SYNTHESIS AND USE OF NANOCRYSTALLINE ZEOLITES

Inventors: Sarah Larsen, Iowa City, IA (US); Vicki Grassian, Iowa City, IA (US); Weiguo Song, Beijing (CN); Gonghu Li, Evanston, IL (US)
(Continued)
Assignee: University of Iowa Research Foundation, Iowa City, IA (US)
(Continued)
Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

Appl. No.: 12/510,776
Filed: Jul. 28, 2009

Prior Publication Data

Related U.S. Application Data
Division of application No. 11/379,015, filed on Apr. 17, 2006, now Pat. No. 7,585,490.
Provisional application No. 60/671,837, filed on Apr. 15, 2005.

Int. Cl.
B01D 53/56 (2006.01)
B01D 53/86 (2006.01)
B01D 47/00 (2006.01)
B01D 53/94 (2006.01)
B01J 8/00 (2006.01)
B01J 8/02 (2006.01)
C01B 21/00 (2006.01)
B01J 29/08 (2006.01)

U.S. Cl. 423/239.2, 423/239.1; 423/235; 423/212; 423/213.2; 502/79

Field of Classification Search 423/700, 423/210, 212, 213.2, 235, 239.1, 239.2; 502/79
See application file for complete search history.

References Cited
U.S. PATENT DOCUMENTS
4,330,518 A 5/1982 Kostiako
(Continued)
FOREIGN PATENT DOCUMENTS
CA 2106170 3/1994
(Continued)
OTHER PUBLICATIONS
(Continued)
Primary Examiner—Karl E Group
Assistant Examiner—Noah S Wiese
Attorney, Agent, or Firm—Schwegman, Lundberg & Woessner, P.A.

ABSTRACT
Embodiments of the present invention relate to a method for synthesizing nanocrystalline zeolites, the method comprising contacting starting products that comprise a solvent, a silicon source, a cation base, an organic template, and an aluminum source, or any combination thereof sufficient to produce a zeolite gel by hydrolysis, heating the zeolite gel sufficient to produce a first batch of zeolite crystals and a first clear solution, separating the first batch of zeolite crystals from the first clear solution, heating the first clear solution sufficient to produce a second batch of zeolite crystals and second clear solution and separating the second batch of zeolite crystals from the second clear solution. In addition, embodiments relate to a method of using nanocrystalline zeolites, the method comprising contacting a nanocrystalline zeolite with a reductant sufficient to produce a nanocrystalline zeolite with adsorbed reductant and exposing the nanocrystalline zeolite with adsorbed reductant to reactant gases sufficient to obtain reaction products and the nanocrystalline zeolite.

19 Claims, 16 Drawing Sheets
**FOREIGN PATENT DOCUMENTS**

<table>
<thead>
<tr>
<th>CN</th>
<th>DE</th>
<th>EP</th>
<th>JP</th>
<th>JP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1230466</td>
<td>19715475</td>
<td>219854 A</td>
<td>002000</td>
<td>0022335</td>
</tr>
<tr>
<td>234441 A</td>
<td>326667 A</td>
<td>0662450 A</td>
<td>11147801 A</td>
<td>11711798</td>
</tr>
</tbody>
</table>

