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Vapor-Phase Isomerization of *o*-Chlorotoluene over H-Mordenite Treated with CF_3Cl

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Vapor phase-isomerization of *o*-chlorotoluene was somewhat promoted by H-mordenite (HM). The catalytic activity was appreciably enhanced by treatment with CF_3Cl and other chlorofluorocarbons such as CF_2ClCF_2Cl and CF_2ClCF_3. In particular, maintenance of the HM catalyst activity was remarkably improved by CF_3Cl treatment. The CF_3Cl-treated HM also promoted vapor phase isomerizations of *p*- and *m*-chlorotoluene. The catalytic activity was relatively long-lasting for the isomerization of *p*-chlorotoluene. Enlargement of the HM pore size on treatment with CF_3Cl and other chlorofluorocarbons may contribute to increasing the catalytic activity and then maintaing it.

Chlorotoluene is an important intermediate for syntheses of agricultural chemicals, dyes, and pharmaceuticals. It is prepared, in general, by chlorination of toluene, in which ortho isomer is preferably formed together with some para isomer owing to the directing effect of the methyl group. Accordingly, when *m*-chlorotoluene (MCT) is required in large amounts, it is desirable to isomerize the *o*-chlorotoluene (OCT) to MCT. In addition, the isomerization of OCT to *p*-chlorotoluene (PCT) is important because the para isomer is especially useful as a raw material for agricultural chemicals.

Hitherto isomerizations of halotoluenes have been known to occur only in the presence of a strong acid catalyst such as $HF-BF_3$[1] and $AlCl_3$.[2] However, these catalysts are unstable, and they are very difficult to recover. Furthermore, they are remarkably corrosive to reaction vessels.

Recently, acidic zeolites such as a proton-exchanged mordenite (HM) and H-ZSM-5 have been reported to be useful as a catalyst for the isomerization of chlorotoluene.[3] However, the isomerization, as catalyzed by the acidic zeolite, is carried out only in the liquid phase at a high temperature in a closed system.

From an industrial viewpoint, it is desirable for isomerization to proceed in the gas phase by using a continuous flow system under an atomospheric pressure. Hence, a search was carried out to seek a suitable catalyst for the gas phase isomerization of OCT. For comparison with the OCT isomerization, the vapor phase isomerizations of MCT and PCT were attempted in the presence of the treated HM. The results obtained for these isomerizations of chlorotoluenes are compared with those of the xylene isomerization, which is performed over the same catalyst, i.e., the CF_3Cl treated HM.[4]

Experimental

Materials. The HM used in this study was prepared by the heat-treatment of the NH_4 mordenite at 500 °C for 3 h. The NH_4 mordenite was prepared from a commercial Na mordenite (Toyo Soda Co., TSZ, SiO_2/Al_2O_3 mol ratio=9.75, 15.4, 19.0 or 22.7) by ion exchange with 1.0 M NH_4Cl (1 M=1 mol dm^{-3}) solution followed by the necessary washing. The proton-exchanged Y type zeolite (HY) was supplied by Toyo Soda Co. (TSZ 352). Before use as a catalyst or treatment with CF_3Cl, the HY was heat-treated in air at 500 °C for 3 h, similar to HM and other metal oxides. The treatments with CF_3Cl and other halocarbons were carried out by the previously reported methods.[4—6] Unless otherwise noted, the treatments were run at 450 °C for 15 min.

The Al_2O_3 catalyst was obtained by hydrolysis of aluminum isopropoxide (Wako Chemical Co.) followed by heat-treatment in air at 600 °C for 3h. The $SiO_2-Al_2O_3$ (Nikki Chemical Co., N-631L, Si/Al (atomic ratio)=85/15) was used to evaluate the catalytic activity of typical solid acid.

Reaction Procedure. The isomerization was carried out under ordinary pressure using a continuous flow reactor. The products were collected every 30 min and analyzed by gas chromatography using a column (3 mm×6.3 m) packed with 4,4′-azoxydianisole supported on Uniport HP (60—80 mesh) at 100 °C (oven temperature). Unless otherwise noted, the value representing the catalyic activity and activity maintenance was the one obtained for the first 30 min period.

