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Transition-Metal Ion Exchange Using Poly(ethylene glycol) Oligomers as Solvents

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Poly(ethylene glycol) oligomers have been found to be effective as alternative solvents for the ion exchange of Mn^{2+}, Fe^{2+}, and Co^{2+} into hydrated and dehydrated Zeolite X ($Na_{80}Al_{80}Si_{112}O_{384}\cdot nH_2O$). When attempted in aqueous solutions, the exchange of these cations quickly leads to destruction of the zeolite structure within 1−2 exchange cycles. However, in PEG oligomer solvents, the structure can be maintained and exchanges of 48% (Co^{2+}), 80% (Mn^{2+}), and 91% (Fe^{2+}) are observed after one cycle under hydrated conditions. When rigorous steps are taken to remove all water from the zeolite before exchange, absorption of the oligomers into the zeolite pores is promoted, which hinders ion exchange; a maximum of 6% exchange is seen under dehydrated conditions. However, improved catalytic efficiency toward NO decomposition is observed for these samples, with turnover frequencies of 0.0237 s^{-1} for Dehyd Na/Mn-X oligomer, 0.0213 s^{-1} for Dehyd Na/Fe-X oligomer, and 0.0190 s^{-1} for Dehyd Na/Co-X oligomer. Use of these PEG oligomers as reaction media has also been expanded to the ion exchange of layered oxides such as Dion−Jacobson perovskite phases.

Introduction

Poly(ethylene oxide), or PEO, is a mass-produced, nontoxic, inexpensive polyether $HO(CH_2CH_2O)_nH$ available in a wide range of molecular weights; the lower-molecular-weight variants are commonly referred to as poly(ethylene glycol), or PEG. PEG-related molecules such as glymes ($CH_3O(CH_2CH_2O)_nCH_3$ ($n = 1-4$)) are used as solvents for organometallic reactions requiring highly dissociated and activated salts.[1] PEG oligomers have also found use as reactive solvents in the polyol process for formation of metal nanoclusters, both solvating salts and reducing their cations.[2] However, the most well-known use of PEG or PEO compounds is in polyelectrolytes in solid-state lithium batteries. Lithium salts are dissolved in melts of high-molecular-weight PEO that, when solidified, act as the electrolytes in batteries, transporting Li^+ cations between the electrodes.[3] Given their ability to dissolve salts and transport cations to and from the graphitic carbon or layered metal-oxide electrodes of lithium batteries, it is somewhat surprising that PEG compounds have not been investigated as media for ion exchange processes in other inorganic porous or layered compounds. The lower-molecular-weight PEG oligomers are liquid at room temperature and have a wider range of accessible reaction temperatures than more commonly used low-boiling ethers such as tetrahydrofuran (THF) or diethyl ether.

Zeolites are a suitable class of materials to test the applicability of PEG oligomers as solvents for ion exchange. These open-framework aluminosilicate compounds have a variety of structures featuring ordered arrays of pores or channels.[4] Every aluminum oxide unit within the framework carries a negative charge that is balanced by a cationic species residing in the cages or channels. In industrial processes, such as hydrocarbon cracking or isomerization, and environmental pollutant control, such as NO_x abatement, a reactant contacts a cation in the zeolite cages, which catalyzes a reaction.[5−8] To render a zeolite catalytically active, the cations present in the as-synthesized material (usually Na^+) must be exchanged for more active species such as transition-metal ions. This is traditionally performed using aqueous ion exchange. However, the acidic hydrated metal complexes that form when transition-metal salts are dissolved in water can degrade the zeolite framework.

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Transition-metal ions can also form metal hydroxide precipitates on the surface or within the pores of the zeolite.[5,9] Elemental analysis of such samples will often show >100% ion exchange (referred to as over-exchange), producing uncertainty about the actual nature of the metal sites involved in catalysis. To avoid these problems, nonaqueous ion exchange solvents such as acetonitrile, dimethyl sulfoxide, and formamide have been investigated in the past with little to no exchange observed.[10] Ion exchange in ammonia and glacial acetic acid occurs more readily, but these solvents are difficult to handle and are not suited for zeolites of low Si:Al ratio.[11]

Since PEO is known to solvate lithium salts, initial tests were conducted on the ion exchange of Li^+ into sodalite, $Na_6(AlSiO_4)_6 \cdot 8H_2O$, using a variety of PEG oligomers; this proved to be quite successful.[12] We have now expanded this area of research to ions with more complex behavior and materials of industrial importance, investigating the ion exchange of transition metals (Mn^{2+}, Fe^{2+}, and Co^{2+}) into hydrated Na Zeolite X ($Na_{80}Al_{80}Si_{112}O_{384} \cdot 212H_2O$, denoted as Hyd Na-X) and dehydrated Na Zeolite X ($Na_{80}Al_{80}Si_{112}O_{384}$, denoted as Dehyd Na-X), using PEG oligomer solvents. Transition-metal ion exchange of hydrated Zeolite X in PEG solvents was found to be particularly convenient and effective, maintaining the zeolite structure and allowing for up to 91% exchange. However, zeolites exchanged under more rigorously dehydrated conditions were found to be better catalysts for the decomposition of NO into N_2 and O_2, a reaction of industrial interest known to be facilitated by zeolite catalysts.[7,8,13] The success of ion exchange of porous oxide systems in PEG solvents has led to exploration of their use in the ion exchange of layered materials. Preliminary data from investigation of PEG-mediated exchange of Dion−Jacobsen perovskites indicate that the use of these solvents for ion exchange may be expanded to a wide variety of layered and porous solids.