* cited by examiner

---

**OTHER PUBLICATIONS**


FIG. 1

1. STARTING PRODUCTS

3. MIX & STIR

5. ZEOLITE GEL

7. HEAT

9. ZEOLITE CRYSTALS IN FIRST CLEAR SOLUTION

11. SEPARATE

13. FIRST BATCH ZEOLITE CRYSTALS

15. FIRST CLEAR SOLUTION

17. HEAT

19. ZEOLITE CRYSTALS IN SECOND CLEAR SOLUTION

21. SEPARATE

23. SECOND CLEAR SOLUTION

FIG. 2

23. NANOCRYSTALLINE ZEOLITE

25. CONTACT WITH REDUCTANT

27. NANOCRYSTALLINE ZEOLITE WITH ADSORBED REDUCTANT

29. EXPOSE TO REACTANT GASES

31. REACTION PRODUCTS

29. NANOCRYSTALLINE ZEOLITE
FIG. 3

FIG. 4
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>BATCH</th>
<th>Si/Al</th>
<th>SURFACE AREA (m²/g)ᵃ</th>
<th>CRYSTAL SIZE (nm)ᵇ</th>
<th>PRODUCT YIELD (%)ᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>SILICALITE-1</td>
<td>1</td>
<td>NA</td>
<td>165</td>
<td>20</td>
<td>6.8</td>
</tr>
<tr>
<td>SILICALITE-1</td>
<td>2</td>
<td>NA</td>
<td>158</td>
<td>20</td>
<td>13.6</td>
</tr>
<tr>
<td>SILICALITE-1</td>
<td>3</td>
<td>NA</td>
<td>160</td>
<td>20</td>
<td>22.4</td>
</tr>
<tr>
<td>SILICALITE-1</td>
<td>4</td>
<td>NA</td>
<td>148</td>
<td>22</td>
<td>32.5</td>
</tr>
<tr>
<td>SILICALITE-1</td>
<td>5</td>
<td>NA</td>
<td>126</td>
<td>26</td>
<td>41.8</td>
</tr>
<tr>
<td>NaY</td>
<td>1</td>
<td>1.87</td>
<td>168</td>
<td>26</td>
<td>4.0</td>
</tr>
<tr>
<td>NaY</td>
<td>4</td>
<td>1.74</td>
<td>141</td>
<td>31</td>
<td>15.8</td>
</tr>
<tr>
<td>NaY</td>
<td>7</td>
<td>1.80</td>
<td>217</td>
<td>20</td>
<td>28.8</td>
</tr>
<tr>
<td>NaY</td>
<td>10</td>
<td>1.83</td>
<td>178</td>
<td>25</td>
<td>43.3</td>
</tr>
</tbody>
</table>

ᵃ SURFACE AREA OF AS–SYNTHESIZED SAMPLE ᵇ CRYSTAL SIZE CALCULATED FROM EXTERNAL SURFACE AREA AS DESCRIBED PREVIOUSLY ᶜ CUMULATIVE PRODUCT YIELD

**FIG. 5**
<table>
<thead>
<tr>
<th>PHASE</th>
<th>ASSIGNMENTS</th>
<th>$v^{14\text{N}}$</th>
<th>$v^{15\text{N}}$</th>
<th>$\Delta v$</th>
<th>$v^{14\text{N}}/v^{15\text{N}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAS PHASE</td>
<td>HNCO</td>
<td>2268</td>
<td>2260</td>
<td>8</td>
<td>1.004</td>
</tr>
<tr>
<td></td>
<td>$^3\text{NCO}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^3\text{NN}$</td>
<td>2224</td>
<td>2201</td>
<td>23</td>
<td>1.010</td>
</tr>
<tr>
<td></td>
<td>$^3\text{NO}$</td>
<td>1285</td>
<td>1270</td>
<td>15</td>
<td>1.012</td>
</tr>
<tr>
<td></td>
<td>$^3\text{NH}_3$</td>
<td>965</td>
<td>960</td>
<td>5</td>
<td>1.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ADSORBED IN NANOCRYSTALLINE NaY</td>
<td>HNCO</td>
<td>~2276</td>
<td>~2258</td>
<td>~18</td>
<td>1.008</td>
</tr>
<tr>
<td></td>
<td>$^3\text{NCO}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OCN$^-$</td>
<td>2169</td>
<td>2153</td>
<td>16</td>
<td>1.007</td>
</tr>
<tr>
<td></td>
<td>$^3\text{NC}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(NH$_2$)$_2$CO</td>
<td>1527</td>
<td>1522</td>
<td>5</td>
<td>1.003</td>
</tr>
<tr>
<td></td>
<td>$^3\text{CNH}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(NH$_2$)$_2$CO</td>
<td>1271</td>
<td>1266</td>
<td>5</td>
<td>1.004</td>
</tr>
<tr>
<td></td>
<td>$^3\text{CNH}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ADSORBED IN COMMERCIAL NaY</td>
<td>HNCO</td>
<td>~2282</td>
<td>~2250</td>
<td>~32</td>
<td>1.014</td>
</tr>
<tr>
<td></td>
<td>$^3\text{NCO}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OCN$^-$</td>
<td>2175</td>
<td>2159</td>
<td>16</td>
<td>1.007</td>
</tr>
<tr>
<td></td>
<td>$^3\text{NC}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(NH$_2$CO)$_2$NH</td>
<td>1759</td>
<td>1751</td>
<td>8</td>
<td>1.005</td>
</tr>
<tr>
<td></td>
<td>$^3\text{CO}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(HNCO)$_3$</td>
<td>1735</td>
<td>1727</td>
<td>8</td>
<td>1.005</td>
</tr>
</tbody>
</table>

