JOURNAL OF CATALYSIS 26, 451-454 (1972)

The Nature of Active Sites on Zeolites

XIII. The Acidity and Catalytic Activity of Magnesium Ammonium Y Zeolite*

JOHN W. WARD

Union Oil Company of California, Union Research Center, Brea, California 92621

Received February 1, 1972

Catalytic activity measurements of *ortho*-xylene isomerization over magnesium ammonium Y zeolite have been made as a function of calcination temperature. A maximum activity is observed after calcination at 570–580°C. This temperature falls within the calcination temperature range for maximum Bronsted acidity. It is also below the temperature at which marked dehydroxylation occurs.

The catalytic results can be explained simply in terms of Bronsted acid site concentrations and there appears to be no need to invoke Lewis acid sites or defect sites. The results and conclusions are in marked contrast to those found with ammonium Y zeolite. The difference may be due to the absence of complications involving the thermal instability of the ammonium Y zeolite.

INTRODUCTION

The relationship between catalytic activity and surface acidity of molecular sieve zeolites has been subject to considerable study. Several studies have been made relating the properties of ammonium Y zeolite and its decomposition product, hydrogen Y zeolite, as a function of calcination temperature (*1–12*). Changes in calcination temperature influence the degree of dehydroxylation of the surface and hence the nature of the acid sites. The nature of the surface has been studied by various techniques including infrared studies, electron spin resonance, oxidation of adsorbed ammonia and thermal analyses. Attempts have been made to relate these observations to catalytic measurements made by various workers (*4–12*). It has generally been concluded from infrared studies (*1–4*) that the hydroxyl group population reaches a maximum after calcination around 350°C, remains constant to about 550°C and then declines as dehydroxylation occurs. The concentration of Bronsted acid sites as measured by pyridine adsorption follows a similar trend. On the contrary, the concentration of Lewis acid sites starts to increase until at about 650–700°C approximately equal numbers of the two types of sites exist. By electron spin resonance studies of adsorbed nitric oxide, Lunsford (*6*) has shown that the maximum spin concentration is observed near 600°C after some dehydroxylation has occurred. Similarly, Hildebrandt and Skala (5) studied the oxidation of adsorbed ammonia as a function of calcination temperature. The concentration of one type of adsorbed ammonia increased from zero at 400°C to a maximum near 600°C, and then declined to a minimum at 750°C: it was considered to be indicative of Bronsted acidity. The concentration of a second type of adsorbed ammonia increased linearly from being zero at 600°C and was attributed to Lewis acidity.

Benesi (*8*) initially reported maximum activity for toluene disproportionation near 600°C. Venuto *et al.* (*7*) showed a similar dependence exists for the ethylene–benzene

---

* Previously presented in part before the Division of Petroleum Chemistry, American Chemical Society, 161st National Meeting, Los Angeles, March 1971.

alkylation reaction. Hopkins (*9*) has shown that the cracking of hexane and heptane pass through a maximum at about 550°C and Hickson and Csicsery (*12*) observed a maximum in the activity for the isomerization of methyl ethyl benzene near 620°C. On the other hand, Turkevich (*10*) studied cumene cracking and *o*-xylene isomerization. He observed constant activity from 350 to 450°C. Higher calcination temperatures caused a rapid activity decline.

Comparison of the results with physical parameters strongly suggests that Bronsted acid sites are necessary for catalytic activity since catalytic activity generally declines rapidly with decreasing Bronsted acidity for calcination temperatures above 600°C. Under these conditions, the dehydroxylation is occurring with the resultant decrease in Bronsted acid sites and increase in Lewis acid sites. Although this broad conclusion is probably justifiable the results are far from conclusive and it is still a matter of controversy as to whether Bronsted acid sites alone, Lewis acid sites, a mixture of the two sites or some uncharacterized sites in the structure are responsible for catalytic activity. It has recently been shown by Pink *et al.* (*13*) that for cyclopropane isomerization over hydrogen Y zeolite, two distinct optimum calcination temperatures are observed near 320 and 660°C. These results indicate that both types of sites can function in this reaction.

Part of the difficulties in interpreting the results arise because (1) the physical and catalytic measurements have not been made on the same samples, (2) measurements have often only been made at 100°C intervals which appears to be insufficient to establish the calcination temperature effects, and (3) complications due to total or partial loss of crystal structure at high temperatures appear to have been neglected.

In order to eliminate some of these uncertainties, a study of the physical and catalytic properties of a magnesium stabilized ammonium Y zeolite have been made. This study eliminates the difficulties of interpretation due to (1) and reduced those due to (2) and (3). Magnesium stabilized zeolites have been shown to be stable up to at least 800°C (*14*).

