

CHAPTER 8

SUMMARY AND CONCLUSIONS

This thesis was written based on work from two separate and unrelated projects. In the first part of the thesis, the synthesis and characterization of alkali azide occluded zeolites was investigated as a route towards a novel zeolite supported super—basic material capable of carbon—carbon additions of olefins to alkyl—aromatics. Combining the shape selectivity of a zeolite support with the product profiles available to base catalyzed reactions would be of great use in fine chemical syntheses and greatly improve the economics for the production of polyethylene naphthalate, a high performance thermoplastic polyester currently limited to specialty applications due to its high manufacturing cost.

Precursor materials were prepared by impregnation of alkali—metal azides into the pores of alkali exchanged zeolite X. It was believed that depending on the choices of alkali—metal azide precursor and alkali exchange cations in the zeolite, neutral alkali—metal clusters or mixed alkali—metal alloys could be formed during thermal treatment of the materials. Characterization by FTIR showed a splitting of the azide stretching vibration when the alkali—metal azides were occluded within the zeolite pores, indicating successful inclusion of the azide precursors. The results of high speed, solid—state ^{23}Na 1D MAS, and 2D MQMAS NMR verified that the azides were indeed occluded within the pores of the zeolite. Simulation of the 1D spectrum of sodium exchanged zeolite X allowed the exchange cations to be assigned to crystallographic locations within the zeolite and their

distribution among the sites to be determined. It was shown that azide loading caused a redistribution of cation sites which became more severe as azide loading was increased. Redistribution of the cations upon azide impregnation was confirmed by the results of ^{23}Na 2D MQMAS spectra which showed a decrease in the number of discernible spin—spin interactions. Thermal activation of the materials resulted in further cation redistribution. No evidence of neutral metallic clusters could be found by NMR techniques. Instead, it is possible that a small number of inactive, NMR silent ionic clusters were formed.

Thermally treated materials were tested for their ability to promote the base catalyzed semi—batch alkenylation of *o*-xylene with 1,3-butadiene, the gas—phase alkenylation and ethylation of *o*-xylene, and the gas—phase isomerization of 1-butene to *cis*- and *trans*-2-butene. Trace catalytic activity was observed for the alkenylation of *o*-xylene with 1,3-butadiene in the semi—batch phase over the material $(4)\text{NaN}_3/\text{NaX}$, but could not be reproduced. The same catalyst was not able to catalyze the alkenylation of *o*-xylene with 1,3-butadiene in the gas phase, but did show trace activity for the less rigorous reaction of *o*-xylene and ethylene. Again, this reactivity could not be reproduced across catalyst batches. The thermally decomposed alkali azide containing materials were also not able to catalyze the fairly non-demanding isomerization of 1-butene. Controls of alkal—metal oxides occluded in zeolite X were able to catalyze the reaction with a strong selectivity to *cis*-2-butene, indicating a base catalyzed reaction.

The combined results of characterization and reactivity studies demonstrated that the active site of the catalyst was not consistently formed during thermal decomposition of the azide. An insufficient number of neutral metallic clusters characteristic of active catalysts reported in the literature were formed. It was hypothesized that inactive NMR

silent alkali—metal ionic clusters may also have been formed. Numerous attempts to encourage the formation of neutral metallic clusters by synthesis and activation techniques did not result in an active catalyst. Thus, it was concluded that using the thermal decomposition of alkali—metal azides impregnated into zeolite X is not a robust method for the creation of a novel zeolite supported super-basic material.

The second part of this thesis examined the use of partially reduced heteropolyanions for the oxidative dehydrogenation of ethane to ethylene and acetic acid at atmospheric pressure. The activity of these catalysts towards the oxidation of ethylene and ethanol was also examined. It was found that following thermal activation at 420°C, the materials NbPMo₁₁VPyr and NbPMo₁₂Pyr were able to catalyze the oxidation of ethane to ethylene and acetic acid in yields comparable to those reported in the literature for the most active mixed metal oxide ethane oxidation catalysts. Both catalysts were also extremely active for the oxidation of ethylene to acetic acid. Unlike other mixed metal oxides reported in the literature, the presence of vanadium is not required for an active material. Instead, the presence of vanadium in the catalytic material inhibits both conversion and selectivity in the oxidation of ethane. The presence of niobium, in tandem with pyridine, greatly enhances the activity and selectivity of ethane oxidation. The transition metals iron, gallium, and antimony were not able to reproduce the beneficial effect of niobium in the catalytic materials.

