JOURNAL OF CATALYSIS 116, 279–284 (1989)

NOTES

Base Catalysis by Alkali-Modified Zeolites

II. Nature of the Active Site

INTRODUCTION

The synthesis and partial characterization of alkali-modified X and Y zeolites for use as base catalysts are presented in our accompanying report (*1*). From this work, it is shown that upon impregnation of CsNaX and CsNaY with identical loadings of cesium acetate, the acetone activity (activity of catalyst which manifested in the yield of acetone) of the CsNaY zeolite is an order of magnitude greater than that found for the CsNaX zeolite. Also, the propylene activity of the impregnated CsNaX zeolite is considerably higher than that observed from CsNaY, and as a result yields only a 62% selectivity to acetone. In contrast, virtually no propylene activity is found for the impregnated CsNaY zeolite and thus gives a 97% selectivity to acetone. This dissimilarity in activity between the identically prepared X and Y zeolites is not fully understood as yet. However, this behavior is not uncommon. Rode *et al.* (*2, 3*) observed also a significant difference in activity between identically prepared rhodium X and Y zeolites for hydroformylation. On a surface area basis, the impregnated CsNaY zeolite shows an acetone activity which is comparable to that observed for MgO. This high activity and selectivity for the impregnated CsNaY zeolite are due to a base site formed by the decomposition products of the cesium acetate (*1*).

The purpose of this work is to investigate the nature of the base site formed by the decomposition of cesium acetate in CsNaY.

EXPERIMENTAL

Materials and preparation. The synthesis of NaY and the exchange procedure have been given elsewhere (*1*). Cesium carbonate (99.9%) and isopropanol (99.5%) were obtained from Aldrich. Cesium oxide (Cs_2O) at 99% purity was obtained from AESAR. CO_2 (99.8%) and helium containing 1% CO_2 were obtained from AIRCO and used with no further purification.

Impregnation. In a manner similar to that described in Ref. (*1*) CsOH was impregnated onto silica gel and activated carbon at ~2.0 wt%.

In our accompanying report, strong evidence is provided to suggest that cesium acetate is occluded into CsNaY by leaving the zeolite unrinsed after exchanging NaY with cesium acetate (*1*). Catalysts studied here which have been prepared by this technique will be specified as CsNaY–Ace-UR (unrinsed, acetate-exchanged Y zeolites).

Analysis. ESR spectroscopy was performed on a Varian E3 spectrometer. Samples were heated in helium and sealed in quartz tubes.

Elemental analyses were performed in our laboratories by inductively coupled plasma and atomic absorption spectrometry.

Reactor and procedure. The reactor and procedure used in this work are described elsewhere (*1*), however, a brief description follows. An isopropanol and helium mixture was contacted with the catalyst in a fixed bed microreactor at 350°C and atmospheric pressure. Reaction products were analyzed by an on-line gas chromatograph. For partial pressures of CO_2 below 0.16 Torr, helium containing 1% CO_2 was introduced into the feed. For experiments requiring a partial pressure of 5 Torr, CO_2 (99.8%) was used. In both cases, the carrier

0021-9517/89 $3.00

gas (helium) was reduced to maintain a constant partial pressure of isopropanol.

RESULTS AND DISCUSSION

Several candidates for the active site generated by the decomposition of the cesium acetate in CsNaY are considered in this investigation. They are cesium metal, carbonate, hydroxide, and oxide. It should be noted that both the acetone and the propylene activities of the CsNaY–Ace-UR zeolite are always highest at initial reaction times (see for example Ref. (*1*, Fig. 5)). We, therefore, assume that after calcination the active site is present before the onset of the reaction and is not formed as a result of contact with the reaction environment.

Cesium metal. Sodium clusters in large pore zeolites were recently investigated by Martens *et al.* (*4*) by *in situ* ESR and IR spectroscopy. They suggested that framework oxygen anions in the neighborhood of neutral sodium clusters were the active base site. Wood *et al* (*5*) investigated the decomposition of Cs_2CO_3 by Knudsen cell mass spectroscopy and observed cesium metal in the vapor phase. Garces *et al.* (*6*) postulated that similar behavior should be observed with KNaX, RbNaX, and CsNaX, and, in fact, detected K, Rb, and Cs metal vapor over these materials at temperatures above 327°C. In light of these observations, it seems plausible that cesium metal could form upon calcination of our impregnated CsNaY zeolite and may, therefore, promote the base-catalyzed dehydrogenation of isopropanol.

