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The Nature of Active Sites on Zeolites

XV. The Influence of Nickel Cations on the Catalytic Activity of Hydrogen Y Zeolite

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Rate constants for *o*-xylene isomerization and the infrared spectra of the surface structure of a series of nickel hydrogen Y zeolites have been measured. The nickel content of the hydrogen zeolite was varied from 0 to 100% of the exchange capacity. The nature and population of the structural hydroxyl groups, the surface acidity and the catalytic activity are interpreted in terms of probable locations of the nickel cations. The results are compared with similar studies of Group IIA Y zeolites and with information about nickel Y zeolites derived from other techniques.

INTRODUCTION

Many studies have now been reported which relate the catalytic activity of zeolites in reactions involving carbonium ions to the presence of acid sites (*1*). In particular, the active centers appear to be related to the presence of Bronsted acid sites rather than Lewis acid sites or to the influence of the electrostatic field associated with the exchangeable cations.

Most of the discussions of relationships between catalytic activity and acidic properties of the zeolites have considered the concentration of acidic sites. Although in many cases good relationships have been found between the acid site concentration and the catalytic activity, a sufficient number of exceptions has been reported that it appears desirable to investigate other factors which might be contributing significantly to the catalytic activity.

One of the many possible factors which could influence the catalytic activity is the environment and strength of the acid sites. Few studies have been made of this phenomenon in zeolites although its importance has been suggested several times.

Hirschler (*2*) has suggested that "the polarizing action of the field of the cation tends to free (make acidic) a proton of a hydroxyl group attached to an adjacent silicon or aluminum atom, or a proton of a water molecule adsorbed on the cation itself. The greater the field strength of the cation, the stronger would be the resultant acidity." Thus, the acid strength should increase with increasing charge and decreasing size of the cation. Hence, it would seem that water molecules associated with the cations could become acid centers and that the cations could influence the acid strength of hydroxyl groups already present in the structure.

Richardson (*3*) has discussed a somewhat similar concept in relating catalytic activity for cumene cracking to cation properties. He considered that the ionic potential (*e*/*r*) of the cation results in a shift of electron charge distribution towards the vicinity of the cation via a conduction band model. Such an interaction would weaken the O–H bonds on the surface of the supercages and thus modify the acidity of the hydroxyl groups. Both of these proposals consider the role of the cation in modifying the nature of hydroxyl groups existing already in the zeolite structure (*2*,*3*) or of water associated with the cation without specific formation of new structural hydroxyl groups (*2*). An interesting portion of the proposals of Richardson is that modifications of the activity of hydrogen Y zeolite can be anticipated. Thus, whereas the discussion of cation and hydrogen Y zeolites above would lead to expectation that hydrogen Y zeolite would be the most acidic faujasite type zeolite, introduction of a cation with a high ionic potential into a hydrogen Y zeolite could produce a more acidic faujasite (*3*). Studies of rare earth hydrogen and alkaline earth hydrogen Y zeolites (*4*,*5*,*10*) have indicated such an effect. The proposals of Richardson also suggest that a distribution of acid site strengths exists which is compatible with the necessity for only a small fraction of the total acid site population being necessary for catalytic conversions. Tung and McIninch (*6*,*7*) have discussed a different type of mechanism for the modification of acid site strengths. They visualized the existence of a dynamic (time variant) surface field and Bronsted acidity. Movements of the ion exchanged cations were visualized as generating changes in the surface field strengths and in the strengths of proton acid sites. These considerations stemmed from the studies of dielectric constants of the zeolites in the presence of an alternating electrostatic field. Variations in the acid site strength have also been reported by Benson *et al.* (*8*). Lunsford (*9*) has proposed that defect sites formed in the zeolite structure have important modifying effects upon the acidity of the structural hydroxyl groups.

