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The Nature of Active Sites on Zeolites

XII. The Acidity and Catalytic Activity of Transition Metal Y Zeolites

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Infrared spectra of pyridine chemisorbed on several transition metal-ion Y zeolites have been studied as a means of characterizing the acidity of the surface. After calcination at 480°C, all of the zeolites studied are proton acids. No Lewis acidity was detected. The Y zeolites were more acidic than the X zeolites. No simple relationship was found between the proton acid concentration of the zeolites and their physical parameters. The catalytic activity of the various zeolites was measured for *o*-xylene isomerization and compared with literature data for other reactions. The order of activity of the various zeolites was different for the various reactions investigated. There is little relationship between the catalytic activity and the proton acid concentration.

INTRODUCTION

The influence of the exchangeable cations on the catalytic activity of molecular sieves has been the subject of a number of studies. However, few reports of the properties of the transition metal exchanged zeolites are available.

Richardson (*1*) has studied the electron spin resonance spectra of adsorbed polycyclic aromatic hydrocarbons on cadmium and silver–Y zeolites together with measurements of their activities for cumene cracking. Angell and Schaffer (*2*) and Hall (*3*) have studied the adsorption of several molecules by infrared spectroscopy. Hattori and Shiba (*4*) and Ward (*5*) have recently studied the acidic properties of X zeolites. The locations of nickel ions in nickel faujasite have been discussed by Olson (*6*). Ward has also recently studied the infrared spectra of structural hydroxyl groups and adsorbed water on transition metal Y zeolites (*7*). The catalytic activity of various transition metal cation Y zeolites has recently been reported by Merrill and Arey (*8*). They showed that there were relationships between the catalytic activity and the polarizing power of the cations. Cross, Kemball, and Leach (*9*) recently reported on the isomerization of *n*-butenes over some transition metal X zeolites. The results suggested that a radical mechanism was operative with NiX and in some cases with ZnX in contrast to the other forms examined.

In this paper, studies of the catalytic activity and acidity of a number of transition metal zeolites are reported. So that comparisons can be made with other studies, both partial and fully exchanged Y zeolites were investigated.

EXPERIMENTAL

Materials

All forms of the Y zeolite studied were prepared from a single sample of sodium–Y zeolite by ion exchange in the conventional manner. The NaY had the following properties: $SiO_2:Al_2O_3$ ratio 4·9; 10.3% Na; surface area 903 m^2g^{-1}. X-Ray diffraction studies showed it to be highly crystalline. Exhaustively exchanged samples were prepared by repeated ion exchange at 90–100°C with 10–20% solutions of the appropriate salts. Care was exercised to prevent precipitation of the metal hydroxides and decomposition of the zeolite by use of an unsuitable pH. Partially exchanged samples were prepared by three successive 2-hr exchanges at room temperature (*8*). Retention of crystal structure, after exchange, was confirmed by X-ray diffraction and nitrogen surface area measurements. The physical properties of the samples are listed in Table 1. Pyridine was the heart-cut fraction obtained by distillation of research grade material. It was further dried over activated Linde 4A zeolite. *o*-Xylene was Eastman research grade and was used without further purification.

TABLE 1
Analysis of Zeolite Samples

Cation	Exchanged (%)		Surface area m^2g^{-1}
Mn	91	Exhaustive exchange	843
Co	95		794
Ni	92		824
Cu	99		742
Zn	98		799
Ag	99		690
Cd	93		755
Cr	78	Partial exchange	467
Mn	74		832
Fe	78		644
Co	76		834
Ni	70		839
Cu	78		825
Zn	80		846

Apparatus and Technique

The infrared cell used in this study was the same as reported previously (*5*). A Cary-White 90 infrared spectrophotometer was used. The spectral resolution was 4 cm^{-1} and the scan speed 1 cm^{-1} sec^{-1}.

The zeolite samples were studied in the form of thin wafers. About 0.05 g of powdered zeolite was compacted at 5000 psi in a 1-in. diameter metallurgical die. The resulting wafers had an optical thickness of 6–10 mg cm^{-1}. The samples were inserted in the cell and evacuated to 10^{-3} Torr. The temperature was then slowly raised to 480°C and maintained for 16 hr. The sample was then cooled to room temperature and its spectrum recorded. The sample was then allowed to equilibrate with pyridine at 1-Torr pressure for 2 hr. The gas phase and physically adsorbed pyridine were then removed by evacuation for 2 hr at 250°C and, after cooling to room temperature, the spectrum of the chemisorbed pyridine was recorded.