$\Delta v = v^{14\text{N}} - v^{15\text{N}}$

**FIG. 6**
<table>
<thead>
<tr>
<th>CATALYST</th>
<th>INITIAL RATE (μmol L⁻¹ min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH₃</td>
</tr>
<tr>
<td>NANOCRYSTALLINE NaY</td>
<td>10.3</td>
</tr>
<tr>
<td>COMMERCIAL NaY</td>
<td>2.4</td>
</tr>
<tr>
<td>COMMERCIAL NaY b</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*a* The initial rate of NO loss during the UREA-SCR of NO₂ over commercial NaY zeolite was measured from t = 9 min to t = 18 min.

*b* Thermal decomposition of urea in the presence of O₂

**FIG. 7**

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>CONCENTRATION (μmol L⁻¹)³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH₃</td>
</tr>
<tr>
<td>NANOCRYSTALLINE NaY</td>
<td>56</td>
</tr>
<tr>
<td>COMMERCIAL NaY</td>
<td>17</td>
</tr>
<tr>
<td>COMMERCIAL NaY b</td>
<td>53</td>
</tr>
</tbody>
</table>

³ The concentration of gas-phase NH₃ was measured at T=473K, the concentrations of gas-phase CO₂, NO and N₂O were measured at T=298K.

*b* Thermal reaction of urea in the absence of NO₂

**FIG. 8**
FIG. 9

FIG. 10
FIG. 11
FIG. 13
FIG. 14
FIG. 15
FIG. 16
FIG. 20
SYNTHESIS AND USE OF
NANOCRYSTALLINE ZEOLITES

RELATED APPLICATION

This application is a divisional under 37 C.F.R. 1.53(b) of U.S. patent application Ser. No. 11/379,015 filed Apr. 17, 2006, now U.S. Pat. No. 7,585,490, which claims the benefit of U.S. Provisional Patent Application Ser. No. 60/671,837 filed Apr. 15, 2005, the contents of which are incorporated herein by reference in their entirety.

STATEMENT OF GOVERNMENT RIGHTS

This invention was made, at least in part, with a grant from the Government of the United States of America (Grant No. EPA-R82960001 from the Environmental Protection Agency). The Government has certain rights in the invention.

FIELD OF TECHNOLOGY

Embodiments of the present invention relate to the fields of nanocrystalline zeolite synthesis and applications thereof. Specifically, the embodiments relate to methods of efficiently synthesizing nanocrystalline zeolites and the use of nanocrystalline zeolites as catalysts and reaction sites for selective catalytic reduction of reactant gases.

BACKGROUND OF THE INVENTION

Zeolites have well-defined, crystalline structures with pores that are in molecular size range, ion exchangeable sites, and high hydrothermal stability. These properties enable zeolites to be widely used as catalysts in petrochemical processing. Nanocrystalline zeolites (with crystal sizes of 100 nm or less) can have advantages over conventional micron-sized zeolites in that they have larger external surface areas, shorter diffusion path-lengths, and lower tendencies to form coke. The improved properties of nanocrystalline zeolites can lead to new applications in catalysis, environmental protection, and chemical sensing. Pure silica nanocrystalline zeolites are promising low-dielectric constant materials for electronics applications. Composite polymer zeolite nanocomposite membranes can be useful in air separation applications.

Current methods to synthesis nanocrystalline zeolites involve terminating the synthesis while the zeolite crystals are still in the nanometer range, thus prohibiting further crystal growth. Such methods synthesize nanocrystalline zeolites at low temperature and ambient pressure which leads to low product yields and long synthesis times. The long synthesis times are a result of the low temperature causing slow nucleation and crystal growth. Typical product yields for the nanocrystalline zeolites are less than 10% of the synthesis gel composition, as compared to near 100% yields for conventional micron-sized zeolites. Once synthesis is complete, nanocrystalline zeolites are present in colloidal suspensions and powder products are then recovered by centrifugation. The remaining synthesis solution is usually discarded after the nanocrystalline zeolites are recovered resulting in adverse environmental effects and the disposal of valuable chemical materials. Previous attempts at reusing the original synthesis solution has required the addition of template species, silicon and/or aluminum sources. In addition, many attempts at reusing the original synthesis solution have failed due to reactants polymerizing and the impurity of the nuclei for subsequent crystal growth.