Determination of Surface Properties. In order to know whether the Brönsted or the Lewis type acid site should promote the isomerization, the effect of 2,6-lutidine pretreatment[7] on the catalytic activity for the isomerization was examined together with that of pyridine pretreatment. In addition, CO_2 addition was examined for its effect on the basic sites of HM.

To evaluate the acid amount and acid strength, temperature-programmed desorption (TPD) of NH_3 (5 ml) was carried out on a sample (50 mg, 32—42 mesh) which was heat-treated in air at 500 °C for 3 h. Immediately before the TPD, the samples were heat-treated in the test apparatus at 500 °C for 1 h in an atmosphere of He. The temperature was raised to 500 °C at a rate of 40 °C min^{-1}.

Structure and Surface Composition. The structure of HM before and after treatment with CF_3Cl was determined from the powder-diffraction patterns obtained with a Rigaku Geigerflex X-ray diffractometer using filtered Cu *Kα* radiation. The compositions in the surface layer were dertermined by XPS using a Shimadzu ESCA-750 apparatus. The spectra were measured with Mg *Kα* radiation. The base pressure of the spectrometer was usually below 10^{-7} Torr (1 Torr=133,322 Pa) during the experiments. The compositions were calculated from the areas of the spectral peaks (i.e., the maximum in the counting rate) on the basis of the photoionization cross section at 1254 eV in units of the C 1s cross section of

22200 barns.[8)]

Results and Discussion

Comparison of Catalytic Activities of Various Solid Acids. Table 1 shows the results of the isomerization of OCT to other chlorotoluenes over various solid acids. Among these solid acids, HM exhibited the highest catalytic activity. HY also showed some catalytic activity, though the typical solid Lewis acid Al_2O_3 and the strong solid acid, $SiO_2 \cdot Al_2O_3$ were catalytically inactive. These facts are in contrast to observations that the isomerization of *o*- and *p*-xylenes are readily promoted by Al_2O_3–HX (X=halogen)[9)] or SiO_2–Al_2O_3.[10)]

After treatment with CF_3Cl at 450 °C, HM became much more active, and SiO_2–Al_2O_3 became somewhat active. On the other hand, Al_2O_3 was still inactive as a catalyst, and HY completely lost its catalytic activity. It has been observed that Al_2O_3 becomes strongly acidic and catalytically active for paraffin isomerization[6)] and CH_3OH conversion to olefins,[5)] which are promoted by only extremely strong solid acids. So, the evidence that the CF_3Cl-treated Al_2O_3 was unable to promote the isomerization suggests that strong acidity is not the only essential factor for catalytic activity. Some other factors, for example the zeolytic structure, are needed for catalytic activity in the chlorotoluene isomerization. The loss of the catalytic activity of HY after the CF_3Cl-treatment is then explicible by the collapse of the zeolytic structure during the treatment with CF_3Cl, which was observed by XRD.

Table 1. Activities of Various Catalysts

	Conversion (mol%)	
	Before treatment	After treatment[a)]
H-mordenite[b)]	11.7	41.9
SiO_2–Al_2O_3	0	5.0
Al_2O_3	0	0
Y type zeolite	3.4	0

a) The treatment was carried out by using CF_3Cl at 450 °C for 8 min. b) SiO_2/Al_2O_3 mol ratio=19.0.

Effects of Treatment with Various Fluorochlorocarbons or HF Acid. Table 2 summarizes the results relating to the effect of treatment using various simple fluoro- or fluorochlorocarbons, CCl_4 or HF acid.

As is shown in this table, CF_3Cl was the most effective treatment agent, while other chloropolyfluorocarbons such as CF_2ClCF_3, CF_2ClCF_2Cl, and CF_2Cl_2 also showed some effect. Abrupt increases in temperature were observed during the treatment of HM with these agents. Approximate values of the increase in temperature for the different agents were as follows: $CFCl_3$, 60 °C; CF_2ClCF_2Cl, 50—60 °C; CF_2Cl_2, 40 °C; CF_3Cl, 30—40 °C; CF_3CF_2Cl, 20 °C; CF_4, CF_3CF_3, 0 °C. For the CCl_4-treatment, the value could not be measured since the increase was too rapid and too sudden.