The zeolite acidity was also studied after partial hydration. Water was allowed to equilibrate with the zeolite for 1 hr, and then the excess water was removed by evacuation at 250°C. After cooling, the spectra were again recorded. Under these conditions, the zeolites contain about 2% water.

The surface areas of the zeolites were measured after dehydration for 4 hr at 400°C. Measurements were made at a nitrogen pressure of p/p_0 of about 0.018 using a Perkin Elmer Sorptometer.

Catalytic activity of the zeolites for *o*-xylene isomerization was measured in the microreactor and using the conditions described previously (*5*). The zeolite was used in the form 20- to 40-mesh granules. Helium was used as the carrier gas. Activity data, for comparison, were also taken from the literature (*8*).

The electrostatic fields in the zeolite were calculated from the data of Rabo *et al.* (*12*) and Dempsey (*13*).

Results

The use of pyridine to characterize the surface of acidic catalysts is now well established (*4, 5, 14*). Briefly, an absorption band at 1545 cm^{-1}, due to pyridinium ions, is indicative of Brönsted acidity while a band at 1451 cm^{-1}, due to coordinately bound pyridine, is characteristic of Lewis acidity. A band due to coordinately bound pyridine between 1450 and 1435 cm^{-1} is due to pyridine–cation interactions. A number of other bands are observed in the spectrum of chemisorbed pyridine, but these are not as useful for diagnostic purposes.

The spectra of pyridine adsorbed on the transition metal Y zeolites were qualitatively similar to those observed on transition metal X zeolites (*5*) and, therefore,

TABLE 2
ACIDITY AND PHYSICAL PARAMETERS OF EXCHANGED Y ZEOLITES

Cation		Ionic radius A°	Electrostatic field (V/Å)	Electrostatic potential (e/r)	Ionization potential (V)	Pyridine–cation frequency (cm^{-1})	Proton acidity (arbitrary units) Dry	Proton acidity (arbitrary units) Hydrated
Exhaustive exchange	Mn	0.80	4.8	2.50	15.7	1448	2.2	6.3
	Co	0.78	4.9	2.58	17.3	1446	2.1	8.9
	Ni	0.78	4.9	2.58	18.2	1447	1.1	4.5
	Cu	0.69	5.4	2.90	20.3	1448	2.3	4.7
	Zn	0.74	5.1	2.70	17.9	1449	2.6	5.8
	Cd	0.97	4.2	2.06	16.8	1447	1.3	5.7
Partial exchange	Cr	0.69	—	4.35	30.9	—	5.0	5.6
	Mn	0.80	4.8	2.50	15.7	1448	1.6	7.4
	Fe	0.76	5.1	2.63	16.2	—	3.3	7.0
	Co	0.78	4.9	2.56	17.3	1446	1.9	8.5
	Ni	0.78	4.9	2.56	18.2	1447	0.3	9.5
	Cu	0.69	5.4	2.90	20.3	1448	6.9	6.5
	Zn	0.74	5.1	2.70	17.9	1449	1.4	5.2

will not be illustrated here. Absorption bands due to pyridinium ions and pyridine–cation interactions were observed. The concentrations of pyridinium ions and the frequencies of the cation–pyridine bands are listed in Table 2. The concentration of proton acid sites (arbitrary units) as a function of the ionization potential, electrostatic potential, and electrostatic field are shown in Figs. 1 and 2.

The catalytic activities of the various zeolites for the *o*-xylene isomerization are also listed in Table 3. Rate constants at 260°C were calculated from Arrhenius plots of the xylene conversion data. Data for the cracking of methylcyclopentane and disproportionation of toluene from Ref. (*8*) are also listed in Table 3. The data for the three reactions are plotted as a function of the physical parameter in Figs. 3–6.