SELECTIVE CATALYTIC REDUCTION (SCR) using ammonia or hydrocarbons is a promising technology for post-combustion treatment of NOx (NO and NO2). Selective catalytic reduction utilizing ammonia (NH3—SCR) has been developed and used worldwide for the control of NOx emissions in fuel combustion from stationary sources due to its efficiency, selectivity and economics. However, NH3 is not a practical reducing agent for NOx emissions from mobile sources due to its toxicity and difficulties in its storage, transportation and handling. A great deal of interest has focused on using urea as a safer source of ammonia in automotive applications. Currently, a solution of urea in water is the preferred choice among different precursors for ammonia. It is generally accepted that urea thermally decomposes in two steps (reaction 1 and 2) to form ammonia and carbon dioxide.

\[
\text{(NH}_3\text{)}_2\text{CO} \rightarrow \text{NH}_3 + \text{HCONH}_2
\]  
(1)

\[
\text{HCONH}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2
\]  
(2)

Transition metal-containing zeolites have been extensively studied as SCR catalysts. Several recent studies have also used alkali and/or alkaline earth substituted Y zeolites as selective oxidation catalysts and deNOx catalysts. In the absence of transition metals, zeolite Y potentially offers novel SCR pathways different from those that occur in transition metal containing catalysts. Nanocrystalline Y zeolites and metal oxides with particle sizes less than 100 nm, can be particularly useful in environmental applications due to the small crystal sizes and large internal and external surface areas. The influence of intracrystalline diffusion on SCR reaction rates has been previously investigated for transition metal-exchanged zeolites with different crystal sizes.

SUMMARY OF THE INVENTION

Embodiments of the present invention demonstrate the synthesis of nanocrystalline zeolites in a higher yield than performed or contemplated before, by periodically removing nanocrystals from the synthesis solution and reusing the synthesis solution. Since the yield of nanocrystalline zeolite product is very low, only a small portion of nutrients in the synthesis are consumed and the clear solution composition is very close to the original synthesis solution composition. In addition, since only zeolite crystals that are heavy enough to be separated from the clear solution are removed, very small zeolite crystals are still present in the clear solution and can serve as nucleation sites, directly growing into larger crystals. Long nucleation and growth times are thus eliminated. Embodiments of the present invention synthesize nanocrystals more efficiently, more quickly, with higher yields and obtain more consistent crystal sizes than previously known.

Embodiments of the present invention include a method accomplishing the selective catalytic reduction (SCR) of NOx with urea in nanocrystalline NaY. The reaction rate for urea-SCR of NOx in nanocrystalline NaY zeolite is significantly greater than in commercial NaY zeolite with a larger crystal size. In addition, a dramatic decrease in the concentration of undesirable surface species is observed on nanocrystalline NaY compared to commercial NaY after urea-SCR of NOx. The increased reactivity for urea-SCR of NOx is attributed to silanol groups and extra-framework aluminum (EFAL) species located on the external surface of nanocrystalline NaY. Specifically, NOx storage as NO$_2$ on the internal zeolite surface was coupled to reactive de-NOx sites on the external surface. The increased external surface area (up to ~40% of the total surface area) of nanocrystalline zeolites can be utilized as a reactive surface with unique active sites for catalysis.
BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention can be best understood by referring to the following description and accompanying drawings which illustrate such embodiments. The numbering scheme for the Figures included herein are such that the leading number for a given reference number in a Figure is associated with the number of the Figure. Reference numbers are the same for those elements that are the same across different Figures. For example, a block flow diagram depicting the starting products (1) can be located in FIG. 1. However, reference numbers are the same for those elements that are the same across different Figures. In the drawings:

FIG. 1 illustrates a block flow diagram depicting a method for synthesizing nanocrystalline zeolites.

FIG. 2 illustrates a block flow diagram depicting a method for selective catalytic reduction of reactant gases with a nanocrystalline zeolite.

FIG. 3 illustrates X-ray diffraction patterns of five consecutive batches of silicate-1 zeolite crystals synthesized from the same synthesis solution.

FIG. 4 illustrates X-ray diffraction powder patterns of four selected batches of Y zeolite crystals synthesized from the same synthesis solution.

FIG. 5 illustrates a table depicting physical properties of synthesized nanocrystalline zeolite crystals.

FIG. 6 illustrates a table depicting vibrational frequencies of nitrogen-containing gas-phrase and adsorbed species which showed an isotopic shift upon substitution of 15N for 14N in the adsorbed urea (NH4CO), precursor.