The increases in temperature are assignable to the surface reaction of HM with the treatment agent. Infact, the compositions were remarkably changed by the treatment. For example, as Table 3 shows, F and Cl components were incorporated in the surface layer by the treatment with CF_3Cl, and were retained after use as a catalyst. For the sample treated with fluoropolychlorocarbons or polychlorocarbon such as $CFCl_3$ and CCl_4, an extensive degradation of mordenite structure was confirmed by XRD determination. This probably resulted from the violent reaction between the HM surface and these polychlorocarbons which have a relatively weak C–Cl bond.[11)] On the other hand, perfluorocarbons such as CF_4 and CF_3CF_3 were unable to react with the HM surface because of the very strong C–F bond in their molecules.[12)] Thus the high bond strength in CF_4 and CF_3CF_3 may account for the inertness of the perfluorocarbons as a treatment agent for the HM surface.

Finally, chloropolyfluorocarbons such as CF_3Cl, CF_2ClCF_2Cl, and CF_2ClCF_3 may gently and moderate-

Table 2. Catalytic Activities of H-Mordenite Treated with Various Halocarbons or HF Acid

Treatment agent	Conversion mol%	Treatment agent	Conversion mol%
$CFCl_3$	9.5	CF_2ClCF_2Cl	28.4
CF_2Cl_2	19.1	CF_2ClCF_3	34.9
CF_3Cl	41.9	CF_3CF_3	7.8
CF_4	15.3	HF acid	7.4
CCl_4	tr.	no treatment	11.7

Table 3. Surface Composition of H-Mordenite[a)]

Sample	Composition/atomic%					
	Si	Al	O	F	Cl	F/Al
Before treatment	28.7	3.7	67.6	0	0	—
After CF_3Cl treatment[b)]	30.2	3.2	55.4	10.9	0.2	3.4
After use for 3 h	27.4	5.7	52.1	14.0	0.7	2.5

a) SiO_2/Al_2O_3 mol ratio=19.0. b) The treatment was carried out at 450 °C for 8 min.

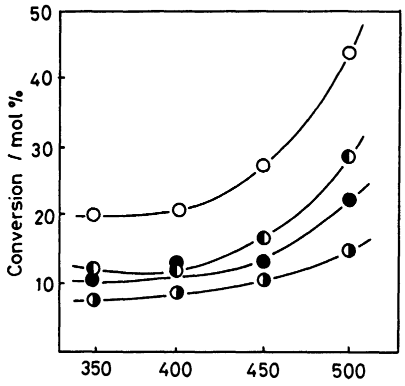


Fig. 1. Effect of reaction temperature on conversion of OCT. HM catalyst having SiO_2/Al_2O_3 mol ratio of 19.0 was used as a catalyst after treatment with CF_3Cl; the treatment was carried out at 450 °C for 8 min. W/F=64.9 gh/mol. Symbols used in this figure are as following.

O: Total conversion to MCT and PCT, ◐: conversion to MCT, ◑: conversion to PCT, ●: conversion to CB.

ly react with the HM surface through their C–Cl bonds of the right strength. That is, since these chloropolyfluorocarbons have a C–Cl bond which is fairly strong compared to those of chlorocarbons (such as CCl_4) and fluoropolychlorocarbons (such as $CFCl_3$), they are not so reactive as to destroy the mordenite structure. Similarly the C–F bond in the CF_2X group is fairly strong compared to that in the CFXY group (X and Y are atoms other than F),[12] although it is not as excessively strong as that in perfluorocarbon. Also this moderately high strength in the C–F bond should contribute to prevention of the violent reaction of the treatment agent with mordenite. Thus, CF_3Cl and chlofluoroethanes, containing not CFXY, but the CF_2X group may be the most suitable treatment agent for HM.

Although HF acid is widely used as the treatment agent for Al_2O_3, SiO_2–Al_2O_3 and various other metal oxides,[13] it was unsuitable for HM treatment. A significant formation of crystalline aluminum fluoride was observed by XRD measurement for the HF acid-treated HM, thus partial degradation of mordenite structure or deposition of the crystalline fluoride in the pores or channels of the mordenite may be the reason for the pronounced decrease in the catalytic activity.

Effect of Reaction Temperature. As Fig. 1 shows, the conversions of OCT to MCT and PCT considerably increased at temperatures higher than 400 °C. However, dechlorination or CB formation became important at high temperatures like 500 °C. So, the selectivity of the isomerization was maximal around 450 °C. Although the data are not shown here, other products such as benzene and polychloro aromatic compounds were formed in small amounts at temperature higher than 500 °C.