DISCUSSION

Variation of Acidity with Cation

It has been shown previously that several of the transition metals studied possessed structural hydroxyl groups (*7*). This is understandable in terms of the accepted need of hydroxyl groups to satisfy the electrical neutrality and charge distribution

TABLE 3
CATALYTIC ACTIVITY OF TRANSITION METAL Y ZEOLITES

Cation	Rate constant for xylene isomerization: Partial exchange	Rate constant for xylene isomerization: Exhaustive exchange	Wt % cracking of methylcyclopentane at 50% conversion (*8*)	% C_{8^+} in C_{7^+} fraction: toluene disproportionation (*8*)
Cr	0.8	—	26	39
Mn	0.4	0.3	17	36
Fe	2.5	—	23	26
Co	1.7	2.5	33	25
Ni	21.9	58.9	34	27
Cu	5.6	6.6	34	30
Zn	3.6	9.3	28	20
Cd	—	0.3	—	—

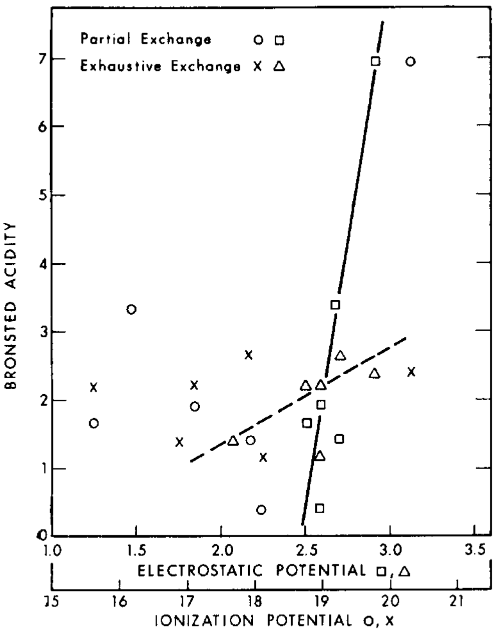

FIG. 1. Variation of Brönsted acidity concentration with ionization potential and electrostatic potential.

of the zeolite lattice when multivalent cations are introduced,

$$M^{2+} + H_2O \rightarrow MOH^+ + H^+.$$

Hence it is to be expected that the transition metal ion zeolites studied should possess acid centers. Chemisorption of pyridine reveals the presence of proton acid sites in all the ion-exchanged forms studied as shown by the presence of an absorption band near 1545 cm^{-1}. Since all of the transition metal ion zeolites contain hydroxyl groups with an infrared absorption band frequency near 3640 cm^{-1} (*7*), the acid sites are probably formed by a fission of adsorbed water under the influence of the electrostatic field in a manner analogous to that proposed for alkaline-earth zeolites (*3*, *5*) and for transition metal ion X zeolites (*5*). Figure 2 shows the relationship between the calculated electrostatic field and the proton acid concentration for the partially and exhaustively exchanged zeolites. It is seen that for both cases, a fairly good relationship between acid site concentration and field is observed which supports the dissociation mechanism,

$$M^{2+} + H_2O \rightleftharpoons MOH^+ + H^+.$$

The stronger the field, the greater would be the concentration of protons because of the greater interaction of the cations with adsorbed water.

In Fig. 1, the acid site concentration is shown as a function of the electrostatic potential and ionization potential. Again, a good correlation is observed with the electrostatic potential, but a poor relationship is observed with the ionization potential.

From these results, it appears that the factors involved in the formation of proton acid sites are far more complicated for transition metal zeolites than for alkaline-earth zeolites (*15*) and merit further investigation. In particular, it is surprising to observe that some of the partially exchanged zeolites have more acid sites than the exhaustively exchanged zeolites. A possible explanation is that accessible acidic hydroxyl groups are replaced by non or weakly acidic cations at the higher degrees of exchange.

With the exceptions of copper- and chromium-exchanged zeolites, all of the forms studied had fewer acid sites than magnesium and calcium–Y zeolites. They

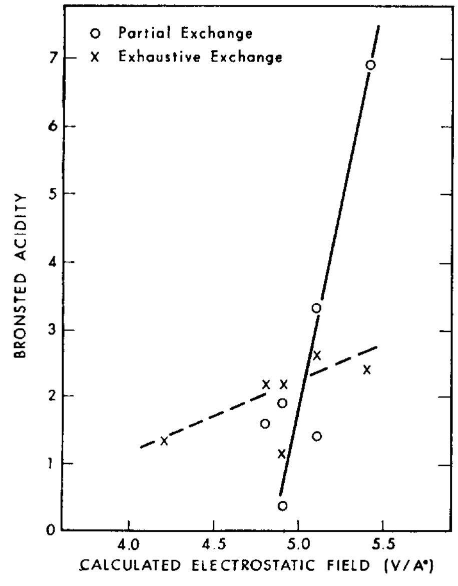

FIG. 2. Variation of Brönsted acidity concentration with electrostatic field.

had, however, more sites than the corresponding X zeolites which would be expected by comparison with the corresponding alkaline-earth forms (*5*).