FIG. 7 illustrates a table depicting rates for formation of gas-phase NH3, CO2, and N2O and loss of gas-phase NO during urea-selective catalytic reduction (SCR) of NOx and thermal decomposition of urea.

FIG. 8 illustrates a table depicting gas-phase product distribution after urea-SCR of NOx and thermal reaction of urea.

FIG. 9 illustrates a scheme depicting thermal decomposition of urea on silanol (SiOH) and EFAL (AlOx) in nanocrystalline NaY zeolite.

FIG. 10 illustrates a scheme depicting 15N-urea SCR on silanol (SiOH) and EFAL (AlOx) in nanocrystalline NaY zeolite.

FIG. 11 illustrates a Fourier Transform-Infrared (FT-IR) spectrum of commercial NaY with adsorbed urea.

FIG. 12 illustrates FT-IR difference spectra of nanocrystalline NaY with adsorbed urea and commercial NaY zeolite with adsorbed urea following adsorption of NOx.

FIG. 13 illustrates FT-IR spectra of the gas phase upon adsorption of NOx in commercial NaY zeolite with adsorbed 15N-urea, nanocrystalline NaY zeolite with adsorbed 15N-urea, commercial NaY zeolite with adsorbed unlabeled urea, and nanocrystalline NaY zeolite with adsorbed unlabeled urea.

FIG. 14 illustrates FT-IR spectra of the gas phase as a function of reaction time in 15N-urea SCR of NOx over nanocrystalline NaY zeolite.

FIG. 15 illustrates FT-IR spectra of the gas phase as a function of reaction time in urea-SCR of NOx over commercial NaY zeolite.

FIG. 16 illustrates charts depicting the evolution of gas-phase NH3, CO2, and H2O during urea-SCR of NOx in nanocrystalline NaY zeolite, urea-SCR of NOx in commercial NaY zeolite, and thermal decomposition of urea in commercial NaY zeolite.

FIG. 17 illustrates charts depicting the evolution of gas-phase NO and N2O during urea-SCR of NOx in nanocrystalline NaY zeolite and in commercial NaY zeolite.

FIG. 18 illustrates FT-IR difference spectra of zeolite samples following 15N-urea SCR of NOx in nanocrystalline NaY for 30 minutes, urea-SCR of NOx in nanocrystalline NaY for 2 hours, urea-SCR of NOx in commercial NaY for 2 hours and thermal decomposition of urea in commercial NaY for 2 hours.

FIG. 19 illustrates MAS NMR spectra depicting 13C single pulse and 15N single pulse of labeled urea, NO and O2 adsorbed in nanocrystalline NaY at various temperatures.

FIG. 20 illustrates FT-IR spectra of surface hydroxyl groups in nanocrystalline NaY and commercial NaY zeolite.

DETAILED DESCRIPTION OF THE EMBODIMENTS OF THE PRESENT INVENTION

References in the specification to “one embodiment”, “an embodiment”, “an example embodiment”, etc., indicate that the embodiment described can include a particular feature, structure, or characteristic, but every embodiment may not necessarily include the particular feature, structure, or characteristic. Moreover, such phrases are not necessarily referring to the same embodiment. Further, when a particular feature, structure, or characteristic is described in connection with an embodiment, it is submitted that it is within the knowledge of one skilled in the art to affect such feature, structure, or characteristic in connection with other embodiments whether or not explicitly described.

The embodiments of the present invention relate to the synthesis and the use of nanocrystalline zeolites. When describing such methods, the following terms have the following meanings, unless otherwise indicated.

DEFINITIONS


As used herein, “zeolite gel” refers to a composition capable of forming zeolite crystals. The zeolite gel can contain template molecules and compounds providing silicon and/or aluminum sources.

As used herein, “hydrolysis” or “hydrolyzing” refers to the reaction of salt with water to form an acid and base; decomposition of organic compounds by interaction with water, either in the cold or on heating alone in the presence of acids or alkalis. Bennett, H. Concise Chemical and Technical Dictionary, 4th Ed., New York, 1986, p. 631.

As used herein, “nanocrystalline” refers to crystals in the range of nanometers. For example, nanocrystalline zeolites can be zeolite crystals with a size smaller than 100 nm.

As used herein, “synthesis” refers to the formation of a chemical compound from more elementary substances. Bennett, H. Concise Chemical and Technical Dictionary, 4th Ed., New York, 1986, p. 1096. For example, nanocrystalline zeolites can be synthesized from molecules serving as templates, silicon sources, aluminum sources, etc.