Experimental Section

Synthesis. Hydrated Zeolite X, $Na_{80}Al_{80}Si_{112}O_{384} \cdot 212H_2O$ (Hyd Na-X), was synthesized from a basic solution of sodium aluminate and sodium silicate, according to the literature.[14] A solution of 4.51 g (0.055 mol Na, 0.055 mol Al) $NaAlO_2$ (Strem Chemicals) and 38.0 g (0.95 mol) NaOH (Fisher Chemicals, 99.8%) in 250 mL of deionized water (DI H_2O) was prepared and added to a solution of 61.2 g (0.214 mol Na, 0.275 mol Si) sodium silicate (Sigma−Aldrich, 14% NaOH, 27% SiO_2) in 250 mL of DI H_2O in a polyethylene bottle with stirring. An amorphous gel mixture formed immediately; this was stirred at room temperature for 7 h and was then heated to 88 °C overnight. The precipitated product was filtered and washed with DI H_2O, rinsed with acetone, and dried. Dehydrated Zeolite X, $Na_{80}Al_{80}Si_{112}O_{384}$ (Dehyd Na-X), was produced by heating the sample to 400 °C under a vacuum of 10^{-3} Torr overnight and then under a vacuum of 10^{-5} Torr for 5 h. The resulting zeolite was stored in the drybox for subsequent experiments.

Hydrated zeolite exchange reactions were performed by adding the hydrated zeolite to a solution of the transition-metal chloride, (0.10 M anhydrous $MnCl_2$ (Alfa Aesar, 97%), 0.25 M $FeCl_2 \cdot 4H_2O$ (Fisher Scientific), or 0.10 M anhydrous $CoCl_2$ (Alfa Aesar 99.7%)), in either DI H_2O, polyethylene glycol 600 (PEG 600, Acros Organics, $HO{-}[CH_2CH_2O]_n{-}H$, $n \approx 12{-}14$), or polyethylene glycol methyl ether 750 (PEGME 750, Acros Organics, $HO{-}[CH_2CH_2O]_n{-}CH_3$, $n \approx 15{-}17$), in a ratio of >1 g/100 mL. These solutions were then heated in sealed polypropylene bottles at 100 °C overnight. The samples were filtered, washed with DI H_2O, and rinsed with acetone. This process was repeated to observe changes in the zeolite unit-cell parameters after two cycles of exchange.

Anhydrous ion-exchange reactions were conducted using the dehydrated zeolites in a glovebox with the previous anhydrous metal salts, anhydrous $FeCl_2$ (Alfa Aesar, 99.5%), and oligomer solvents purged with N_2 and dried over molecular sieves. These reactions followed the same method as that previously described, except they were sealed in glass vials with stir bars and then set in an aluminum block on a hot plate in the glovebox and heated/stirred at 100 °C overnight. These samples were filtered in the glovebox, rinsed with anhydrous ethylene glycol and anhydrous THF (Sigma−Aldrich, 99.9%). This process was repeated for 2 cycles of exchange.

Powder X-ray Diffraction (XRD). Each sample for diffraction was mixed with a small amount of silicon powder as an internal standard (Strem Chemicals, 99+%). Dehydrated zeolite samples were prepared inside a glovebox and placed in an air-tight sample holder sealed with Kapton film. The powder patterns of these exchanged zeolite samples were obtained on a Rigaku Ultima III X-ray powder diffractometer. The patterns were indexed and unit-cell parameters were determined by fitting the diffraction peak positions (corrected for errors in 2θ with the internal standard), using the accompanying MDI Jade software package.

Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). The zeolite Na, Al, Si, Mn, Fe, and Co concentrations were determined quantitatively with a FinniganMat ELEMENT 1 high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) at the Isotope Geochemistry Division, NHMFL, Florida State University (FSU). The instrument is equipped with a CD-1 guard electrode for enhanced sensitivity ($1{-}1.6 \times 10^6$ cps ^{115}In for 1 ppb In solution). Sample introduction was

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performed with a 100 uL/min self-aspirating Teflon nebulizer (Elemental Scientific) and a Teflon spray chamber. Solutions of the exchanged zeolite samples were prepared by dissolving the material in nitric acid and then diluting with deionized water to ~10 ppm Al in 2% HNO_3. A standard solution of similar concentration and stoichiometry to the analyzed samples was prepared from 1000 μg/mL stock solutions of each element (Alfa Aesar, SpecPure) with the following composition: 5 ppm Na, 10 ppm Al, 10 ppm Si, 3 ppm Mn, 3 ppm Fe, and 3 ppm Co in 2% HNO_3. The isotopes ^{23}Na, ^{27}Al, ^{29}Si, ^{55}Mn, ^{57}Fe, and ^{59}Co were measured in medium resolution mode ($m/\Delta m = 4000$) to eliminate isobaric interferences and the maximum standard deviation for these measurements was 5%. Elemental concentrations were determined by the standard-sample bracketing method.

^{27}Al Solid-State Nuclear Magnetic Resonance (NMR). Aluminum coordination in the Dehyd Na/Fe-X oligomer exchanged and Hyd Na/Fe-X aqueous exchanged samples was characterized on a Varian wide-bore Inova 500 MHz NMR at 25 °C. Dehydrated samples were loaded into a 4-mm zirconia rotor in the drybox while the hydrated sample was loaded under ambient conditions. Data were collected with the following parameters: spin rate, 12 kHz ; pulse, 5.0 μs; and recycle delay, 1.0 s (with 2000 scans).