None of the samples had any detectable Lewis acidity at the conditions of examination. By analogy with other proton acid-containing zeolites, calcination at higher temperatures would be expected to convert proton acid sites into Lewis acid sites.

All of the zeolites studied showed an absorption band in the spectrum of chemisorbed pyridine due to cation–pyridine interaction. The band near 1440–1450 cm^{-1} varies in frequency with the cation, but there seems to be no direct relationship with the calculated electrostatic field or potential. The frequencies are similar to those observed previously for transition metal X zeolites and are all higher than those observed for alkaline-earth cation zeolites (*5*, *15*). The latter indicates stronger bonding of the pyridine to the zeolite cations, possibly involving *d*-electrons, for the transition metal ion zeolites.

Measurement of the acidity under hydrated conditions resulted in an increased number of sites for all forms except the partially exchanged copper zeolite. In this case, a slight decrease in acid site concentration was observed. These results are similar to those reported previously for transition metal X zeolites (*5*). Since no Lewis acid sites are observed on the dehydrated zeolites, the increase in proton acidity is not due to conversion of Lewis acid sites to proton acid sites as observed for silica-alumina and decationized Y zeolite. Since a decrease in the absorption band due to cation–pyridine interaction is observed on hydration, the change in acidity may be due to the movement of cations from accessible to inaccessible positions in the structure with the resultant formation of additional proton acid sites in accessible positions.

Variation of Catalytic Activity with Exchangeable Cation

The rate constants at 260°C for the *o*-xylene isomerization reaction vary by a factor of almost 200 from the least to the most active ion-exchanged forms studied. Nickel was by far the most active and manganese and cadmium the least active. As would be expected, the exhaustively exchanged samples, with the exception of manganese, were more active than the partially exchanged samples. The order of activities is Ni $>$ Zn $>$ Cu $>$ Co $>$ Mn,Cd for the exhaustively exchanged samples and Ni $>$ Cu $>$ Zn $>$ Fe $>$ Co $>$ Cr $>$ Mn for the partially exchanged samples. It is seen that, apart from the reversal of the copper and zinc, the orders for the two series are the same. The difference could be due to the reversal in degree of exchange. Where comparisons can be made, the order of catalytic activity is the same as that reported previously for X zeolites (*5*). However, in all cases, the Y forms are more active than the corresponding X forms. Of the cation forms examined, only nickel, zinc, and copper were more active than conventional amorphous silica-alumina (*19*, *20*).

Silver–Y zeolite was also studied, but the sample reduced to silver metal in the presence of xylene at reaction temperatures, and no satisfactory results were obtained. For all other samples, no decomposition of the zeolites was detected.

An interesting observation is that the activation energy for the exhaustively exchanged samples is 33 ± 1 kcal $mole^{-1}$ compared to 20 ± 1 kcal $mole^{-1}$ for the partially exchanged samples. The former value corresponds to the values found previously for exhaustively exchanged transition metal X zeolites while the latter corresponds to the value found for alkaline-earth X and Y zeolites. The significance of these different values is under investigation. At this time, is is only possible to suggest that different types or strengths of sites or different mechanisms may be involved. Schwab and Kral (*10*) found comparable differences for cumene cracking over various ion-exchanged zeolites. In a study of xylene isomerization and disproportionation over rare-earth zeolites, Matsumoto and Morita (*11*) found that the activation energy for isomerization was independent of the extent of rare-earth ion exchange, whereas the activation energy for disproportionation decreased with increasing extent of ion exchange. This change in activation energy is opposite to that observed in the present study. Moreover, for the experimental conditions of this study, the contribution of the disproportionation reaction to the conversion of the *o*-xylene is insignificant.