In previous papers, the influence of alkaline earth cations on the catalytic activity and surface properties of hydrogen Y zeolite were studied. It was shown that the cation field had an indirect influence on the catalytic activity which varied in an irregular manner with the extent of exchange (*10*). It was also shown (*11*) that the nature of the alkaline earth cation, even at the same level of exchange, also influenced the activity of the zeolite. The activity was directly related to the electrostatic field or potential of the exchanged cation.

In this paper, the influence of the transition metal ion, nickel, on the properties of the surface active sites is reported. Nickel was chosen since the chemisorption of carbon monoxide studied by infrared (*12*), gas adsorption (*13*) and X-ray diffraction techniques (*14*) suggested that the locations of the divalent nickel ions may be considerably different from those of magnesium and calcium. Later, magnetic studies suggested that cobalt ions had a lower site preference than calcium (*15*). More recent studies (*16*–*18*) have shown that nickel has a lower preference for hidden sites than calcium. It was also shown that the locations of the nickel ions are sensitive to residual moisture and also that the nickel ions can be induced to migrate by adsorbents such as carbon monoxide.

EXPERIMENTAL METHODS

Ammonium Y zeolite was prepared by conventional ion exchange of sodium Y zeolite ($SiO_2/Al_2O_3 = 4.9$). The ammonium Y zeolite had a sodium content of 0.1 wt%. Nickel ammonium Y zeolites were prepared by controlled ion exchange of the parent ammonium Y (surface area = 965 $m^2\ g^{-1}$) with dilute nickel nitrate solutions. The extent of exchange was controlled by the quantity of nickel nitrate used in the ion exchange. Exchange levels for the various samples are given in Table 1. All samples had crystallinities greater than 95% relative to a standard sample and had surface areas greater than 800 $m^2\ g^{-1}$.

Techniques

Catalytic activities of the various zeolite samples for *o*-xylene conversion were

TABLE 1
Analysis of Nickel Ammonium Y Zeolites

Sample	% Ni exchanged
1	8.7
2	20.2
3	28.7
4	31.3
5	35.0
6	61.5
7	70.8
8	71.2
9	71.8
10	91.3
11	100.0

measured as reported previously (*5*). Conversion of *o*-xylene was measured at a series of temperatures. From the Arrhenius plots, the rate constant at 260° was calculated. The catalyst samples were activated under conditions such that hydrothermal effects were eliminated.

The surface acidity was measured by means of the infrared spectra of chemisorbed pyridine using the previously reported procedure (*5*). The types and population of surface hydroxyl groups were also studied by infrared techniques.

RESULTS

Spectral Studies

Typical spectra of the structural hydroxyl group are observed on the nickel ammonium Y zeolites after calcination in vacuum at 450°C. Typical characteristic hydroxyl absorption bands are observed near 3740, 3680, 3635 and 3540 cm^{-1}. In Fig. 1, the peak heights of the two major bands near 3635 and 3540 cm^{-1} are shown as a function of the percentage exchange with nickel ions.

Adsorption of pyridine on Bronsted acid sites results in the formation of pyridinium ions with a characteristic absorption band near 1540 cm^{-1}. Adsorption on Lewis acid sites produces a band at about 1451 cm^{-1} while interaction with the exchangeable cations produces bands at a slightly lower but variable frequency.

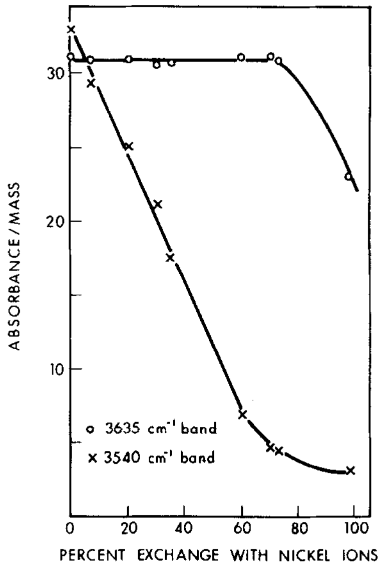

Fig. 1. Variation of hydroxyl group band intensities with percentage nickel exchange.