Infrared Analysis. Zeolites exchanged in oligomer solutions were prepared as 10%, by mass, samples in KBr (Fluka, spectrometer-grade), and measured on a Thermo-Nicolet Avatar 360 FT-IR using a Harrick Praying Mantis diffuse reflectance sampling device. All hydrated Na/TM-X oligomer exchanged samples were heated to 100 °C and all calcined Na/Co-X oligomer exchanged samples to 150 and 300 °C under a flow of oxygen gas using a Harrick temperature-controlled high-temperature cell and measured in situ.

Thermogravimetric Analysis (TGA). Zeolite samples were heated to 450 °C at a rate of 10 °C/min under a flow of oxygen gas in an SDT 2960 Simultaneous DSC-TGA. Percent weight loss was determined for each sample using the accompanying TA Universal Analysis 2000 software package. These samples were saved for determination of the unit-cell parameters of the calcined compounds using powder X-ray diffraction.

Electron Paramagnetic Resonance. Dehyd Na/TM-X samples that been exchanged in PEGME (2×) were analyzed at room temperature on a Bruker ELEXSYS 500 Q-Band EPR spectrometer at a power of 1.0 mW and a modulation amplitude of 5 or 10 G, to verify the oxidation state of the transition metal in the zeolite after exchange.

Catalysis. Catalytic activity of the samples was measured using a fixed-bed flow reactor described in the Supporting Information. For each set of transition-metal reactions, one sample from each type of exchange was measured for comparison. For example, in the manganese reactions, one sample from the Hyd Na/Mn-X aqueous, Hyd Na/Mn-X oligomer, and Dehyd Na/Mn-X oligomer exchanges were measured. Approximately 0.053 g of dried, ground samples were placed into the reaction tube, calcined under an oxygen flow at 450 °C for ~3 h, and subsequently placed under a helium flow as the system was cooled to 200 °C overnight. Reactant gas, 4% NO in helium (AirGas South), was flowed through the zeolite bed at a rate of 10 mL/min. Several experimental runs (3−5) were taken for each data point from 200 °C to 450 °C, at 50° intervals for each sample. Catalytic activity was measured for each sample by monitoring the area of the N_2 product peak formed from NO decomposition using an HP 5890 Series II gas chromatograph. The number of N_2 molecules formed was determined from a calibration curve using 0.50%, 1.0%, and 2.0% N_2 in helium balance standard gas mixtures (AirGas South). From this information, the turnover frequency (which is the number of molecules of a given product formed per the number of active catalytic sites per second; denoted by the acronym TOF) was calculated for each sample over the given temperature range.

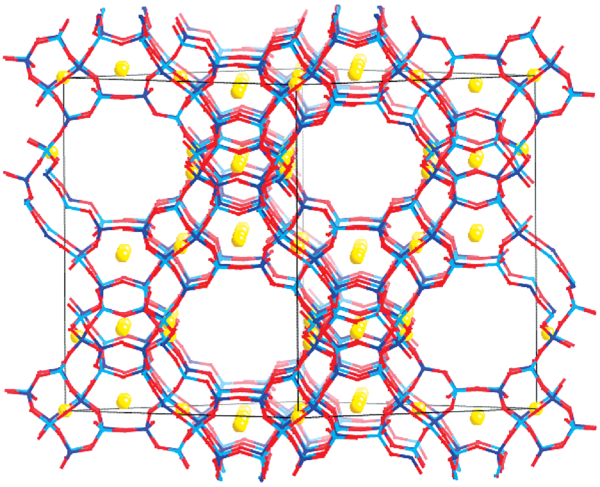

Figure 1. Framework of the faujasite-type zeolite structure viewed down the (110) direction, showing β-cages joined through hexagonal prisms creating larger α-cages. Cation sites are represented by yellow spheres.

Results and Discussion

Zeolite X and Zeolite Y are isostructural faujasite-type zeolites (shown in Figure 1), varying only in their Si:Al ratio. This structure consists of β-cage units connected by hexagonal prisms to form a larger α-cage; this creates five different types of cation sites.[4,5,8] The framework Si:Al ratio ranges are 1−1.5 for Zeolite X and 1.5−∞ for Zeolite Y. As the ratio increases, the amount of Al within the structure decreases, along with the cation content and the size of the unit cell. In these experiments, Hyd Na-X was synthesized with a Si:Al ratio of 1.4, $Na_{80}Al_{80}Si_{112}O_{384}.212H_2O$, with a unit-cell parameter of 24.92(1) Å. Because of the low Si:Al ratio, Zeolite X is susceptible to proton exchange and eventual structure degradation under aqueous exchange, but, at the same time, it can potentially incorporate a larger number of catalytically active cations, compared to higher-silica zeolites if hydrolysis can be avoided.