Changes of Catalytic Activity and Selectivity with Time on Stream. As is shown by the total conversion of OCT to other chlorotoluene in Fig. 2, the catalytic activity of HM abruptly decreased with reaction time. On treatment CF_3Cl at 450 °C, the catalytic activity was significantly enhanced, and a decrease in activity with process time became less prominent.

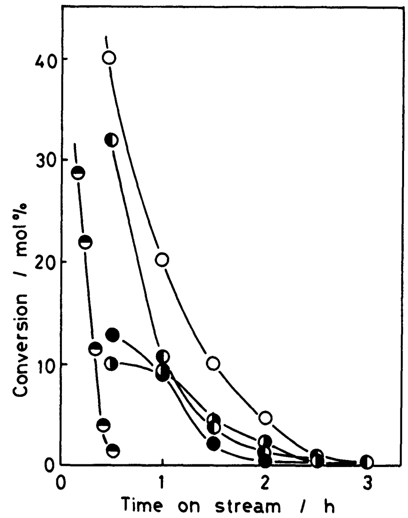


Fig. 2. Effect of process time on conversion of OCT. HM catalyst (SiO_2/Al_2O_3 mol ratio=19.0) was used after CF_3Cl-treatment. The CF_3Cl-treatment and the catalytic reactions were carried out under the same conditions as those described above (Fig. 1). Symbols are as following.

O: Total conversion to MCT and PCT, ◓: total conversion to MCT and PCT in the presence of untreated HM, ◐: conversion to MCT, ◑: conversion to PCT, ●: conversion to CB.

As Fig. 2 shows, at the beginning of OCT isomerization, MCT was preferentially formed. Then the amount of MCT product remarkably decreased with time, and finally became less than that of PCT.

It is probable that the pore size was decreased by the deposition of decomposed materials or carbonized products. So, transfer of the product from active sites by diffusion through the pore become more difficult for MCT than for PCT, because the former molecules have a larger cross-sectional area.

Isomerizations of MCT and PCT. As Figs. 3 and 4 show, the isomerizations of MCT and PCT were promoted by the CF_3Cl-treated HM as well as that of OCT. Furthermore, for these isomerizations of MCT and PCT, the activity maintenance of the treated HM catalyst was better than that for the OCT isomerization. Especially for the isomerization of MCT, the amount of PCT formation was still high even 3 h after the reaction was begun. This is explained as follows. Namely, the para isomer, which has the smallest cross-sectional area among the chlorotoluenes, should be most readily and easily transferred from the pores as soon as it is produced there. Thus, clogging of the pore is fairly slow in the isomerization of MCT when PCT is the main reaction product.

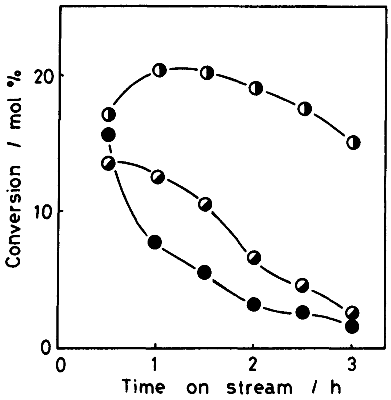


Fig. 3. Effect of process time on conversion of MCT. The HM catalyst (SiO_2/Al_2O_3=19.0) was used also in this reaction. The conditions employed in this reaction were the same as those employed in the OCT isomerization (shown in Figs, 1 and 2). The symbols used here were as following.
◑: Conversion to PCT, ◒: conversion to OCT, ●: conversion to CB.