As used herein, “clear solution” refers to the zeolite gel solution once a batch of zeolite crystals have been removed. The presence of zeolite crystals creates a cloudy solution, which in turn, becomes clear after the removal of formed zeolite crystals.

As used herein, “separate” or “separating” refers to isolating from a mixture. Gove, Philip Babcock, ed. Webster’s
Silicon and Aluminum Sources

Zeolites are generally aluminosilicate structures in which silicon and aluminum are used to form the framework of the molecule (although zeolites can be formed using only silicon, such as silicalite-1). Suitable compounds used as silicon and/or aluminum sources will hydrolyze (decompose with water) to free up silicon and aluminum to form the framework in the zeolite synthesis and subsequent crystal. Examples of silicon sources include, e.g., tetraethylorthosilicate (TEOS) (C₂H₅O₂Si), colloidal or fumed silica (amorphous silica, such as Ludox LS30), and disodium metasilicate (Na₂O·SiO₂).

Examples of aluminum sources include, e.g., aluminum isopropoxide (C₃H₇AlO₂), sodium aluminate (Al₂O₃·3Na₂O·6H₂O), and aluminum sulfate (Al₂O₃·3H₂O). TEOS can be used as the silicon source for the formation of silicalite-1 zeolite. TEOS can be used in an amount by mol percentage of about 1.7-5.2%, preferably about 3.1-3.8%, of the starting products (1). TEOS and aluminum isopropoxide can be used as the silicon and aluminum sources, respectively, for the formation of NaY zeolite. TEOS can be used in an amount by mol percentage of about 0.69-2.1%, preferably about 1.23-1.51%, of the starting products (1). Aluminum isopropoxide can be used in an amount by mol percentage of about 0.34-1.03%, preferably about 0.62-0.76%, of the starting products (1). Equivalent silicon and aluminum sources can be found in the Aldrich catalog, incorporated herein by reference. *Aldrich Handbook of Fine Chemicals*, 2003-2004 (Milwaukee, Wis.).

Cation and Base

An additional element of the starting products (1) is a compound, such as sodium hydroxide, that provides the metal cation and also the alkaliinity needed for the formation of the zeolite. The sodium cation released forms a part of the zeolite structure by stabilizing the charge and interlocking with the pore structure. Other metal cations (transition metals, alkali and alkaline earth metals, for example) can be used to form a zeolite, but are usually exchanged with sodium after the formation of the zeolite. Potassium hydroxide (KOH) can be an example of a cation and base that can be used in place of sodium hydroxide. Sodium hydroxide can be used in the formation of silicalite-1 zeolite. Sodium hydroxide can be used in an amount by mol percentage of about 0.008-0.024%, preferably about 0.0015-0.0018%, of the starting products (1). Sodium hydroxide can also be used in the formation of NaY zeolites. Sodium hydroxide can be used in an amount by mol percentage of about 0.024-0.071%, preferably about 0.043-0.052%, of the starting products (1). Equivalent cations and bases can be found in the Aldrich catalog, incorporated herein by reference. *Aldrich Handbook of Fine Chemicals*, 2003-2004 (Milwaukee, Wis.).

Solvent

Water is most often used as a solvent to facilitate the formation of zeolites. Water is used in excess and can be used in the formation of silicalite-1 and NaY zeolites. Water can be used in an amount by mol percentage of about 91-99%, preferably about 94-96.5%, of the starting products (1) for silicalite-1. For NaY zeolites, water can be used in an amount by mol percentage of about 91.0-99.0%, preferably about 94.0-98.0%, of the starting products (1).

The starting products (1) are mixed and stirred (3) for a sufficient time and at an appropriate temperature to ensure hydrolysis of the silicon and/or aluminum sources. For example, TEOS can be the silicon source and aluminum isopropoxide can be the aluminum source. Room temperature can be an example of an appropriate temperature for hydrolysis. Overnight, or about 12 hours, can be an example of sufficient time to ensure hydrolysis. Ethanol and iso-propanol
are the respective hydrolysis products of TEOS and aluminum isopropoxide. Once hydrolysis has occurred, a zeolite gel (5) can be formed.