Comparison of Exchange Methods. Traditional aqueous exchange of Mn^{2+}, Fe^{2+}, and Co^{2+} into hydrated Na-X was attempted first for comparison with the results of exchange in PEG solvents. After aqueous exchange, the Hyd Na/TM-X samples turned from a white powder to light brown, reddish brown, and pink powders for Mn, Fe, and Co, respectively. Elemental compositions for the aqueous exchanged samples (Tables 1−3) show decreases in the Si:Al ratios from 1.4 to 1.27, 0.18, and 1.29 after two exchanges with Mn and after one exchange with Fe and Co, respectively. This is due to the degradation of the zeolite structure caused by the acidic aqueous environment (the iron solutions have pH values as low as 3.1). Aluminum is leached from the framework and reacts to form transition-metal and aluminum oxide/hydroxide

Table 1. Unit-Cell Parameters and Elemental Composition Data for Mn-Exchanged Zeolite X[a]

solvent	condition	unit cell/unit cell (calcined) (Å)	composition
water	**1× aqueous**	**24.79(2)***	$\mathbf{Na_{8.80}Mn_{36.88}Al_{80.8}Si_{111.2}O_{384}}$
water	2× aqueous	24.686(3)	0.03 Na:0.54 Mn:1.0 Al:1.27 Si
PEG 600	1× hydrated	24.892(3)	$Na_{19.46}Mn_{28.45}Al_{80.0}Si_{112.0}O_{384}$
PEG 600	2× hydrated	24.818(3)/24.828(3) (calcined)	0.08 Na:0.38 Mn:1.0 Al:1.30 Si
PEG ME 750	**1× hydrated**	**24.92(4)***	$\mathbf{Na_{25.15}Mn_{32.03}Al_{80.2}Si_{111.8}O_{384}}$
PEG ME 750	2× hydrated	24.848(3)/24.843(4) (calcined)	0.17 Na:0.46 Mn:1.0 Al:1.31 Si
PEG 600	1× dehydrated	25.005(1)	$Na_{62.40}Mn_{1.52}H_{14.6}Al_{80.8}Si_{111.2}O_{384}$
PEG 600	2× dehydrated	24.99229(1)/24.950(4) (calcined)	$Na_{65.81}Mn_{2.23}H_{9.7}Al_{81.9}Si_{110.1}O_{384}$
PEG ME 750	1× dehydrated	25.02(1)*	$Na_{67.47}Mn_{1.08}H_{10.4}Al_{79.5}Si_{112.5}O_{384}$
PEG ME 750	**2× dehydrated**	**25.036(3)/24.91854(1) (calcined)**	$\mathbf{Na_{64.57}Mn_{1.89}H_{11.6}Al_{82.4}Si_{109.6}O_{384}}$

[a] Compositions of samples with extensive degradation are given as metal molar ratios; full stoichiometries are given for zeolites that maintained their structure during exchange. Averaged data are indicated by an asterisk (*); the term "(calcined)" indicates data that were obtained after calcination; bold font indicates samples used for catalysis measurements.

Table 2. Unit-Cell Parameters and Elemental Composition Data for Fe-Exchanged Zeolite X[a]

solvent	condition	unit cell/unit cell (calcined) (Å)	composition
water	**1× aqueous**	**structure collapsed**	**0.01 Na:0.30 Fe:1.0 Al:0.18 Si**
water	2× aqueous	structure collapsed	0 Na:5.79 Fe:1.0 Al:0.61 Si
PEG 600	**1× hydrated**	**24.978(9)*/24.77(2)* (calcined)**	$\mathbf{Na_{11.34}Fe_{36.45}Al_{81.4}Si_{110.6}O_{384}}$
PEG 600	2× hydrated	24.994(3)	0.03 Na:0.60 Fe:1.0 Al:0.60 Si
PEG ME 750	1× hydrated	24.960(4)	0.14 Na:0.71 Fe:1.0 Al:0.66 Si
PEG ME 750	2× hydrated	24.979(8)	0.06 Na:0.50 Fe:1.0 Al:0.59 Si
PEG 600	1× dehydrated	25.041(3)	$Na_{59.92}Fe_{1.10}H_{16.8-17.9}Al_{80.5}Si_{111.5}O_{384}$
PEG 600	2× dehydrated	25.063(2)	$Na_{50.57}Fe_{1.63}H_{24.5-26.2}Al_{79.6}Si_{112.4}O_{384}$
PEG ME 750	1× dehydrated	25.06(2)*	$Na_{59.12}Fe_{1.04}H_{17.8-18.8}Al_{80.1}Si_{111.9}O_{384}$
PEG ME 750	**2× dehydrated**	**25.05294(1)/24.931(3) (calcined)**	$\mathbf{Na_{51.63}Fe_{2.17}H_{21.9-24.0}Al_{80.2}Si_{111.8}O_{384}}$

[a] Compositions of samples with extensive degradation are given as metal molar ratios; full stoichiometries are given for zeolites that maintained their structure during exchange. Averaged data are indicated by an asterisk (*); the term "(calcined)" indicates data that were obtained after calcination; bold font indicates samples used for catalysis measurements.

Table 3. Unit-Cell Parameters and Elemental Composition Data for Co-Exchanged Zeolite X[a]