To investigate the formation of cesium metal upon calcination of the modified CsNaY zeolite, ESR spectroscopy was employed. The CsNaY catalyst, impregnated at ~2.0 cesium acetate molecules per unit cell (~2.4 wt%), was calcined at 550°C in helium. The sample temperature was then lowered to 77 K for ESR analysis. Blazey *et al.* (*7*) studied alkali clusters in zeolites X and Y and concluded that these clusters are chemically stable at room temperature. Therefore, any clusters formed upon calcination in this study were expected to remain during the cooling for ESR analysis. No ESR signals were detected that could be assigned to either cesium metal or ionic clusters (*7*, *8*). From this result, we exclude cesium metal or charged clusters as the active site for isopropanol dehydrogenation.

Cesium carbonate. Using infrared spectroscopy, carbonates have been identified on alkali-exchanged X zeolites (*9*, *10*). We observed carbonates on our CsNaY–Ace-UR zeolite as well (*1*). To investigate the potential of the carbonate ions as the active species for the catalytic decomposition of isopropanol, bulk cesium carbonate was employed. Cesium carbonate ($99^{+}\%$) was loaded into the reactor, heated to 350°C in flowing helium, and subjected to the reactant flow specified earlier (*1*). Only trace acetone was detected and no propylene was observed. To further analyze for the presence of carbonates after calcination an IR spectrum of the CsNaY–Ace-UR zeolite was recorded at 550°C in air using an *in situ* cell. No bands assignable to carbonate species were observed. Note that calcined (550°C) CsNaY–Ace-UR zeolite is active for acetone formation showing that the active site is present after calcination at 550°C. In light of these results, we exclude cesium carbonate as the active site.

Cesium hydroxide. From our previous activity results (*1*), both the unrinsed cesium acetate- and the hydroxide-exchanged Y zeolites showed higher activities than their rinsed analogs. Furthermore, strong evidence is given to suggest that unrinsed samples contain occluded alkali salts (*1*). One can speculate that the acetate and hydroxide in the unrinsed CsNaY zeolite are converted to an identical base site. An alternative explanation could be that the occluded cesium acetate may decompose to form a hydroxide and, therefore, show similar activity.

If CsOH in the CsNaY zeolite remains intact and serves as the active site, then we might expect supported hydroxide to be catalytically active in the decomposition of isopropanol. Therefore, cesium hydroxide was impregnated into both silica gel and activated carbon at ~2.0 wt%. Both catalysts were first calcined at 450°C in helium and then subjected to start-up procedure 1 of Ref. (*1*) for reaction rate measurements. No activity was observed from the silica-supported cesium and only trace acetone activity was found from the carbon-supported cesium. Although we cannot exclude the possibility that the CsOH supported on silica and carbon decomposes during calcination or exposure to the reaction environment, we expect similar catalytic activity on the zeolite, silica, and carbon if CsOH acts as the active site. Therefore, at this time we do not believe that CsOH is the active site.

Cesium oxide. We now discuss the possibility that upon decomposition of the cesium acetate, a cesium oxide forms. A first step is to simply test the catalytic properties of cesium oxide denoted Cs_xO_y for isopropanol decomposition. Because water readily reacts with Cs_xO_y to form CsOH, all efforts were made to minimize any exposure to water vapor prior to loading the reactor. Therefore, Cs_xO_y crystals were ground to a fine powder in a glove box. The powder was quickly transferred into the reactor which was purging with helium. The reactor temperature was then elevated from room temperature to 350°C at ~4°C/min. At 350°C the oxide was subjected to the reaction environment as before (*1*) and F/W at 0.98 mol isopropanol · h^{-1} · g^{-1}. The initial yield of acetone from Cs_xO_y was 3.6% but slowly fell to 0.5% over 3 h. Propylene activity was detectable at 5 min, but fell below the detection limits as the reaction proceeded. The selectivity to acetone 5 min into the reaction was 99.1%. In light of these results, two points are brought to the readers attention. First, the selectivity to acetone for CsNaY impregnated with ~2.0 cesium acetate molecules per unit cell is 97.4%. Second, the CsNaY–Ace-UR zeolite has very high initial activity, but also slowly falls to lower levels of conversion (Fig. 1). Owing to the similarity in both the start-up kinetics and the high selectivity, it would appear that cesium oxide is a likely candidate for the active site formed by the decomposition of cesium acetate in CsNaY.

The decline in activity for the CsNaY–Ace-UR zeolite and Cs_xO_y is consistent with the behavior of other oxides as well.

