CHAPTER 4

DISCUSSION AND CONCLUSION

SYNTHESIS, CHARACTERIZATION, AND BASE CATALYSIS OF NOVEL ZEOLITE SUPPORTED SUPER—BASIC MATERIALS

4.1 Discussion

Extensive characterization of the alkali—metal azide impregnated zeolites confirms the presence of the azide species within the pores of the zeolite. Results of FTIR analysis indicate that only a small portion of the azide species remains on the surface of the zeolite. The majority of the azide species is partitioned between the supercages and sodalite cages of the zeolite, which is consistent with other studies.[1-3] High speed, solid-state ^{23}Na MAS NMR spectra reveal the presence of five cation sites in dehydrated NaX which are assigned according to previous reports.[4-7] Simulation of the spectra confirms the site assignment and determines the distribution of cations at the crystallographic locations I (6.6%), I' (27.5%), II (32.2%) and III (34.2%).

Upon the addition of sodium azide to the system, a redistribution of cation sites is observed at the expense of sites I', II, and III'(1,2). The redistribution becomes more severe as more azide species is loaded into the zeolite. The addition of azide to the catalyst does not significantly affect the intensity of the NMR signal, precluding removal of free cations to NMR silent ionic clusters.[8-12] Redistribution of cation sites may only occur if the azide species are located within the pores of the zeolite, as indicated the results of FTIR investigations. Thus, the results of ^{23}Na 1D MAS NMR confirm the presence of the azide species within the zeolite pores.

The presence of azide within the pores is further verified by the results of ^{23}Na 2D MQMAS NMR. Spectra taken for dehydrated NaX show distinct and easily discernible spin-spin interactions of the sodium cations, indicating that the cation sites are well defined and relatively isolated from each other. The addition of azide to the zeolite results in a collapse of the discernible spin-spin interactions. The collapse of discernible spin-spin interactions becomes more severe as azide loading is increased, consistent with studies indicating that cation location and clustering is sensitive to guest species.[4,7,13,14] Thus, ^{23}Na 2D MQMAS NMR demonstrates that the azide species affects cations within the pores of the zeolite and therefore must be present in the pores. Furthermore, no phase separation is noted following the impregnation of zeolites with alkali azide species and the results of TGA analysis confirm the expected amount of azide is present in the zeolite following synthesis.

Thus, the results from observations during synthesis, FTIR, and ^{23}Na NMR indicate that the lack of reproducible catalytic activity cannot be due to the absence of azide species or localization of the azide species to the surface of the zeolite following synthesis. Additionally, catalytic activity of these materials with azide loadings identical to, or lower than, those investigated here has been observed for 1-butene isomerization,[3,15-18] ethylation of *o*-xylene and toluene,[15-17] and alkenylation of *o*-xylene.[17,19] Therefore, insufficient azide loading is not the cause of poor activity in the catalyst system.

Small variations in the synthesis of the catalytic materials cannot explain the lack of reproducible activity. Although calcination of sodium X zeolite to remove trace contaminants prior to ion exchange can be perfomed,[3,16,20] no difference to the reactivity of

the catalyst system was observed following calcination in this study. Hence, the lack of catalytic activity is not due to the presence of trace organics during thermal activation of the catalyst. The distribution and identity of cations within the zeolite prior to the introduction of an alkali—metal is responsible for the type and size of resulting metal clusters.[8,9,21-24] Furthermore, the distribution of cations is affected by the level of hydration of the catalyst.[25] Therefore, prior to impregnation with alkali—metal azides, ion exchanged azides were aged at various temperatures, dehydrated, aged and then dehydrated, or not treated in any way. Azides were impregnated in a methanolic or aqueous solution. Following alkali azide impregnation, the catalysts were used as made or aged further at various temperatures allowing further cation redistribution. Despite these attempts to affect formation of the active metal centers prior to thermal decomposition of the azide, no active catalyst was found. Thus, consistent with results of FTIR and ^{23}Na NMR, the method of alkali—metal azide impregnation is not responsible for the lack of reproducible catalytic activity.

Variation of the activation procedure does not result in materials which are catalytically active. Results of FTIR and TGA analyses demonstrate that alkali—metal azides are slowly decomposed within the zeolite, and removed beyond detection by FTIR by 700^{o}C. The azide species are still visible, although partially decomposed, by 400^{o}C. Absorption bands characteristic of N-O species are detected by FTIR after thermal decomposition of the alkali—metal azides for 10 hours at 550^{o}C under helium, but these bands were rendered undetectable by thermal treatment to 700^{o}C. Other studies suggest that N-O species anchor metallic clusters within the zeolite pores and impart thermal stability to the metallic clusters.[4,7,12,14,25] However, variations in the temperature of

activation to adjust the ratio of N-O species to azide species present in the catalyst after thermal decomposition did not result in the production of active materials for any of the catalyst precursors. Annealing time spent at the final activation temperature can also affect the cation and metal center distribution due to the high level of cation mobility in zeolite X at elevated temperature,[13,25] and the ability of cations and metallic clusters to interact by electron transfer to form alloys.[11,26] Variations in annealing time, however, also failed to produce a catalytically active material. Thus, the inactivity of the catalysts investigated cannot be due to the effects of thermal treatment during activation.