solvent	condition	unit cell/unit cell (calcined) (Å)	composition
water	**1× aqueous**	**24.897(6)***	**0.24 Na:0.41 Co:1.0 Al:1.29 Si**
water	2× aqueous	24.910(3)	0.07 Na:0.61 Co:1.0 Al:1.13 Si
PEG 600	1× hydrated	25.05463(1)	$Na_{37.32}Co_{14.68}H_{13.3}Al_{81.9}Si_{110.1}O_{384}$
PEG 600	2× hydrated	25.035(2)/24.939(5) (calcined)	$Na_{22.23}Co_{19.50}H_{18.8}Al_{80.9}Si_{111.1}O_{384}$
PEG ME 750	**1× hydrated**	**25.04(1)***	$\mathbf{Na_{43.77}Co_{15.02}H_{6.2}Al_{82.0}Si_{110.0}O_{384}}$
PEG ME 750	2× hydrated	25.02217(1)/24.893(5) (calcined)	$Na_{35.28}Co_{18.63}H_{7.5}Al_{81.2}Si_{110.8}O_{384}$
PEG 600	1× dehydrated	25.059(2)	$Na_{63.91}Co_{1.35}H_{13.4}Al_{81.8}Si_{110.2}O_{384}$
PEG 600	2× dehydrated	25.052(3)/24.91014(1) (calcined)	$Na_{59.19}Co_{2.00}H_{16.8}Al_{81.9}Si_{110.1}O_{384}$
PEG ME 750	1× dehydrated	25.050(8)*	$Na_{63.09}Co_{1.42}H_{14.1}Al_{82.2}Si_{109.8}O_{384}$
PEG ME 750	**2× dehydrated**	**25.076(4)/24.922(4) (calcined)**	$\mathbf{Na_{57.48}Co_{2.42}H_{17.7}Al_{82.3}Si_{109.7}O_{384}}$

[a] Compositions of samples with extensive degradation are given as metal molar ratios; full stoichiometries are given for zeolites which maintained their structure during exchange. Averaged data are indicated by an asterisk (*); the term "(calcined)" indicates data that were obtained after calcination; bold font indicates samples used for catalysis measurements.

precipitates; the silicon forms soluble sodium silicates, which are lost during filtration. The compositions of extensively degraded zeolite samples in Tables 1−3 are stated as molar ratios of metals in the solid remaining after exchange; full stoichiometries are given for zeolites that maintained their structure. Collapse of the zeolite structure is illustrated in Figure 2a, which shows the powder diffraction pattern for the Hyd Na/Fe-X aqueous exchanged sample. Nearly all of the Zeolite X diffraction peaks have disappeared and have been replaced by broad FeOOH diffraction peaks that are due to the formation of this compound on the sample surface.

In the next set of experiments, Hyd Na-X was exchanged with Mn^{2+}, Fe^{2+}, and Co^{2+} using the PEG oligomer solvents. These samples became off-white, light brown, and purple/blue (turning pink over time with hydration) after Mn, Fe, and Co exchange, respectively. The Hyd Na/Co-X exchanged samples remained intact through two cycles in PEG solutions with 48% Co^{2+} ion exchange, according to elemental analysis results (see Tables 1−3). The Hyd Na/Mn-X oligomer exchanged samples remained intact at the end of the first cycle with 80% Mn^{2+} ion exchange; however, they began to decompose slightly during the second cycle, as indicated by the reduced Si:Al ratio of 1.30. According to the elemental analysis of the Hyd Na/Fe-X oligomer exchanged samples, the PEG 600 exchanged sample remained intact with 91% exchange after one cycle (XRD pattern shown in Figure 2b) before collapse in the second cycle. In contrast to this, the PEGME 750 exchanged sample began to collapse during the first cycle, resulting in a Si:Al ratio of 0.66. However, enough of the structure remained

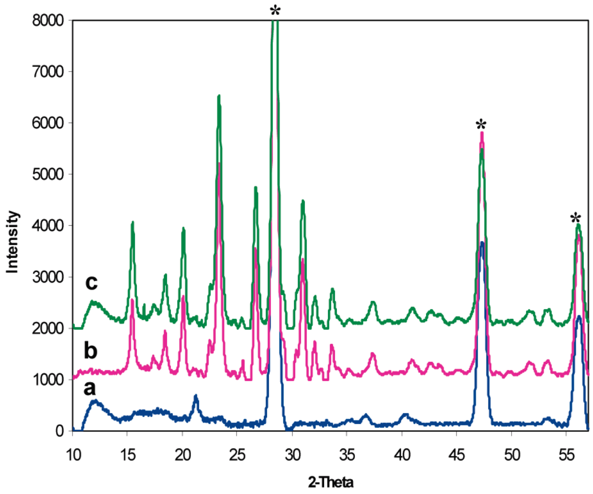

Figure 2. Powder XRD patterns for Hyd Na/Fe-X exchanged in (a) water, (b) PEG 600, and (c) PEGME 750, after one cycle. Si reference peaks are marked with an asterisk.

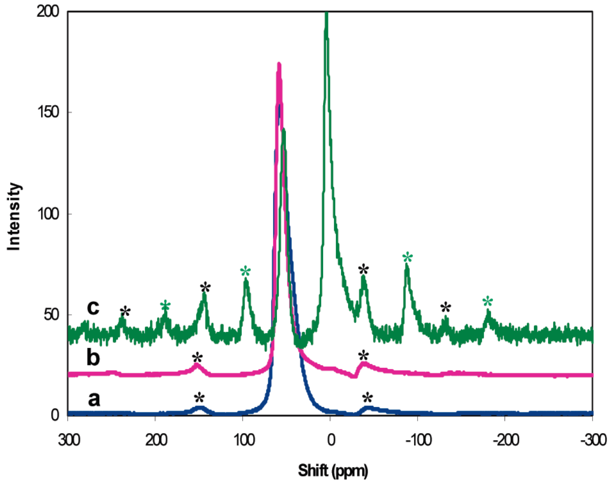

Figure 3. ^{27}Al solid-state NMR of (a) Dehyd Na-X, (b) Dehyd Na/Fe-X exchanged in PEG 600 (2×), and (c) Hyd Na/Fe-X exchanged in water (2×). Spinning side bands are marked with asterisks.