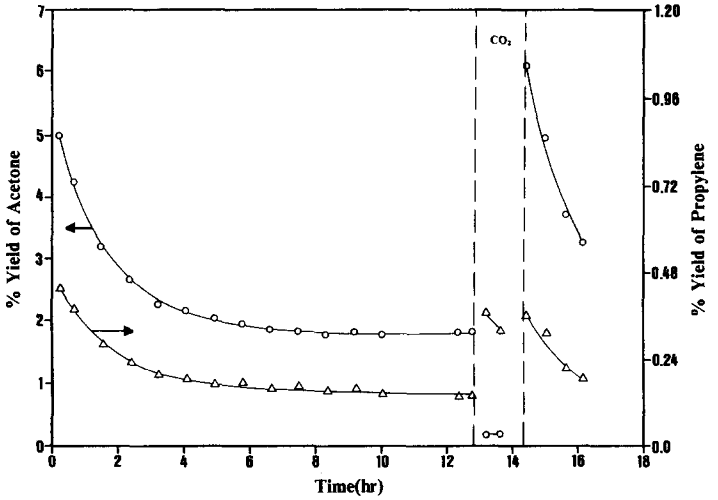

FIG. 1. Effect of CO_2 contact on activity of the CsNaY–Ace-UR zeolite. ○, acetone; △, propylene. F/W = 2.41 mol isopropanol · h^{-1} · g, temperature = 350°C, total pressure = 1 atm, and partial pressure of isopropanol = 152 Torr (STP). Start-up procedure 2.

Several factors are attributed to the loss in activity such as site blockage by carbonate formation (*11*) or a reduction of the oxide surface by dehydroxylation (*12*). Another factor which could compliment site blockage or reduction could be a change in the order of the kinetics with site loss. Akiba *et al.* (*13*) showed that over ZnO, the initial isopropanol kinetics were second order but as the reaction proceeded, the kinetics convert to first order thus lowering activity. For the CsNaY–Ace-UR zeolite, the exact loss in activity is not clear. However, from our studies involving CO_2, a consumption of the active site by the reaction environment could explain the observed loss. As illustrated in Fig. 1, we see that when the CsNaY–Ace-UR zeolite is contacted with CO_2, the base activity is quenched. However, upon removal of CO_2 from the feed, the high activity observed at initial times is reestablished suggesting that the active base site is regenerated. Promotion of the base activity by CO_2 contact was also shown to occur in the synthesis of methanol over Cu/ZnO (*14*). In that study, Klier *et al.* suggested that CO_2 may act as an oxidizing agent which oxidizes sites reduced by the reaction environment. CO_2 was also reported to reactivate the activity for methane coupling over Li/MgO (*15*). Korf *et al.* suggested that the lithium reacts with the CO_2 to form a carbonate which then decomposed to the active site.

Further evidence which supports the case for cesium oxide as the active site is provided by the activity data obtained with the different calcination atmospheres (*1*). The CsNaY–Ace-UR zeolite was calcined in both an oxygen (99.5%) and a helium (99.995%) atmosphere at 500°C to investigate the effect of O_2 on the decomposition of the cesium acetate. By exposing the CsNaY–Ace-UR zeolite to such an oxidizing atmosphere we expect an oxide to result from the decomposition of the cesium acetate. The results listed in Table 2D of Ref. (*1*) show that the catalytic activity for formation of acetone and propylene is, in fact, higher when the catalyst is calcined in oxygen as opposed to helium. However, the calcination atmosphere has little effect on selectivity which may suggest that the cesium acetate decomposition products are similar for both atmospheres, but the oxygen atmosphere is more effective in generating the active site.

Another characteristic of metal oxides is their ability to dehydrate alcohols over base sites. It has been shown that alcohols can dissociatively adsorb on metal oxides to form alkoxides (*16–18*). These alkoxides have been suggested to decompose further to form dehydrogenation products (ketones/aldehydes) or dehydration products (olefins) (*12, 19–22*). We might, therefore, expect the loss in acetone activity to be paralleled by a loss in propylene activity if, in fact, an alkoxide is the reaction intermediate. Figure 1 shows the acetone and propylene activity before and after CO_2 contact. The results show that the high acetone activity is paralleled by the propylene activity both before and after CO_2 contact. Furthermore, the selectivity to acetone before and after CO_2 contact never deviated more than 0.43 and 0.18%, respectively.