Figure 2 shows the absorbance of bands near 1540 and 1447 cm^{-1} due to chemisorbed pyridine on Bronsted acid sites and interacting with the nickel ions as a function of the nickel exchange level. No bands near 1451 cm^{-1} attributable to ad-

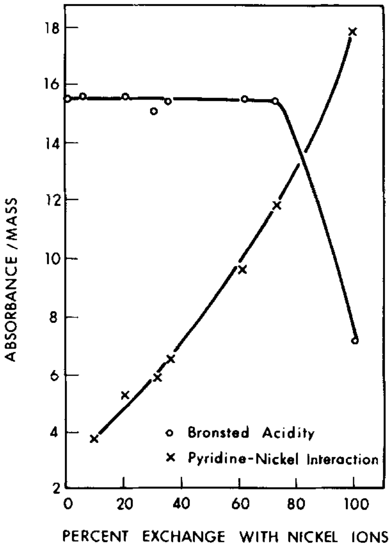

Fig. 2. Variation of Bronsted acidity and pyridine-nickel interaction with percentage nickel exchange.

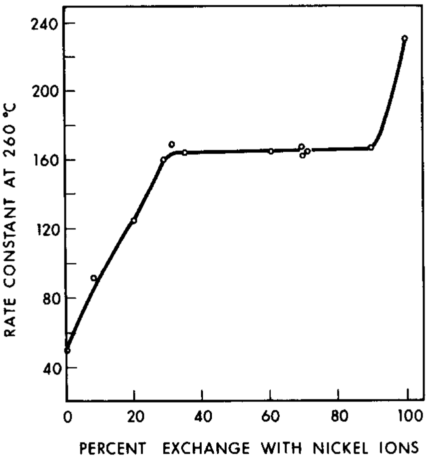

FIG. 3. Influence of percentage of nickel exchange on the activity for *o*-xylene isomerization.

sorption on Lewis acid sites were detected, indicating that the zeolite had not been partially dehydroxylated to form such sites.

Activity Measurements

The rate constants at 260°C for xylene isomerization are plotted as a function of the nickel in Fig. 3. The activation energy was found to be 20 ± 1 kcal/mole. No variation of activation energy with degree of exchange was found.

DISCUSSION

Nature of Hydroxyl Groups

The spectra of the nickel hydrogen Y zeolites with less than 50% of the exchange capacity occupied by nickel ions are similar to those of the parent hydrogen Y zeolite. The two characteristic bands near 3635 and 3540 cm^{-1} are readily detected.

As the nickel ions are introduced into the zeolite, the intensity of the 3540 cm^{-1} decreases steadily until at about 60% exchange, the intensity is only one-fifth of the initial value. As the level of exchange is increased to 95%, the intensity declines more slowly to about one-tenth of the initial value. The initial decline is comparable to that of calcium and magnesium hydrogen Y zeolites but differs in that for the alkaline earth cases at 60% exchange, the intensity has declined to one-tenth of the initial value and to zero at 90% exchange.

The initial decline in intensity is probably due to the replacement of hydroxyl group precursors in the hexagonal prism portions of the structure by nickel ions either in the initial exchange or in the subsequent calcination. This result is similar to that previously reported for the alkaline earth cation. The process can probably be represented by the following scheme:

$$2NH_4Y + Ni^{2+} + H_2O \rightarrow Ni^{2+}Y + NH_4{}^+Y + H_2O + NH_4{}^+ \rightarrow NiOHY + HY + NH_3.$$