Zeolite Gel
The zeolite gel is the clear solution that is produced by the hydrolysis of the silicon and/or aluminum sources of the starting products (1). The stirring and mixing (3) of the starting products (1) ensures hydrolysis and frees up silicon or other metal to form the zeolite framework. Hydrolysis also produces by-products such as ethanol or isopropanol, which can contribute to the physical properties of the zeolite gel, but do not take part in the formation of the zeolite. For example, in the formation of silicate-1, the hydrolysis of TEOS uses water to free up silicon and produces ethanol as a by-product. Starting products, such as the organic template, the cation/base such as sodium hydroxide, and an excess of water still remain after hydrolysis of the metal source. In the formation of NaY zeolite, the hydrolysis of TEOS frees up silicon and the hydrolysis of aluminum isopropoxide frees up aluminum, in turn, producing ethanol and isopropanol as by-products, respectively. The ethanol and isopropanol are then part of the zeolite gel, but do not effectively participate in the formation of the zeolite from the gel.

For silicate-1 zeolites, the zeolite gel (5) can comprise water, sodium hydroxide (NaOH), tetrapropyl ammonium hydroxide (TPOH) (C₄H₁₀O), silicon (Si) and ethanol (C₂H₅OH). Specifically, the zeolite gel (5) can comprise about 50.0-92.0% water, about 0.012-0.038% sodium hydroxide (NaOH), about 0.72-2.15% tetrapropyl ammonium hydroxide (TPOH) (C₄H₁₀O), about 1.99-5.96% silicon (Si) and about 7.35-23.84% ethanol (C₂H₅OH) by mol percentages. Further, the zeolite gel (5) can comprise about 70.81-86.55% water, about 0.022-0.028% sodium hydroxide (NaOH), about 1.28-1.57% tetrapropyl ammonium hydroxide (TPOH) (C₄H₁₀O), about 3.57-4.37% silicon (Si) and about 14.30-17.48% ethanol (C₂H₅OH) by mol percentages.

For Y zeolites, the zeolite gel (5) can comprise water, sodium (Na), tetramethyl ammonium hydroxide (TMAOH) (C₄H₁₀N), i-propanol (C₃H₇OH), silicon (Si), aluminum (Al) and ethanol (C₂H₅OH). Specifically, the zeolite gel (5) can comprise comprises about 74.0-94.0% water, about 0.024-0.071% sodium (Na), about 0.81-2.43% tetramethyl ammonium hydroxide (TMAOH) (C₄H₁₀N), about 1.01-3.03% i-propanol (C₃H₇OH), about 0.68-2.03% silicon (Si), about 0.34-1.01% aluminum (Al) and about 2.70-8.09% ethanol (C₂H₅OH) by mol percentages. Further, the zeolite gel (5) can comprise about 80.01-94.00% water, about 0.042-0.052% sodium (Na), about 1.46-1.78% tetramethyl ammonium hydroxide (TMAOH) (C₄H₁₀N), about 1.82-2.22% i-propanol (C₃H₇OH), about 1.22-1.49% silicon (Si), about 0.60-0.74% aluminum (Al) and about 4.85-5.92% ethanol (C₂H₅OH) by mol percentages.

The zeolite gel (5) is heated (7) to obtain zeolite crystals in a first clear solution (9). The mechanism for forming zeolite crystals is not clear in the art. The zeolite gel (5) can be heated (7) in a glass flask with a magnetic stirrer, for example. The zeolite gel (5) for silicate-1 can be heated to about 30-90°C for about 120-360 hours. For example, about 60°C and about 240 hours can be used. The zeolite gel (5) for Y zeolite can be heated to about 45-135°C for about 72-216 hours. For example, about 90°C and about 144 hours can be used. The formation of zeolites from the zeolite gel can be monitored visually. As the zeolite crystals form, the solution becomes increasingly cloudy. The duration of the heating can depend on reaching the desired cloudiness which would indicate the completion of crystal formation.

Zeolite crystals in a first clear solution (9) are separated (11) to obtain a first batch zeolite crystals (13) and a first clear solution (11). Separation (11) can be accomplished by centrifugation for example. The centrifugation can be accomplished at about 14,000 rpm for about thirty minutes as an example. The first, second and subsequent batches of zeolites can contain from about 75-100%, preferably at least about 85%, of the target zeolite. The undesirable structures formed can be alternative zeolites or some amorphous structure.