If it is assumed that a propoxide intermediate exists on the CsNaY–Ace-UR zeolite during the reaction, then both the acetone and the propylene activities could possibly be poisoned by an electrophilic adsorbate. MgO, which was suggested to adsorb alcohols dissociatively to form alkoxides (*17, 19, 23*), was contacted with CO_2 at a partial pressure of *ca.* 5 Torr in an attempt to poison both the acetone and the propylene activities. As illustrated in Fig. 2, both the acetone and the propylene activities of MgO are poisoned upon exposure to CO_2. With removal of the CO_2 from the feed stream, the acetone and propylene activities recover immediately to their steady-state activities. For the CsNaY–Ace-UR zeolite (Fig. 1), the acetone activity was suppressed upon CO_2 contact; however, the propylene activity was promoted. This promotion in propylene activity upon CO_2

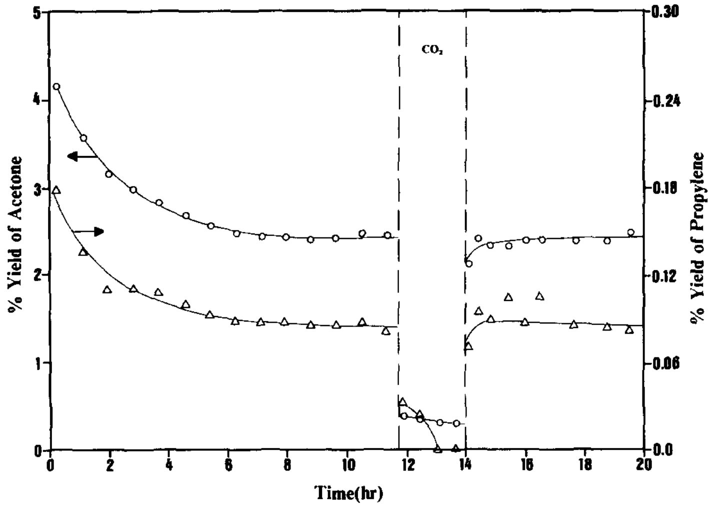

FIG. 2. Effect of CO_2 contact on activity of MgO. ○, acetone; △, propylene. $F/W = 1.07$ mol isopropanol · h^{-1} · g^{-1}, temperature = 350°C, total pressure = 1 atm, and partial pressure of isopropanol = 152 Torr (STP). Start-up procedure 2.

contact has been observed elsewhere (*24–26*). Frilette and Munns (*24*) showed that the propylene activity over NaX increases with increasing partial pressures of CO_2. Mirodatos *et al.* (*25, 26*) suggested from infrared studies on various forms of zeolite Y that CO_2 reacts with hydroxylated divalent cations to form carbonate species and new acidic H^+ sites. Therefore, the possibility exists that any loss in propylene activity associated with the poisoning of a propoxide intermediate via CO_2 could be overshadowed by other types of promotion in propylene activity. In an attempt to circumvent this problem, very low partial pressures of CO_2 were used in order to minimize the possible promotion of propylene activity. Thus, any loss in propylene activity associated with the propoxide decomposition could more likely be observed. Figure 3 shows that with increasing partial pressures of CO_2 both the acetone and the propylene activities are suppressed. Selectivity remained at 96.8 ± 0.18% for P/Po below 11×10^{-5} suggesting that some of the observed propylene activity was resulting from a propoxide intermediate.

CONCLUSIONS

From the results presented in this work, it appears that the active site formed by the decomposition of the cesium acetate in CsNaY is cesium oxide. No evidence is found to suggest that after calcination the final decomposition products of cesium acetate are cesium metal, carbonate, or hy-

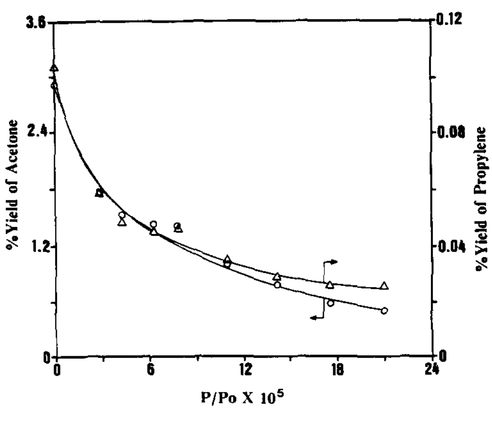

FIG. 3. Effect of CO_2 contact at low partial pressures of CO_2 on activity of the CsNaY–Ace–UR zeolite. ○, acetone; △, propylene. $F/W = 6.53$ mol isopropanol · h^{-1} · g^{-1}, temperature = 350°C, total pressure = 1 atm, and partial pressure of isopropanol = 152 Torr (STP).

droxide. The results also suggest that a portion of the propylene activity may be resulting from a propoxide intermediate.

