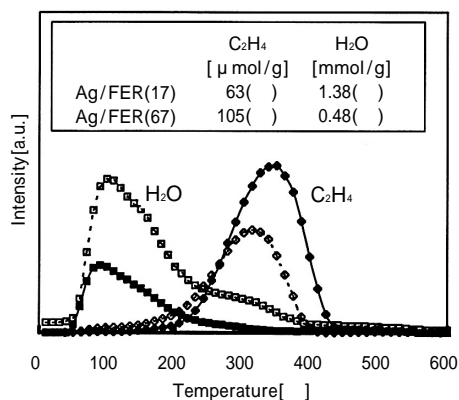


Fig. 6 TPD profiles of (/) C₂H₄ and (/) H₂O on Ag/FER(17) and Ag/FER(67).

capacity of n-C₁₀H₂₂ in our previous study [12]. TPD profiles of n-decane and gas chromatograms at the peak temperature on H-BEA(26) are shown in Fig. 7. It was measured that n-C₁₀H₂₂ was decomposed to lower hydrocarbons, mainly C₃H₆, in the desorption processes. Fig. 8 shows the effect of SiO₂/Al₂O₃ ratio of H-BEA on adsorption-desorption property of n-decane. Adsorbed amounts of n-decane in the absence of water are almost constant. On the other hand, the adsorbed amounts in the presence of water increased with the increase of SiO₂/Al₂O₃ ratio, because of the increase of hydrophobicity. The decomposition rate of n-decane decreased with increasing SiO₂/Al₂O₃ ratio. Namely, if the decomposition of hydrocarbons is desired, BEA zeolites with lower SiO₂/Al₂O₃ ratio can be selected.

However, after the aging, the decomposition rate of n-decane of H-BEA(26) decreased as shown in

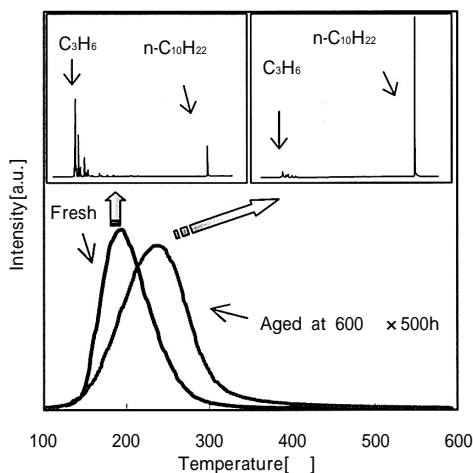


Fig. 7 TPD profiles of n-decane and gas chromatograms at the peak temperature on H-BEA(26).

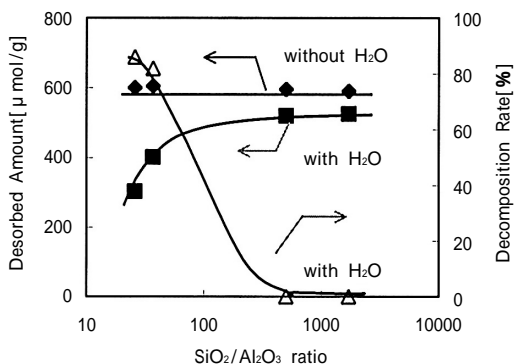


Fig. 8 Effect of SiO₂/Al₂O₃ ratio of H-BEA zeolite on the adsorption-desorption property of n-C₁₀H₂₂.

Fig. 7. The total amount of desorbed hydrocarbons was almost the same in fresh and aged samples. The shift of the desorption peak to higher temperature in the aged sample is due to the decrease of decomposition because of the decrease of acid sites caused by dealumination through aging. Fig. 9 shows the total desorbed amounts and the decomposition rates at the peak temperature of $n\text{-C}_{10}\text{H}_{22}$. It has been reported that the acidic properties of zeolites after impregnation with phosphoric acid and subsequent thermal treatment were changed by dealumination, formation of aluminum phosphates and polyphosphoric acids [13]. The decrease of decomposition rate of H-BEA(37) could be improved by impregnation with $(\text{NH}_4)_2\text{HPO}_4$ and subsequent thermal treatment as shown in P/BEA(37) in Fig. 9. It has been suggested that the acid sites produced by impregnation with $(\text{NH}_4)_2\text{HPO}_4$ and subsequent