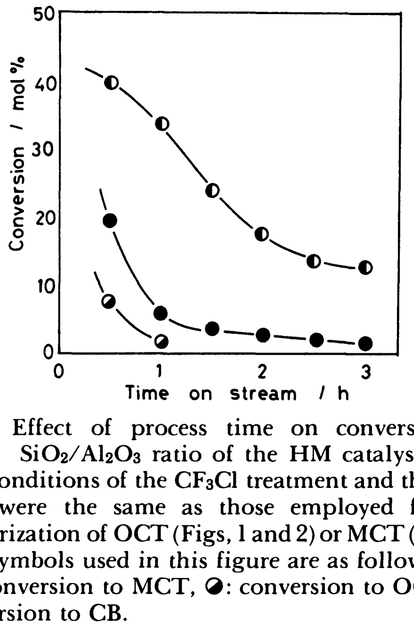


Fig. 4. Effect of process time on conversion of PCT. SiO_2/Al_2O_3 ratio of the HM catalyst=19.0. The conditions of the CF_3Cl treatment and the reaction were the same as those employed for the isomerization of OCT (Figs, 1 and 2) or MCT (Fig. 3). The symbols used in this figure are as following.
◐: Conversion to MCT, ◒: conversion to OCT, ●: conversion to CB.

Table 4. Effect of Poisoning on Isomerization Activity of HM[a)]

	Product distribution/mol%		
	MCT	PCT	Chlorobenzene
Before treatment	31.6	10.8	13.0
Pyridine	4.4	6.0	2.4
2,6-Lutidine	8.1	6.0	9.1
Carbon dioxide	15.3	10.5	14.9
Ref.[b)]	16.6	12.9	13.6

a) SiO_2/Al_2O_3 mol ratio=19.0. b) The reference run was carried out by flowing 80 ml N_2, instead of CO_2, to examine the effect of CO_2 addition.

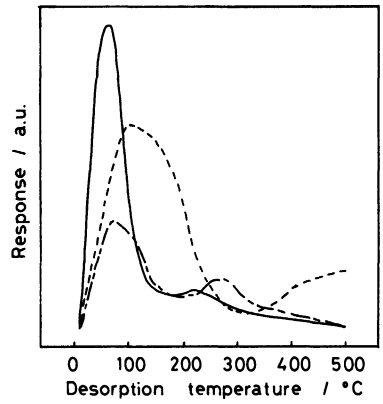


Fig. 5. TPD curves for H-mordenite.
----: Before treatment, ——: after treatment, ——: after use as a catalyst at 450 °C for 3 h. The CF_3Cl treatment was carried out at 450 °C for 8 min.

Appreciably high conversion was obtained at the initial stage of the PCT isomerization process (Fig. 4). This result may be due to the ease with which the PCT molecule is able to reach the active sites in the mordenite pore as compared to other chlorotoluene molecules. However, the conversion decreased somewhat rapidly with reaction time, since the main product, MCT, was not readily removed from the active sites, in accordance with reduction of pore size which occurs with passing reaction time.

Poisoning of Active Sites. The results of poisoning with amines are shown in Table 4 together with those of CO_2 addition used as a reference. The active sites were poisoned with 2,6-lutidine as well as pyridine. It is already known that the 2,6-lutidine molecule is unable to react with Lewis acid sites because the electron-donating N atom in the molecule is sterically hindered by the two adjacent CH_3 groups.[7)] Hence, the fact that the active sites were poisoned by the 2,6-lutidine suggests that the active sites on the treated HM are acid sites of not the Lewis, but the Brönsted type.

On the other hand, CO_2 addition gave almost the same results as that of the dilution with an inert gas, N_2. Thus, it is possible, that the basic sites, if they were present on the CF_3Cl-treated HM, had hardly any effect on the isomerization.

TPD Regarding Acid Strength Distribution. Figure 5 shows the TPD curves of HM before and after treatment with CF_3Cl. The TPD curve of the treated HM after use as a catalyst is also exhibited there.

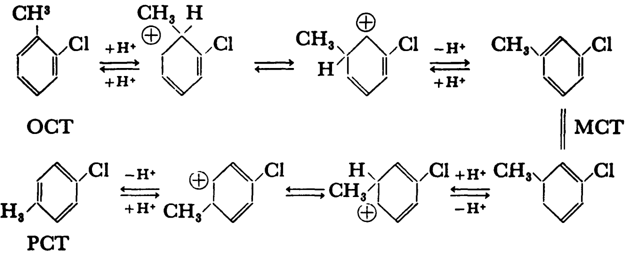
As is represented by the dotted line, a fair amount of NH_3 was adsorbed by the untreated HM even at a temperature as high as 500 °C. For HM treated with CF_3Cl, the adsorption of NH_3 at such a high temperature was no longer observed. Thus, two peaks around 80 and 280 °C became observable in the TPD curve as is represented by the broken line. These facts suggested that excessibly strong acid sites on the untreated HM disappeared and moderately strong acid sites, relating to the peak around 280 °C appeared during CF_3Cl treatment. For the treated HM which became catalytically less active after use as a catalyst for 3 h, the peak at higher temperature almost completely disappeared, and a weak peak became observable around 220 °C. Thus, the moderately strong acid sites represented by the peak around 280 °C, may be most suitable for isomerization promotion.