Experimental

Catalytic Activity Measurements

The catalytic activity for *o*-xylene isomerization was measured as reported previously (*15*) with the exception that the zeolite catalyst was calcined in the reactor at the desired calcination temperature. Conditions were adjusted such that the formation of material analogous to ultrastable Y zeolite was avoided.

Materials

The magnesium ammonium Y was the same as used previously (*14*). It was prepared from a sodium Y zeolite. The starting material had a silica to alumina ratio of 4:9 and a nitrogen surface area (measured at $P/P_0 \approx 0.02$) of 901 m^2g^{-1}. The ammonium form was prepared by repeated exchange of the sodium Y zeolite with a 10% ammonium nitrate solution at 80°C until the residual sodium content was 1%. The zeolite was then washed free of nitrate. The ammonium form was then ion exchanged with sufficient 10% magnesium nitrate solution to yield the magnesium ammonium zeolite containing 2.9% magnesium. X-Ray diffraction and surface area measurements showed the zeolite to be highly crystalline.

Results

The sample studied was shown previously (*14*) to be stable up to at least 800°C. Surface area and crystallinity measurements are tabulated in Table 1 for various calcination temperatures.

The thermal analyses, and the infrared study of the structural hydroxyl groups and acidity, have been presented previously (*14*). The variation of the structural hydroxyl group population and the acidity concentration with calcination temperature are summarized in Figs. 1 and 2.

The percentage conversion of *o*-xylene to *m*- and *p*-xylene as a function of calcination temperature is also shown in Fig. 2.

TABLE 1
SURFACE AREAS AND X-RAY DIFFRACTION PEAK INTENSITIES[a] OF MAGNESIUM AMMONIUM Y ZEOLITES AFTER CALCINATION AT VARIOUS TEMPERATURES

Temperature (°C)	Surface area (m^2g^{-1})	Diffraction peak intensity[a]
300	—	178
410	763	201
470	—	181
510	791	174
570	886	187
600	—	171
620	837	163
660	—	169
740	871	174
800	—	187

[a] Sum of peak heights for (331), (533), (642), and (751, 555) planes.

DISCUSSION

The formation and elimination of structural hydroxyl groups on magnesium ammonium Y zeolite was considered in detail previously (*14*) and is shown in Fig. 1. Briefly it is seen that there are several differences compared to noncation containing ammonium Y zeolite. Firstly, up to 800°C the absorption band near 3737 cm^{-1}, probably due to silanol groups present as impurities, remains constant at a very low level in contrast to the ammonium Y in which it showed a marked increase in intensity above 550°C. This difference is probably a reflection on the much greater structural stability of the magnesium containing zeolite. Secondly, the absorption band near 3560 cm^{-1} decreases constantly from a maximum at 200°C in contrast to the increase, steady state, and decline of the same band in ammonium Y zeolite. The reasons for this difference in behavior are not known. Thirdly, the second strong hydroxyl band is observed at somewhat higher frequency (3660 vs 3640 cm^{-1}). The absorption band reaches a maximum intensity near 425°C, remains constant to 575°C and then decreases rapidly. By comparison, the band at 3640 cm^{-1} on ammonium Y reaches a maximum at 350°, remains constant to 500°C and then rapidly declines. Hence it would appear that the presence of the magnesium ions is influencing the thermal stability of the structural hydroxyl groups as well as improving the structural stability.

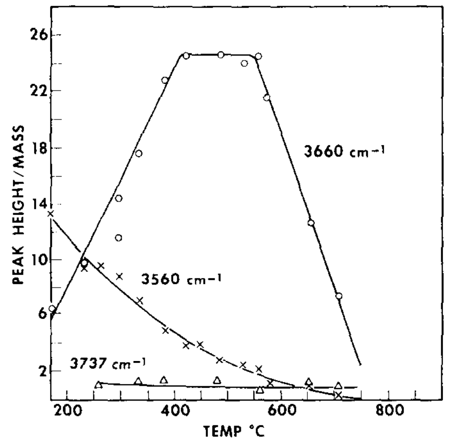

FIG. 1. Hydroxyl group band intensities of magnesium hydrogen Y zeolite as a function of calcination temperature.

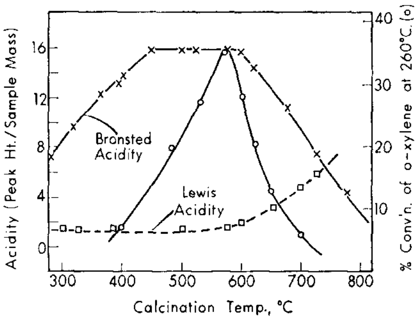

FIG. 2. Acidity and catalytic activity for *o*-xylene isomerization as a function of calcination temperature.