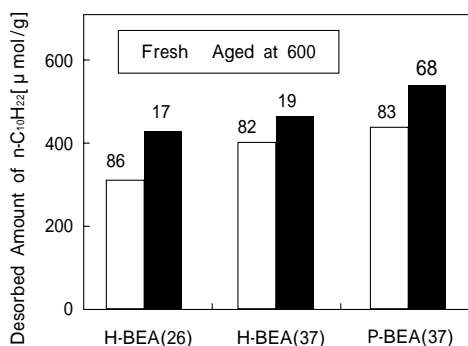


Fig. 9 Adsorption-desorption properties of $n\text{-C}_{10}\text{H}_{22}$ on various BEA zeolites. Numerals in figure refer to the decomposition rates of $n\text{-C}_{10}\text{H}_{22}$.

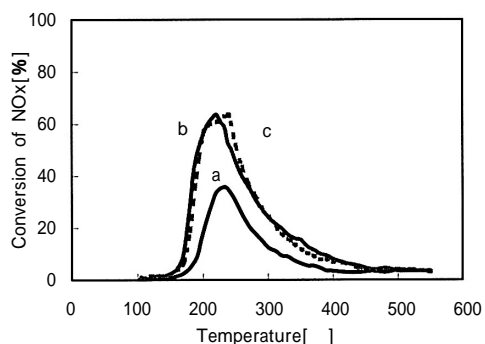


Fig.10 Transient NOx conversions on a; fresh Pt/FER(17), b; fresh hybrid catalyst and c; aged hybrid catalyst at 600 °C for 50h. Feed composition : 200ppm NO, 1000ppmC $n\text{-C}_{10}\text{H}_{22}$, 25ppm SO_2 , 10% O_2 , 7% H_2O , balance N_2 ; GHSV=120,000 hr^{-1} .

thermal treatment result in the enhanced durability for cracking activity of hydrocarbons.

3.3. Lean-NOx catalyst using adsorbed hydrocarbons on zeolite

Lean-NOx catalysts have to possess at least the following two functions, NOx adsorptive-activation and hydrocarbon adsorptive-activation, because NOx is catalytically reduced by hydrocarbons. In our previous study [14], a Pt-loaded Al_2O_3 catalyst showed high durability but low activity, because Al_2O_3 adsorbed only small amount of hydrocarbons. The Pt-loaded zeolites generally show higher conversion of NOx and higher selectivity to N_2 , but lower durability than that of Pt-loaded Al_2O_3 . Pt-loaded FER(17) catalyst showed high conversion of NOx, high selectivity to N_2 , and good durability in the case with C_3H_6 , but low conversion of NOx in the case with $n\text{-C}_{10}\text{H}_{22}$. These results were attributed to the small pore size of FER. The hybrid catalyst physically mixed with Pt-loaded FER(17) and P/BEA(37) was studied in order to obtain both high activity and high durability with $n\text{-C}_{10}\text{H}_{22}$. There were large difference in the NOx conversion with $n\text{-C}_{10}\text{H}_{22}$ between the Pt-loaded FER(17) catalyst and the hybrid one as shown in Fig.10. The NOx conversion could be improved by mixing with P/BEA(37), which has high adsorption capacity and cracking activity of $n\text{-C}_{10}\text{H}_{22}$ as described above.

4 . Conclusion

Fundamental properties of some siliceous zeolites were studied, and adsorptive and catalytic properties of those were investigated for environmental applications. Some siliceous zeolites showed high hydrothermal stability even at the temperature of 850-1000 °C, and high hydrophobicity. Hydrocarbons with high boiling point such as toluene and $n\text{-decane}$ could be adsorbed in channels of siliceous zeolites and be desorbed around their boiling points. Promoting chemical interactions between the hydrocarbons and the surface of zeolites was effective to adsorb light hydrocarbons with lower boiling point. Ag-loaded

FER, especially siliceous and hydrophobic FER, showed excellent performance for adsorption of ethene. The hybrid catalyst composed of Pt loaded FER(17) and P/BEA(37) showed higher activity and durability for NO_x conversion with n-C₁₀H₂₂.

It was shown that some siliceous zeolites were useful for hydrocarbon trap materials and lean-NO_x catalyst materials in automobile emission control. It is also expected that siliceous zeolites will be used for various environmental applications such as adsorption of volatile organic compounds (VOCs) emitted from numerous sources and for removal of contaminants from water.

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