Reactive conditions for 1-butene isomerization, ethylation of *o*-xylene, and alkenylation of *o*-xylene were varied slightly around those adapted from the literature.[15-17,19,27] Neither eliminating the possibility of catalyst leaching nor improving diffusion to the catalyst by performing reactions in the gas—phase improved the catalytic activity of the materials. Aside from the slight reactivity noted for both the gas phase ethylation of *o*-xylene and the semi—batch alkenylation of *o*-xylene over thermally activated (4)NaN_3/NaX, no improvement in activity was observed following variations made to flow rate and reactive flow ratios. Furthermore, the weakly basic alkali acetate impregnated materials were active for 1-butene isomerization, whereas the alkali azide impregnated materials were not active. Thus, the variations in reaction parameters are not the cause of irreproducible catalytic activity

The discussion presented thus far indicates that impregnation of azide into the zeolite, alkali azide loading, synthesis procedure, activation, and reaction parameters cannot explain the absence of catalytic activity for the alkali azide loaded materials. The only remaining possibility is that the active site is either not consistently created or

inaccessible to the reactants. Slight activity was noted for the ethylation of *o*-xylene in the gas phase and the semi—batch alkenylation of *o*-xylene indicating that when the active sites are formed, they are accessible. In the case of semi—batch reaction, the active sites were most likely leached into the solution rather than anchored on the zeolite host. The rapid decrease in ethylation activity in the gas—phase suggests that the active site is quickly deactivated or rendered inaccessible by coking when it is immobilized within the zeolite pore structure. This assertion is supported by the presence of C-H bending vibrations in the FTIR spectra of the catalyst recovered following catalytic reaction. The initial activity observed for the catalytically active material was very low and could not be reproduced in other catalysts. Hence, despite accessibility of the active sites for a short time for a select few catalysts, the active site of the catalyst must not be formed consistently.

The active site in the azide system has been shown to be framework oxygen in the vicinity of neutral metallic clusters located in the supercages of the zeolite.[16] The metallic centers coexist with ionic clusters which can be formed in the sodalite cages[8,9,12,16,18,28] or supercages[8,9,22,29-31] of zeolite X. The type and number of ionic clusters can be manipulated by the identity of guest alkali—metals, the Si/Al ratio of the zeolite, and the method of thermal activation.[8,9,20-24] Neutral metallic clusters resulting from the thermal decomposition of alkali—metal azides have been identified by NMR in faujasite.[2,26,32] However, characterization of the catalytic materials prepared in this study both during and after thermal decomposition suggests that neutral metallic clusters are not consistently formed. Although FTIR and TGA show the presence of N-O anchoring species for neutral metallic clusters following thermal activation at 550^{o}C, no Knight shift of metallic clusters

or alloys was ever observed by ^{23}Na MAS NMR. It follows that a metallic center was never formed, or formed at such a low level as to be undetectable by NMR and reaction. The trace catalytic activity observed for (4)NaN_3/NaX indicates that metallic clusters were likely formed in some of the materials, but in extremely small quantities. The intensity of ^{23}Na 1D MAS NMR spectra before and after thermal treatment of (4)NaN_3/NaX do not show a significant change in the number of cations present within the zeolite. Therefore, decomposition of the alkali—metal azide precursors must not result in a significant amount of silent ionic clusters or neutral metallic clusters. Electron paramagnetic resonance experiments designed to verify the presence of NMR silent ionic clusters were confounded by the presence of iron in the sample. However, the formation of ionic clusters during the decomposition of zeolite supported alkali—metal azides is well documented.[3,9,15-20] Thus, the lack of activity in the investigated catalysts system is explained by the inadequate formation of neutral metallic clusters combined with the possible formation of inactive ionic clusters in the zeolite during activation.

The difficulty of working with supported alkali—metals has been discussed elsewhere.[16,18,33] Alkenylation of *o*-xylene with 1,3-butadiene reported by Doskocil et al. in the semi—batch phase was coupled with a bright red solution the authors attributed to organo—alkali species[17,19] consistent with the mechanism proposed by Eberhardt.[34] The slightly active material (4)NaN_3/NaX in this study also exhibited a light red solution during alkenylation. Hence, even when an active catalyst can be synthesized, activity in semi—batch phase is the result of leaching of the active metallic centers by the reactive mixture rather than controlled catalysis within the pores of the zeolite. When the reaction was attempted in the gas phase with the same catalyst, reproducible activity was not observed.