It is interesting to compare the order of activity found in the study with the partially exchanged samples containing 0.6% Pt reported by Merrill and Arey (*8*). They found, for a series of partially exchanged Y zeolites, that the amount of cracked product at 50% conversion of methylcyclopentane increased with cation in the following order: Cu, Ni > Co > Zn > Cr > Fe > Mn. For toluene disproportionation, they found the order Cr > Mn > Cu > Ni > Fe > Co > Zn. They found fairly good agreements between these orders of activity and the change to radius (*e*/*r*) ratio. Apart from the position of cobalt, the order for methylcyclopentane cracking is in good agreement with the order from the present study. There is little agreement with the toluene disproportionation order. Table 4 ranks, qualitatively, the orders of activity of the catalysts for the three reactions.

In Fig. 3, the rate constants for xylene isomerization are plotted as a function of charge-radius ratio. It is seen that for the partially exchanged samples, with the exception of nickel and chromium, there is an excellent correlation. Nickel zeolite is far more active than would be predicted. Since chromium is the only trivalent ion involved, it is not surprising that it is anomalous. A much poorer correlation is obtained for the exhaustively exchanged samples.

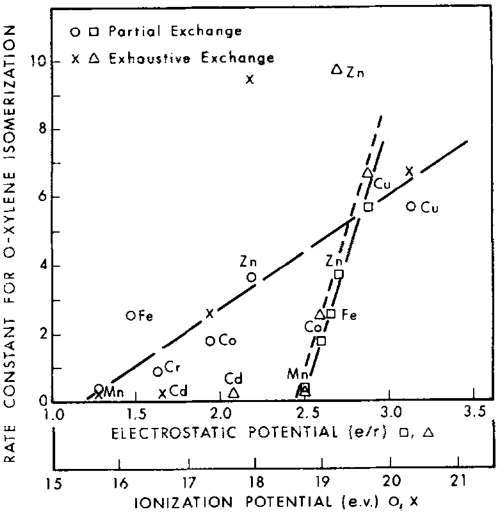

FIG. 3. Rate constant for *o*-xylene isomerization at 260°C as a function of ionization potential and electrostatic potential.

In Fig. 3, the rate constants are also plotted against the ionization potential of the respective metals. Again, with the exception of nickel, a reasonable correlation is observed.

In Fig. 4, the cracking of methylcyclopentane and toluene disproportionation are shown as a function of the electrostatic potential and ionization potential. As ob-

TABLE 4
RANKING OF TRANSITION METAL Y ZEOLITES BY VARIOUS PROPERTIES

Brönsted acidity				*o*-Xylene isomerization		Wt% cracking of methylcyclopentane at 50% conversion	Toluene disproportionation
Partial exchange		Exhaustive exchange					
Dry	Hydrated	Dry	Hydrated	Partial exchange	Exhaustive exchange		
Cu	Ni	Zn	Co	Ni	Ni	Cu	Cr
Cr	Co	Cu	Mn	Cu	Zn	Ni	Mn
Fe	Mn	Mn	Zn	Zn	Cu	Co	Cu
Co	Fe	Co	Cd	Fe	Co	Zn	Ni
Mn	Cu	Cd	Cu	Co	Mn	Cr	Fe
Zn	Cr	Ni	Ni	Cr	Cd	Fe	Co
Ni	Zn			Mn		Mn	Zn

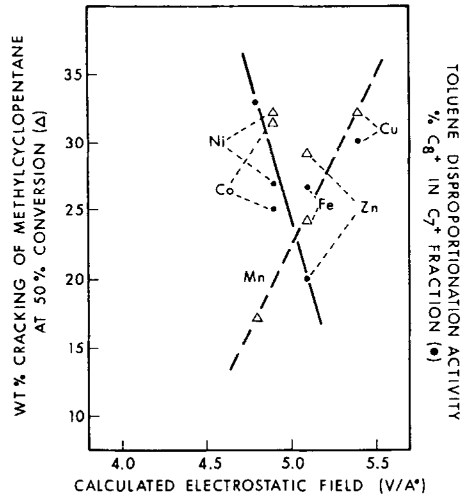

FIG. 4. Catalytic activity for methylcyclopentane cracking and toluene disproportionation as a function of ionization potential and electrostatic potential.

served for the o-xylene reaction, a general trend is observed between the catalytic activity and the physical parameters, but large deviations are found.