ACKNOWLEDGMENTS

Financial support for this project is provided by the National Science Foundation and the Dow Chemical Co. under the Presidential Young Investigator Award to M.E.D. We thank Dr. Steve Suib of the University of Connecticut for the ESR experiments.

REFERENCES

1. Hathaway, P. E., and Davis, M. E., *J. Catal.* **116,** in press.

2. Rode, E. J., Davis, M. E., and Hanson, B. E., *J. Catal.* **96,** 563 (1985).

3. Rode, E. J., Davis, M. E., and Hanson, B. E., *J. Catal.* **96,** 574 (1985).

4. Martens, L. R., Vermeiren, W. J., Huybrechts, D. R., Grobet, P. J. and Jacobs, P. A., "Proceedings of the 9th International Congress on Catalysis Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.) Vol 1, p. 420. The Chemical Institute of Canada, Ottawa, 1988.

5. Wood, B. J., Brittain, R. D., and Lau, K. H., *Amer. Chem. Soc., Div. Fuel Chem.* **28**(1), 55 (1983).

6. Garces, J. M., Vrieland, G. E., Bates, S. I., and Scheidt, F. M. *in* "Catalysis by Acids and Bases" (B. Imelik *et al.*, Eds.), Vol. 20, p. 67. Elsevier, Amsterdam, 1985.

7. Blazey, K. W., Muller, K. A., Blatter, F., and Schumacher, E., *Europhys. Lett.* **4**(7), 857 (1987).

8. Smeulders, J. B. A. F., Hefni, M. A., Klaassen, A. A. K., de Boer, E., Westphal, U., and Geismar, G., *Zeolite* **7**(4), 347 (1987).

9. King, S. T., and Garces, J. M., *J. Catal.* **104,** 59 (1987).

10. Bertsch, L., and Habgood, H. W., *J. Phys. Chem.* **67,** 1621 (1963).

11. Cunningham, J., and Hodnett, B. K., *J. Chem. Soc. Faraday Trans. 1* **77,** 2777 (1981).

12. Kim, K. S., Barteau, M. A., and Farneth, W. E., *Langmuir* **4,** 533 (1988).

13. Akiba, E., Mitsuyuki, S., Takaharu, O., and Tamaru, K., *Z. Phys. Chem.* **119,** 103 (1980).

14. Klier, K., Chatikavanij, V., Herman, R. G., and Simmons, G. W., *J. Catal.* **74,** 343 (1982).

15. Korf, S. J., Roos, J. A., de Bruijn, N. A., van Ommen, J. G., and Ross, J. R. H., *J. Chem. Soc., Chem. Commun.,* 1433 (1987).

16. Zaki, M. I., and Sheppard, N., *J. Catal.* **80,** 114 (1983).

17. Miyata, H., Wakamiya, M., and Kubokawa, Y., *J. Catal.* **34** 117 (1974).

18. Koga, O., Onishi, T., and Tamaru, K., *J. Chem. Soc. Faraday Trans. 1* **76,** 19 (1980).

19. Parrott, S. L., Rodgers, J. W., Jr., and White, J. M., *Appl. Surf. Sci.* **1,** 443 (1978).

20. Bowker, M., Petts, R. W., and Waugh, K. C., *J. Chem. Soc. Faraday Trans. 1* **81,** 3073 (1985).

21. Bowker, M., Petts, R. W., and Waugh, K. C., *J. Catal.* **99,** 53 (1986).

22. Waugh, K. C., Bowker, M., Petts, R. W., Vandervell, H. D., and O'Malley, J., *Appl. Catal.* **25,** 121 (1986).

23. Martinez, R., and Barteau, M. A., *Langmuir* **1**(6), 684 (1985).

24. Frilette, V. J., and Munns, G. W., Jr., *J. Catal.* **4,** 504 (1965).

25. Mirodatos, C., Pichat, P., and Barthomeuf, D., *J. Phys. Chem.* **80**(12), 1335 (1976).

26. Mirodatos, C., Kais, A. A., Vedrine, J. C., Pichat, P., and Barthomeuf, D., *J. Phys. Chem.* **80**(21), 2366 (1976).

PAUL E. HATHAWAY
MARK E. DAVIS[1]

Department of Chemical Engineering
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Received June 12, 1988; revised September 27, 1988

---

[1] To whom correspondence should be addressed.