During calcination, the reaction $Ni(OH_2)^{2+} \rightarrow NiOH^+ + H^+$ probably occurs. Previously, it has been shown that nickel Y zeolites contain hydroxyl groups with frequencies near 3635 and 3540 cm^{-1} analogous to those observed in hydrogen Y zeolites (*19*). A band near 3680 cm^{-1} was also observed and attributed to NiOH groups. The reasons why the intensity of the 3540 cm^{-1} does not decline at zero are not very clear. A possibility suggested from the studies of Olson (*14*) and Egerton *et al.* (*13,15,16*) is that despite the pretreatment in vacuum, the zeolites still contain small amounts of residual water resulting in only partial filling of the hexagonal prisms by nickel ions. The additional ions possibly occupy sites in the S_I' and S_{II}' positions as discussed by Egerton *et al.* (*15*) for cobalt Y zeolite. The data agree reasonably well with the results of Gallezot *et al.* (*20*) who found that the hexagonal prisms are only occupied by 10–12 atoms instead of 16.

The intensity of the 3635 cm^{-1} band remained constant as the nickel content increased to about 70% exchange. The concentration then rapidly decreased as the extent of exchange was increased. This behavior is similar to that of the alkaline earth forms except the point at which the drop in intensity occurs is at a somewhat higher exchange level and that even at close to 100% exchange the band still has greater than one-half of its original intensity. This observation indicates considerable contribution from hydroxyl groups introduced via the nickel ions. Relatively strong absorption bands have been observed previously for NiY (*19*).

The data do not correlate very well with the observations of Egerton and Stone (*17*) who found a marked change in the adsorption of carbon monoxide at about 55% exchange. The decline in the 3635 cm^{-1} hydroxyl band intensity at a higher degree of exchange than predicted from the calcium study (*10*) could be due to many factors. A possibility suggested by Egerton and Stone is that nickel has a lower preference for the accessible sites than say calcium. The difference from Egerton and Stone's data may be due to differences in the degree of hydration or may be due to this study being of the hydrogen–nickel system whereas their study was of the sodium–nickel system.

Adsorption of pyridine was used to determine surface acidity on the various nickel samples. The proton acidity determined from the concentration of pyridinium ions follows very closely the population of the 3635 cm^{-1} hydroxyl groups. The proton acidity remains constant until about 70% exchange has occurred and then declines rapidly. It thus appears that the 3635 cm^{-1} hydroxyl groups are major contributors to the proton acidity of this type of zeolite. No Lewis acid sites were observed using the absence of spectral bands corresponding to coordinately bound pyridine as the criterion. An absorption band near 1447 cm^{-1} indicating pyridine–cation interaction was observed even at low concentrations of nickel ions. The intensity of the band increased continuously with the increasing extent of nickel exchange. This behavior suggests that in some way, some of the nickel ions are available for interaction with large molecules even at low levels of exchange. Hence some ions must be present in the supercages at low levels of exchange. The X-ray and magnetic results support this conclusion if small amounts of water are present. Alternatively, it is possible that the pyridine might interact strongly enough with the nickel ions so as to result in the migration of nickel ions out into the supercages. Such migrations have been suggested previously for pyridine and piperidine on hydrogen Y, for carbon monoxide on nickel Y (*17*) and for pyridine and butene on copper Y (*20*).

The data differ significantly from those previously observed for the alkali and alkaline earths. For these cation hydrogen zeolites, no absorption bands were observed until the extent of exchange was greater than 50%. Then a rapid increase in intensity occurred. The observations were interpreted in terms of cations becoming available in the supercages for interactions with the adsorbing pyridine.

The interpretation of the infrared data in terms of the location and influence of the exchanged nickel ions is difficult and seems to be contradictory. Overall, considering all the data, it appears that the metal ions initially enter the inaccessible parts of the structure (i.e., hexagonal prisms and sodalite units) in preference to the supercages. Such a process continues up to about 70% exchange. The nickel ions then spill out into the supercages as higher degrees of exchange are reached. The data can be reconciled with the pyridine adsorption data if it is assumed that strongly polar adsorbed molecules can induce the migration of nickel ions.