Furthermore, no additional reports of alkenylation or ethylation of *o*-xylene in zeolite supported thermally decomposed alkali—metal azides have been made since the work of Davis and co-workers.[17,19] Therefore, the alkali azide impregnation of zeolites followed by thermal decomposition is not a reliable method towards the synthesis of active zeolite supported super-basic catalysts.

4.2 Conclusions

Despite literature precedent for the alkenylation of *o*-xylene to 5-OTP over catalytic materials formed by the thermal decomposition of alkali—metal azides in zeolite X,[17,19] no reproducible activity over a similar system is observed in the present study. Furthermore, the activity towards alkenylation of *o*-xylene in the semi—batch reaction reported in the literature is attributed to leaching of metallic centers from the catalytic material rather than the formation of a novel super-basic zeolite supported catalyst.[17,19] No reports of alkenylation of *o*-xylene with 1,3-butadiene have been made since this initial report. Other studies, however, have shown that similar catalytic materials promote the base catalyzed reactions of 1-butene isomerization, alkylation of toluene with methanol, and ethylation of toluene and *o*-xylene in the gas phase.[15-20] Despite this, eliminating the possibly of metallic center leaching by reaction in the gas phase failed to produce an active catalyst for alkenylation. Additionally, the isomerization of 1-butene and ethylation of toluene or *o*-xylene could not be reliably reproduced in the current study. The isomerization of 1-butene did give the expected results when performed over alkali-oxide containing catalysts.

Incorporation of the alkali azide precursor into the zeolite pores was confirmed by the results of FTIR, TGA and solid-state ^{23}Na MAS and MQMAS NMR investigation. The results of high speed ^{23}Na MAS NMR showed that incorporation of the alkali azide precursor into the zeolite causes a redistribution of sodium cations within the zeolite pores. During thermal activation, the peak area of the ^{23}Na 1D MAS NMR spectra is not significantly altered and no evidence of metallic clusters is found by monitoring the Knight shift of sodium. Thus, thermal activation of the catalytic materials does not result in the formation of appreciable neutral metallic clusters. The lack of reproducible catalytic activity is therefore attributed to failure of the material to produce neutral metallic clusters during thermal decomposition of the azide precursor, possibly due to the preferential formation of inactive, NMR silent ionic clusters.

Based on the fact that cluster formation is influenced by cation distribution within the zeolite pores and that cation distribution is affected by guest molecules, temperature, and level of hydration,[4,7-9,13,14,21-25] attempts to encourage the production of neutral metallic clusters during thermal decomposition were made. Prior to alkali azide precursor impregnation, alkali exchanged zeolite X was dehydrated, aged at temperatures conducive to cation migration, aged and dehydrated, or not treated at all. In all cases, no improvement of catalytic activity was observed. Additionally, modification of cation distribution and azide location was attempted by both methanolic and aqueous impregnation of the alkali—metal azide precursor. Again, no improvement in catalytic activity was observed. The catalysts were either used as synthesized or were aged further to allow cation redistribution prior to thermal activation and reaction. These treatments also failed to improve the catalytic activity of

the samples. Finally, the distribution of cations and their interaction with guest metals in the pore is affected by the final temperature and annealing time during activation.[11,13,25,26] Variations in these parameters also failed to improve catalytic activity. It is concluded that the use of alkali—metal azides as precursors to metallic centers in faujasite is not a reliable route towards an active super—basic zeolite supported catalyst and that the formation of an active center in the materials is very insensitive to synthesis and activation technique.

Although the impregnation of alkali azide precursors within the pores of zeolite X is easily accomplished, the thermal decomposition of the precursor species to create an active zeolite supported base catalyst is problematic. Neutral metallic clusters, required for an active catalyst, are not reliably formed within the zeolite pores. Furthermore, the formation of neutral metallic clusters is proven to be very insensitive to standard synthesis techniques. Additionally, when active neutral metallic clusters are formed, catalytic activity decreases rapidly with time on stream due to coke formation. Activated catalytic materials are air and moisture sensitive and require careful handling to prevent deactivation. Thus, despite the reports of basic activity over thermally decomposed alkali—metal azides supported in faujasite, this system is not ideal for further investigation as a route to a reliable super-basic zeolite supported catalyst. Furthermore, when leaching of the active metallic species by solution is eliminated by gas—phase reaction, evidence in this report suggests that the active sites in the catalysts may be rendered inaccessible by rapid coke formation on the surface of the catalyst. Thus, even if a successful method for the occlusion of metallic clusters in zeolite X is

developed from the alkali—metal azide precursor system, its use will be severely limited by coking of the catalyst during reaction.

4.3 References

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