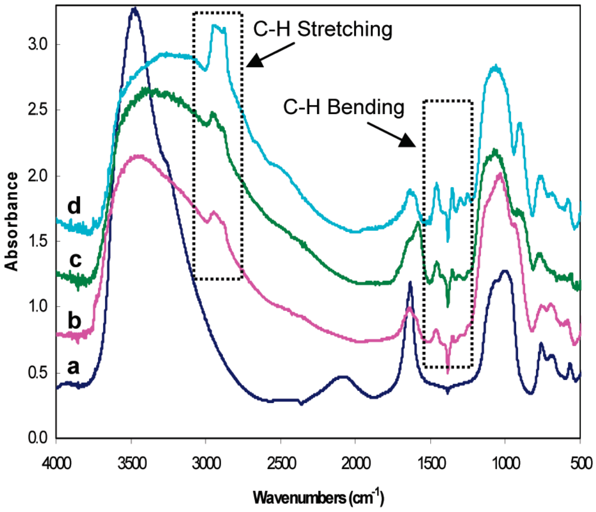

Figure 4. Infrared spectra for (a) Hyd Na-X, (b) Hyd Na/Mn-X exchanged in PEG 600 (2×), (c) Hyd Na/Fe-X (PEG 600, 1×), and (d) Hyd Na/Co-X (PEG 600, 2×). C−H stretching and bending regions are highlighted.

undamaged to produce an indexable powder XRD pattern, shown in Figure 2c.

The final set of exchange experiments explored the use of PEG oligomers as solvents for rigorously anhydrous reactions. Dehyd Na-X was exchanged with anhydrous transition-metal salts using dried oligomers under completely dehydrated conditions within a drybox. After exchange, each of these samples retained the off-white color of the original dehydrated zeolite powder. Each sample's structure was preserved through two exchange cycles. The extent of ion exchange was low; elemental analysis by ICP-MS indicates a maximum of 5.6%, 5.4%, and 6.0% ion exchange for the Mn, Fe, and Co samples, respectively (see Tables 1−3).

Incorporation and Removal of PEG Oligomers. Exchange of Na^+ cations for Mn^{2+}, Fe^{2+}, or Co^{2+} is expected to result in a decrease in zeolite unit-cell parameter from 24.92(1) Å (Hyd Na-X) or 24.93(1) Å (Dehyd Na-X) as the framework bond angles conform around the smaller transition-metal ions. This was observed for the aqueous exchanged samples that maintained some crystallinity and for the Hyd Na/Mn-X oligomer exchanged samples. However, for all of the other samples exchanged in the oligomer solvents, there was an *increase* in the unit-cell size after exchange. In addition, elemental analysis results indicate charge imbalances between the negative framework charge and the sum of the cation charge in the composition of these oligomer exchanged samples. To determine if this was due to amorphous Al compounds resulting from structure degradation forming on the sample surfaces, Na/Fe-X exchanged samples were analyzed using ^{27}Al MAS NMR. As shown in Figure 3, the spectrum of the Dehyd Na/Fe-X oligomer exchanged sample is similar to that of the unexchanged Na-X sample; the 50-ppm peak indicates tetrahedral framework Al. The data for the Hyd Na/Fe-X aqueous exchanged sample are also shown. From powder diffraction and elemental analysis data, this sample is known to have collapsed; accordingly, the NMR spectrum shows a large peak at 0 ppm, which is characteristic of Al in octahedral oxide coordination.[15] The absence of this peak in the oligomer exchanged samples indicates that the charge imbalances are not due to the formation of amorphous aluminum oxide phases.

Diffuse-reflectance Fourier transform infrared (FTIR) analysis was used to determine whether absorption of PEG oligomer was responsible for the charge imbalances and increased unit cell sizes in these samples. Spectra of Hyd Na/TM-X oligomer exchanged samples are shown in Figure 4, along with data for Hyd Na-X for comparison. Similar data collected for zeolites processed under dehydrated conditions can be found in Figure S1 in the Supporting Information. The data show the typical zeolite T−O−T asymmetric stretching vibrations (1250−950 cm^{-1}), the T−O−T symmetric stretching modes (800−650 cm^{-1}), and hexagonal prism breathing modes

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(550 cm^{-1}).[4,8,16] In addition, the broad hydrogen bonded O−H stretch is seen at 3500−3200 cm^{-1}, along with the O−H bending mode at 1645 cm^{-1}, because of water present in the zeolite pores under ambient conditions. Notably, the spectra show C−H stretching vibrations at 2950−2850 cm^{-1} and C−H bending modes at 1450−1150 cm^{-1}.[17] This indicates that the oligomers have adsorbed into the larger α-cages during ion exchange. It is unlikely that the oligomers adsorb into the smaller *β*-cages of the structure; this is confirmed by the lack of C−H stretching and bending modes in IR spectra of similarly exchanged sodalite samples.

To confirm this theory, these samples were further studied using thermogravimetric analysis (TGA). The TGA of Hyd Na-X shows a smooth, continuous weight loss step of 22% from 50 °C to ∼350 °C.[4] However, the TGA of the Hyd Na/TM-X oligomer exchanged samples show two distinct regions of weight loss, with an intermediate weight loss step of 13%−17% at ∼225 °C and a total weight loss of 23%−28% by 450 °C (see Figure S2 in the Supporting Information). This indicates that these samples are losing both water and organic content, at slightly different temperature ranges.[18] The TGA data for dehydrated samples make this point more clearly (see Figure S3 in the Supporting Information), showing a dramatic weight loss of 29%−30% above 250 °C, which can only be due to the loss of organic content in the samples.