Catalytic Activity and Physical Structure

The data in Fig. 3 shows a very complex relationship between catalytic activity and the degree of nickel exchange. In general, the activity increases as the extent of nickel exchange increases. This is a marked difference from the previously reported data for calcium and magnesium which showed a rapid drop in activity after more than about 55% of the exchange capacity was occupied by cations.

The nickel data resembles that obtained for calcium and magnesium at the lower levels of exchange. Rapid increases in activity are observed in three cases from zero cation content up to about 35% exchange. A period of constant activity then occurs. For calcium and magnesium, the constant activity period extended to about 55% exchange whereas with nickel it extended to about 90% exchange. The level of activity is much higher for nickel (rate constant 168) than for magnesium (rate constant 70) and calcium (rate constant 20). Large rate constants (over 100) have previously been observed for hydrogen Y zeolites containing Group IIIB cations (*21*). The major different observation from the alkaline earth cation is at exchange levels above 60%. Whereas for magnesium and calcium (*10*) and for lanthanum and cerium (*21*) the rate constants show a marked decline as the level of exchange is increased, for the nickel-containing zeolite, there is a dramatic increase in activity above 90% exchange. The final level of activity is almost four times that of the initial hydrogen Y zeolite.

The initial increase in activity of the hydrogen Y zeolite is probably due to reasons similar to those responsible for the activity changes in the Group IIA and IIIB hydrogen zeolites, namely, the small multivalent nickel cation is influencing the surface hydroxyl groups of the zeolite so as to provide a stronger acid site. As in the case of the alkaline earth ions, this change in acid site strength is occurring without change in the population of the acidic hydroxyl groups. Since the ionic radius of nickel is less than that of magnesium, the greater effects might be expected.

The initial point on the activity plateau is at a similar level of exchange to that observed for Group IIA (*10*) and IIIB cation hydrogen for zeolites (*21*), namely at about 35% exchange; that is, after about 10–12 cations have been introduced in the case of the divalent ions and 6–8 in the case of the trivalent cations. The reasons for this change in activity exchange level dependence are not readily apparent. Possibly, cations located in certain specific exchange sites have a dominating effect on the structural hydroxyl groups. No particular change in the population of hydroxyl groups or acid sites is seen near the 30–40% exchange level.

No break in the plateau activity is observed near the 50–60% exchange level as might be expected from the data of Egerton *et al.* for cobalt and nickel exchanged Y zeolite (*15,17*) and from the observations with alkaline earth zeolites (*10*). When the break does occur, it is at about 90% exchange. Then in marked contrast to the Group IIA and IIIB cation zeolites, the catalytic activity dramatically increased instead of decreasing. It is difficult to interpret this increase. Unlike other cation hydrogen Y zeolites studied, the catalytic activity does not follow the decrease in proton acidity near 70%. Instead the activity remains constant to near 90% exchange and then increases about 30%, whereas the acidity decreases by 50%. A possibility is that the nickel ions and the xylene can interact via the π electrons of the aromatic nucleus. An interaction of this type has been suggested by Angell and Howell (*22*) to explain infrared spectra of adsorbed benzene. High activities have previously been observed for nickel ions in Y zeolites. For the isomerization of *o*-xylene, catalysts made by exchanging nickel ions into sodium Y zeolite to a level of 70 and 92% were considerably more active than other transition metal ion exchanged zeolite (*23*). Although the 92% exchanged material was substantially less active than the currently studied highly exchanged materials, the lower activity is probably explainable in terms of the much higher sodium contents. Similarly for methylcyclopentane cracking, the nickel zeolites were among the most active (*23*).

In conclusion, nickel hydrogen Y zeolites behave analogously to Group IIA and IIIB hydrogen Y zeolites in physical properties and catalytic activity to some extent but major differences occur at high levels of exchange. The differences may be due to the sensitivity of the nickel ion locations to the extent of dehydration and/or may be due to specific properties of the nickel cations resulting in a lower site preference. Here the possibility of the nickel ions interacting strongly with aromatic molecules also cannot be ignored.

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