Figure 5 shows that, exclusive of nickel, chromium, and the exhaustively exchanged ZnY, a good agreement is obtained between the catalytic activity for xylene isomerization and the calculated electrostatic field, thus indicating a role of the cation in influencing the activity. Figure 6 shows a similar plot for the methylcyclopentane cracking and toluene disproportionation using the data of Merrill and Arey (*8*) for partially exchanged samples. For the methylcyclopentane cracking, the catalytic activity increases with increasing field, analogous to the observations for o-xylene isomerization. However, cobalt and nickel do not fit the correlation for the methylcyclopentane reaction, whereas zinc and nickel did not fit the correlation in the case of the xylene reaction.

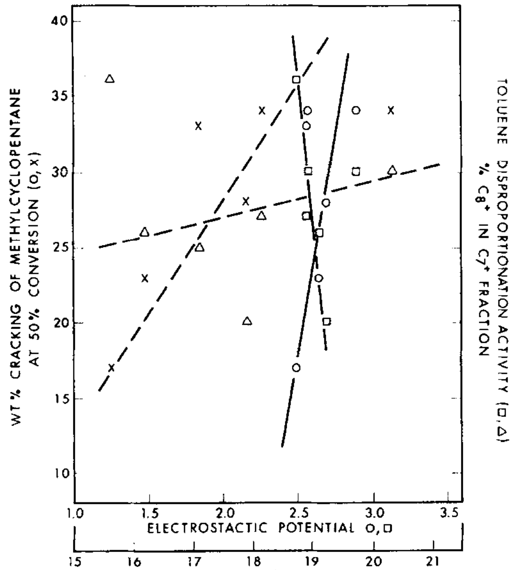

FIG. 5. Rate constant for o-xylene isomerization as a function of electrostatic field.

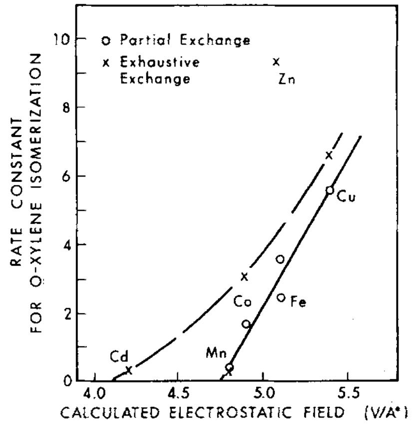

FIG. 6. Catalytic activity for methylcyclopentane cracking and toluene disproportionation as a function of electrostatic potential.

In contrast, for the toluene disproportionation reaction, the activity appears to decrease with increasing electrostatic field. In this case, ferrous iron and copper do not fit the correlation.

Relationship between Catalytic Activity, Acidity and other Physical Parameters

The catalytic activity of zeolites has been attributed to the electrostatic field, Lewis acid sites and Brönsted acid sites by several workers (for a recent evaluation see Ref. *16*). No Lewis acid sites were detected in the samples used in this study, thus making such sites unlikely active catalytic centers. Furthermore, recent studies of nontransition metal ion zeolites have tended to indicate that the electrostatic fields are not the primary cause of catalytic activity, but they may play an important role in promoting the dissociation of water to yield acid sites.

Other studies have indicated that in order to catalyze carbonium ion-type reactions, zeolites usually contain proton acid centers, and that there is, in general, a relationship between the catalytic activity and concentration of acid sites (*15*). Although all of the transition metal ion zeolites studied contain proton acid sites and are catalytically active, there seems to be little relationship between the activity and acid site concentration as shown by the data of Table 3. However, data has been reported suggesting that acid site strength might be an important variable criterion as well as site concentration (*17*). Such a phenomenon may be an important feature of the active sites in transition metal ion zeolites. Another possibility in the case of the presently studied samples is the direct interaction of the transition metal ions with the various molecules studied in the catalytic activity measurements. Thus, Yates (*18*) has shown that specific interactions occur between ethylene and cadmium and silver zeolites which do not occur with nontransition metal ion zeolites.

In summary, transition metal zeolites are proton acid-containing catalysts. However, there is no simple relationship between the concentration of acid sites and the catalytic activity. The order of activity of the various transition metal zeolites differs for different reactions. Further studies are needed to define more specifically the sites responsible for the observed catalytic phenomena.

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