Variations of niobium loading in Nb_xPMo₁₂Pyr showed that while niobium is required for active ethane oxidation catalysts, activity and yield to ethylene and acetic acid were not linear functions of Nb/P. When the data from Nb/P experiments were plotted as selectivity versus conversion, a linear relationship was obtained suggesting that niobium

modifies the active center in balance with another factor which is related to the amount of niobium present. Variations in the reduction potential of the catalysts based on niobium loading could not explain the observed reactivity pattern, most likely due to the strong reduction of the catalyst affected by the desorption of pyridine during thermal activation. However, exchanged niobium replaces exchanged protons in the catalyst during synthesis, and is therefore believed to affect the acidity of the thermally activated catalytic material. Thus, it was concluded that the active site for ethane oxidation is molybdenum in the presence of niobium balanced by acid sites. Similar studies for the oxidation of ethylene showed that niobium is directly involved in the oxidation of ethylene to acetic acid. Niobium also improves the selectivity to acetic acid during ethanol oxidation.

The effect of steam was investigated by varying the partial pressure of steam present during the oxidation of ethane or ethylene. During the oxidation of ethane, increased steam pressure resulted in increased selectivities to ethylene and acetic acid. Conversion, however, passed through a maximum when steam comprised 33% of the total feed to the reactor. Since water is a product of ethane dehydrogenation to ethylene, these studies were repeated for the oxidation of ethylene. It was shown that both activity and selectivity continued to increase with increasing steam feed during ethylene oxidation. Hence, it was concluded that the maximum in conversion observed in the results of ethane oxidation was due to competitive adsorption of steam, ethane, and acetic acid on the surface of the catalyst. Steam studies during ethylene oxidation also suggested that steam aids in the desorption acetic acid from the surface of the catalyst thereby reducing the production of carbon oxides.

It is believed that the formation of ethylene and acetic acid is facilitated by an ethoxy intermediate rather than a surface ethyl group. This result is consistent with temperature studies showing that the production of ethylene, which occurs through β -H elimination, is increased with increased temperature while the production of acetic acid, produced from relatively facile subsequent α -H abstractions, is less affected by temperature changes. The combined data, collected during the oxidation of ethane, ethylene, and ethanol, allowed a reaction network to be proposed for the formation of ethylene and acetic acid from ethane. A minor amount of acetic acid can be formed directly from ethane. However, the primary product of ethane oxidation is ethylene, which is then transformed to acetic acid. This is consistent with the results of ethanol oxidation showing that ethylene is the preferred product of an ethoxy—based intermediate. Ethane, ethylene and acetic acid may all be further oxidized to carbon oxides.

In order to clarify the effect of niobium loading on the catalysts and to verify the hypothesis that niobium affects the acidity of the catalysts, temperature programmed desorption studies of the $\text{Nb}_x\text{PMo}_{12}\text{Pyr}$ series were suggested. These studies could be complemented by simultaneous TGA/DSC/mass spectroscopy measurements to determine by what method pyridine reduces the catalyst during thermal decomposition. The pyridine may desorb intact or in fragments which could be identified by TGA/DSC/MS experiments. EXAFS and XANES studies of the $\text{Nb}_x\text{PMo}_{12}\text{Pyr}$ series during thermal activation and reaction might shed further insight into the role of niobium and the inhibitory effect of vanadium when compared to the studies of $\text{Nb}_{0.4}\text{PMo}_{11}\text{VPyr}$ already performed by this group. Increasing the niobium loading above $\text{Nb/P} = 1.0$ by both polyatom substitution and proton exchange during synthesis may produce a more active

catalyst. Finally, detailed studies of reactivity as a function of space time could aid in the confirmation of the proposed reaction network.