Powder XRD data for the calcined samples demonstrated that their structures remained intact after heating to 450 °C, indicating that removal of the oligomer does not lead to structure degradation and the ion-exchanged zeolite is stable to heating in air or oxygen. The unit-cell data in Tables 1−3 show a significant decrease in size for nearly all of the samples after calcination, associated with loss of the organic oligomer from within the α-cages. However, in the isolated case of the Hyd Na/Mn-X oligomer exchanged samples, there was no change in the unit cell after calcination. This would suggest that the organic was found only on the sample surface in this particular exchange. This was expected, because these samples showed the expected decreases in their original unit cell size after ion exchange.

These data indicate that the PEG oligomer adsorbs into the zeolite pores during ion exchange. It would then be reasonable to conclude that the oligomer degrades, exchanging protons into the structure,[18] thereby accounting for the cation charge imbalance. To verify the presence of acidic −OH groups, the calcined samples were studied using FTIR. Figure 5 shows the spectra of calcined Hyd Na/Co-X oligomer exchanged samples, along with data for the precalcined sample for comparison. Evidence of the organic oligomer, seen in Figure 5a, disappears after calcination; however, the room temperature IR sample shows a great deal of water readsorbed into the zeolite pores. As the sample is heated in the spectrometer, the water is removed and the broad hydrogen bonded O−H peak at ∼3400 cm^{-1} shifts to the sharper isolated O−H peak at ∼3600 cm^{-1}. This region is characteristic of protons or isolated hydroxyls within the structure.[4,8,19] Similar behavior is seen for zeolites exchanged under dehydrated conditions (see Figure S4 in the Supporting Information). Given this result, the elemental compositions of the exchanged samples are listed with the appropriate amount of protons needed for charge balance. This low level of proton exchange was not enough to affect the zeolite structure as severely as in the aqueous exchanged samples. Room-temperature electron paramagnetic resonance (EPR) spectra collected on Dehyd Na/TM-X PEGME exchanged samples confirm a 2+ oxidation state for the Mn and Co samples; however, data for the iron-exchanged sample indicate some Fe^{3+} formation.[20] Therefore, the stoichiometries of Na/Fe-X samples are given as a range in Table 2. Elemental analysis of the Hyd Na/Fe-X PEG 600 (1×) exchanged sample indicates that Fe^{3+} and/or protons are not needed for charge balance. Although the oligomers adsorbed into the sample during exchange, shown by the increase in unit-cell size after exchange and decrease after calcination, it would appear that protons were not exchanged into this sample.

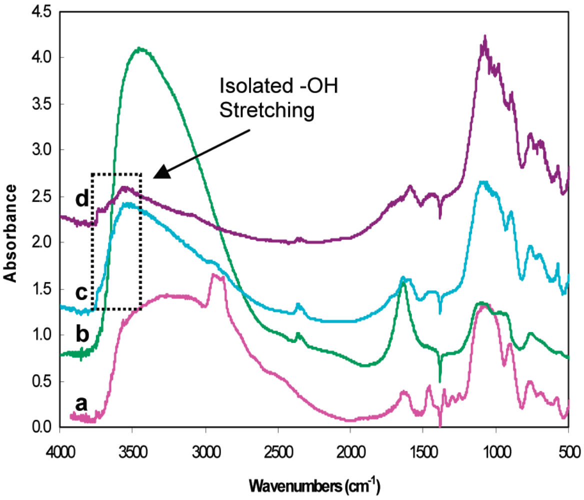

Figure 5. Infrared spectra of Hyd Na/Co-X (PEG 600, 2×): (a) before calcination, (b) calcined (IR at room temperature), (c) calcined (IR at 150 °C), and (d) calcined (IR at 300 °C). Isolated OH stretches are highlighted.

Our previous studies on sodalite ion exchange with Li^{+} in PEG oligomers indicated that these solvent molecules are not required to chaperone the exchanging ion into the zeolite.[12] However, the present investigation shows that the oligomers do adsorb into the larger α-cages of Zeolite X and remain present until they are calcined. This is

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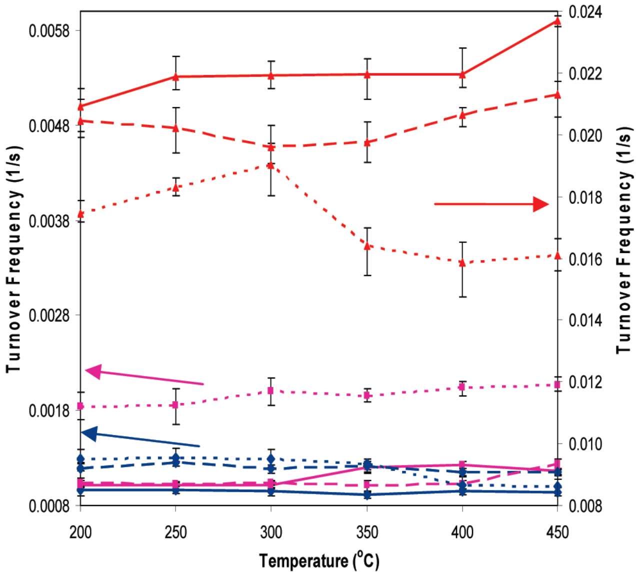