Demethylation. As Figs. 1—4 show, demethylation also occurred in the early stages of the isomerization. The demethylation was especially pronounced at temperatures higher than 450 °C as was exhibited in Fig. 1. On the other hand, hardly any dechlorination occurred under reaction conditions employed in this study, especially at temperatures lower than 500 °C, although the bond strength of Cl–C_6H_5 (88 kcal mol^{-1} [14] (1 cal= 4.184 J)) is less than that of H_3C–C_6H_5 (91 kcal mol^{-1} [14]). So, demethylation is considered to be promoted by acid sites in a manner similar to the isomerization of chlorotoluene. In fact, the demethylation was subject to suppression by poisoning with amines as was already shown in Table 4. However, the acid strength essential to the promotion of demethylation must be fairly high, since demethylation was promoted only in beginning of a run, when appreciably strong acidity can be maintained without poisoning by product formation.

Reaction Pathway. In view of the evidence collected so far, the isomerization of chlorotoluene is expected to proceed similar to the isomerization of xylene.[15] However, the isomerization of chlorotoluene reached levels of 20—40% only with great difficulty at temperatures as high as 450 °C in the presence of the CF_3Cl treated HM, while a conversion level of higher than 50% was obtained at the lower temperature of 300 °C for xylene isomerization promoted by the same catalyst. Such a difference between the reactivities of chlorotoluene and xylene is ascribable to the difference in the activating effects of the substituent on the benzene ring. That is, when a carbon sp^3 orbital is attached to sp^2 orbital of carbon, there is an electron donation in the direction of sp^2 carbon, because the sp^2-hybridized carbon atom is somewhat more electronegative. Thus, a CH_3 group attached to the benzene ring activates it. In particular, the C atom directly bound to the CH_3 group is easily attacked by protons.

On the other hand, the chlorine atom should deactivate the benzene ring because the inductive effect of chlorine (−I) wins out over the resonance effect (+R). Thus, the activity of chlorotoluene is not as high as that of xylene.

Nevertheless chlorotoluene is less active than toluene as mentioned above, the electron-enriched C atom bound to the CH_3 group in chlorotoluene molecule should be first attacked by the Brönsted acid sites as in the case of the xylene isomerization.[4] Then, isomerization of the chlorotoluene can proceed according to the following reaction pathway.



Since the C atom bound to Cl atom is expected to be positive in charge as described above, the C atom may not be attacked by the Brönsted acid on the HM catalyst. In fact, toluene which is produced by the dechlorination was not appreciably formed under the reaction conditions employed in this study.

Effect of CF_3Cl Treatment on Catalytic Activity of HM. In the isomerization of chlorotoluene, excessively strong acid sites are considered to be unsuitable because they do not readily release the product molecule, and thus they promote the decomposition or carbonization of the molecules in the mordenite pores. The treatment with CF_3Cl or some fluorochlorocarbons may be effective for modification of the too strong acidity of some active sites, possibly due to a slight change in the mordenite structure.

Besides the modification of the acid strength described above, the enlargement of the pore size of the HM seems to be another reason for enhancement of the catalytic activity and activity maintenance. It is well known that mordenite has only a one-dimentional channel.[16] Accordingly, resistance to molecular diffusion and clogging of the channel are serious problems in the reaction catalyzed by the mordenite. So, enlargement of the pores or channels through reaction of the CF_3Cl with the Si and Al components in the mordenite may contribute to the improvement of the catalytic activity and activity maintenance in this vapor phase isomerization of chlorotoluene. The enlargement of the pore by the treatment with CF_3Cl has already been seen in the increased amount of formation of the bulky molecule, 1,3,5-trimethylbenzene, in the isomerization and disproportionation of *m*-xylene.[4] Details of the pore enlargement are now being studied by adsorptions of gases of various cross-sectional areas.

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