The Bronsted acidity, determined by pyridine chemisorption, shows a similar trend to the 3660 cm^{-1} band reaching a maximum at about 425°C, remaining constant to about 600°C and then declining rapidly. Simultaneously, the Lewis acidity increases rapidly for samples calcined above 600°C. This can be contrasted with the acidity changes of calcined ammonium Y zeolite. The Bronsted acidity reaches a maximum at 325°C, remains constant to 525°C and then declines. The Lewis acidity increases rapidly above 500°C calcination temperatures. Whereas for the magnesium ammonium Y zeolite, the total acidity (Lewis and Bronsted) remained constant, the acidity of the ammonium Y zeolite declined rapidly after calcination above 550°C. This is a further indication of the greater temperature stability of the magnesium zeolite and suggests that the catalytic evaluation of ammonium Y zeolite as a function of calcination temperature may be complicated by the loss of acid sites. The more stable magnesium zeolite avoids this problem.

The catalytic activity is seen, in Fig. 2, to reach a maximum at about 570–580°C calcination temperature. Above this temperature the activity for xylene isomerization falls off rapidly at roughly the same rate as the decline in Bronsted acidity. There appears to be no indication of an increase in catalyst activity with decreasing Bronsted acidity and decreasing hydroxyl group population. In contrast to the ammonium Y zeolite, the catalytic activity starts to decline at somewhat lower temperature than the Bronsted acidity. The results suggest that only certain hydroxyl groups give rise to acid sites of the required strength as previously suggested by Hopkins (*9*). The relationship found between the calcination temperature, catalytic activity and acidity can be interpreted in terms of the influence of calcination temperature on the Bronsted acid sites. In contrast to the ammonium zeolite, there appears to be no need to involve Lewis acid sites or defect sites left by dehydroxylation.

The reason for the discrepancy between the Bronsted acidity and activity curves below 570–80°C calcination temperature is probably due to reasons discussed previously, namely differences in time of activation and ammonia removal from the catalyst during pretreatment for the acidity and activity measurements (*9*, *16*). Furthermore, pyridine is capable of removing adsorbed ammonia from a catalyst surface; hence the acidity measurements would not show the influence of unremoved ammonia (*17*).

In conclusion, investigation of the acidity and catalytic activity of a magnesium ammonium Y zeolite, stable to at least 800°C, shows that the catalytic activity can be interpreted strictly in terms of the Bronsted acidity. This is in marked contrast to ammonium Y zeolite in which appears to be much more complex. However, the conclusions may be confused by structural collapse of the zeolite in the ammonium Y case.

REFERENCES

1. UYTTERHOEVEN, J. B., CHRISTNER, L. G., AND HALL, W. K., *J. Phys. Chem.* **69**, 2117 (1965).

2. ANGELL, C. L., AND SCHAFFER, P. C., *J. Phys. Chem.* **69**, 3463 (1965).

3. HUGHES, T. R., AND WHITE, H. M., *J. Phys. Chem.* **71**, 2192 (1967).

4. WARD, J. W., *J. Catal.* **9**, 225 (1967).

5. HILDERBRANDT, R. A., AND SKALA, H., *J. Catal.* **15**, 300 (1968).

6. LUNSFORD, J. H., *J. Phys. Chem.* **72**, 4163 (1968).

7. VENUTO, P. B., HAMILTON, L. A., LANDIS, P. S., AND WISE, J. J., *J. Catal.* **4**, 81 (1966).

8. BENESI, H. A., *J. Catal.* **8**, 368 (1967).

9. HOPKINS, P. D., *J. Catal.* **12**, 325 (1968).

10. TURKEVICH, J., AND ONO, Y., *Advan. Chem. Ser.* No. 102, 1971

11. TUNG, S. E., AND MCININCH, E., *J. Catal.* **10**, 175 (1968).

12. HICKSON, D. A., AND CSICSERY, S. M., *J. Catal.* **10**, 27 (1968).

13. FLOCKHART, B. D., MCLOUGHLIN, L., AND PINK, R. C., *Chem. Commun.*, 818 (1970).

14. WARD, J. W., *J. Catal.* **11**, 251 (1968).

15. WARD, J. W., AND HANSFORD, R. C., *J. Catal.* **13**, 364 (1969).

16. WARD, J. W., *Amer. Chem. Soc. Div. Petrol. Preprints* **16**, B6 (1971).

17. BASILA, M. R., AND KANTNER, T. R., *J. Phys. Chem.* **71**, 467 (1967).