Figure 6. Turnover frequency (TOF) data for the catalytic decomposition of NO using zeolite exchanged samples. Different line types represent different transition metals exchanged (solid lines represent Mn exchanged samples, dashed lines represent Fe samples, dotted lines represent Co samples). Different line colors represent different methods of exchange (aqueous exchanged samples in blue and hydrated oligomer samples in pink, both referenced to the left-hand axis; and dehydrated oligomer exchange in red, referenced to the right-hand axis).

especially prevalent under rigorously dehydrated conditions; the vacuum in the cages of Dehyd Na-X draws in large quantities of solvent. This seems to hinder the motion of ions into the samples, resulting in low exchange percentages. If hydrated zeolites are used in these oligomer solvents, the oligomer molecules are not drawn into the cages to as great an extent, because the cages are already somewhat filled with water molecules. This allows for ion motion into the samples, but the amount of water present is not enough to facilitate extensive formation of acidic transition-metal complexes and associated degradation of the zeolite structure. Some attack does occur, however, as indicated by the decomposition seen in further hydrated exchange cycles and in the improved catalytic behavior of zeolites prepared under rigorously dehydrated conditions.

Catalysis of NO Decomposition. Catalysis measurements of NO conversion to N_2 and O_2 were performed for several samples to investigate the effects of different exchange conditions on the properties of the product. For each transition metal, zeolite samples from each type of exchange (aqueous exchange, hydrated oligomer exchange) were investigated, indicated by the bold font in Tables 1−3. The data were converted to TOF (the number of molecules of N_2 produced per active site per second) to compare data normalized with respect to different experimental conditions and amount of exchange.[21] In Figure 6, each point represents the average of 3−5 catalysis measurements; error bars indicate the range in TOF values. Expanded data are provided in the Supporting Information (Figures S5−S7).

Remarkably, the dehydrated exchange samples have TOF values that are an order of magnitude greater than those of the hydrated exchange samples; note the change in scales for the different datasets in Figure 6. The TOF values of 0.0237, 0.0213, and 0.0190 s^{-1} (for Dehyd Mn-, Fe-, and Co-exchanged samples, respectively) are within the range for most heterogeneous reactions of this type.[21] In addition, these values show an improvement over those listed in the literature.[13h] Although the dehydrated exchange samples have the lowest levels of transition-metal ion exchange in this study, their metal loading is comparable to that reported for zeolites with high Si/Al ratios (> 2.5) and corresponding low exchange capacity.[13] The activity of the metal sites created during dehydrated ion exchange in PEG oligomer solvents is improved, compared to previous reports, likely because of the better crystallinity of the zeolite (it is not exposed to acidic aqueous solutions) and the lack of metal hydroxide species. Many ion-exchanged zeolites in the literature are not structurally well-characterized, and many are reported to have an excess of 100% transition-metal exchange from aqueous solution, i.e., they contain metal hydroxide precipitates. It is unclear in these systems if the active catalyst is a transition-metal ion in the zeolite cages, or if it is a metal hydroxide layer. The lack of hydroxide precipitates and framework degradation, in addition to the isolated proton sites found in the dehydrated PEG exchanged samples studied here, leads to a catalyst with the highest activity toward NO decomposition. These significant findings illustrate the advantage of this exchange method and are quite promising, especially for a zeolite of this structure type and low Si/Al ratio. This indicates the potential of the use of PEG solvents for ion exchange in other zeolites and layered oxides.

Conclusions

Poly(ethylene glycol) (PEG) oligomers are well-known to be able to solvate and transport Li^+ cations; this useful behavior can be extended to transition-metal ions. PEG solvents have proven to be convenient media for transition-metal ion exchange into Zeolite X with little degradation of its structure. A high level of ion exchange (up to 91%) is seen in hydrated Zeolite X; this process requires no rigorous preparation of reactants, and the PEG solvents are inexpensive. However, transition-metal sites showing much higher catalytic activity toward NO decomposition are produced by ion exchange in these PEG solvents under rigorously dehydrated conditions. Note that transition-metal ions with low reduction potentials are susceptible to undergoing polyol process chemistry with these solvents.[2] Our attempts to exchange Cu and Ag ions into zeolites in PEG oligomers at 100 °C led to formation of metal nanoparticles. Lower-temperature exchanges were attempted to avoid this, but Ag^+ is reduced by PEG even at 40 °C, and Cu salts have low solubility in these solvents at low temperatures.

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The use of PEG solvents can be extended to ion exchange in other porous and layered inorganic compounds. Similar ion exchange procedures were conducted on a Dion−Jacobson-type perovskite, $KBi_3Ti_4O_{13}\cdot 2H_2O$; results from powder XRD and elemental analysis indicate up to 4% ion exchange of Cs^+ and up to 10% ion exchange of Co^{2+} after one exchange cycle in PEGME (see the Supporting Information). Use of PEG solvents also prevents the exchange of protons produced by the acidic hydrated cobalt complex; these readily exchange into the perovskite layers from aqueous metal solutions, as indicated by a sharp isolated O−H band in the FTIR spectra of samples exchanged in water (see Figure S8 in the Supporting Information).

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Supporting Information Available: Thermogravimetric analysis (TGA) data of the calcination of zeolite samples ion-exchanged under hydrated and dehydrated conditions. FTIR spectra of zeolites exchanged under dehydrated conditions and then calcined. Additional information about catalysis measurements. Unit-cell parameters, elemental analysis, and FTIR spectra of cobalt-exchanged perovskite samples. (PDF file.) This material is available free of charge via the Internet at http://pubs.acs.org.