The remaining first clear solution (15) can be returned to the original flask and heated to temperatures comparable to those mentioned above, sufficient to provide zeolite crystals in a second clear solution (17). The first, second and subsequent clear solutions contain unused organic template and the remaining starting products necessary for zeolite formation. Further, the recycled solution contains precursor zeolites used as nucleation sites to form zeolites faster than by starting with fresh starting products. The time to form zeolite crystals can be significantly reduced. For example, the first clear solution (15) can be heated for about 24-108 hours. Specifically, the first clear solution (15) can be heated for about 72 hours to form silicate-1 zeolites and only about 48 hours to form Y zeolites. For Y zeolites, an amount of sodium hydroxide (NaOH) can be contacted with the first clear solution before heating. For example, the amount of sodium hydroxide (NaOH) contacted can be an amount equal to that found in the original zeolite gel.

The zeolite crystals in the second clear solution (17) can be separated (11) sufficient to provide a second batch zeolite crystals (19) and a second clear solution (21). Separation apparatus and methods can be similar to those mentioned above. The second clear solution (21) can be returned to the original flask and heated sufficient to form zeolite crystals in a third clear solution. The steps of separation and formation can be repeated until the clear solution no longer forms zeolite crystals. For NaY zeolites, sodium hydroxide can be contacted with each clear solution as described above.

Cations used as nanocrystalline zeolites can include alkali, alkaline earth, transition metals or any combination thereof. Further, the Si/Al ratio for nanocrystalline can range from about 1.5-5.0.

Example 1
FIGS. 3 and 4 depict the X-ray diffraction (XRD) powder patterns of silicate-1 and Y zeolites, respectively, obtained from multiple rounds of zeolite synthesis in which the clear solution recovered after removal of zeolite nanocrystals was reused. The patterns (a)-(e) shown in FIG. 3 correspond to consecutive batches (1-5) of silicate-1 zeolites. The patterns (a)-(d) shown in FIG. 4 correspond to the first, fourth, seventh and tenth batch of Y zeolites. Each XRD pattern is consistent with the silicate-1 or Y zeolite structure, respectively. The intensities and line widths of the XRD peaks are similar to each other for each zeolite, suggesting that the different batches of the same zeolite have similar crystal sizes.

The BET surface areas (of as-synthesized samples) and the Si/Al ratios for Y zeolites were measured and are listed in FIG. 5 along with the cumulative nanocrystalline zeolite yields for each batch. The zeolite yield was calculated from the initial synthesis solution composition and the mass of the zeolite nanocrystals recovered for each batch. The BET surface area for the as-synthesized zeolite samples which have template still present in the pores represents the external surface area of the nanocrystalline zeolites. The zeolite crystal size can be estimated from the external surface area and the results are listed in FIG. 5.
For silicalite-1, all five batches of synthesis produced roughly the same amount of silicalite-1 crystals with crystal sizes ranging from 20-26 nm. The crystal size of approximately 20 nm is close to the crystal size of 26 nm estimated from the external surface area. After five batches, the total product yield was 42% and the total time elapsed was 22 days. To produce the same amount of silicalite-1 without recycling the synthesis solution would have required approximately 50 days. The attempt for the sixth round failed to produce a colloidal suspension of nanocrystals.

For NaY, the total product yield was 43% after 10 batches and the time elapsed was 24 days. To produce the same amount of Y zeolite without recycling the synthesis solution would have required approximately 60 days. The Si/Al remained approximately constant at 1.8 for each batch and the crystal size ranged from 20-31 nm for the ten batches. The yield from each round was less than 6%, which appears to be limited by the sodium content in the synthesis gel (7% relative to Al content).

Selective Catalytic Reduction (SCR) on Nanocrystalline Zeolites

Referring to FIG. 2, embodiments of the present invention include a method to reduce reactant gases by selective catalytic reduction. A nanocrystalline zeolite (23) is contacted with reductant (25) sufficient to obtain a nanocrystalline zeolite with adsorbed reductant (27). A nanocrystalline zeolite with adsorbed reductant (27) is exposed to reactant gases (29) sufficient to provide the nanocrystalline zeolite (23) and reaction products (31).

A nanocrystalline zeolite (23) is contacted with reductant (25) sufficient to obtain a nanocrystalline zeolite with adsorbed reductant (27). A nanocrystalline zeolite can comprise NaY zeolite, for example. Transition metal, alkali and alkaline earth substituted nanocrystalline zeolites can also be used as catalysts for the selective catalyst reduction (SCR) reaction. In the absence of transition metals, zeolite NaY potentially offers novel SCR pathways different from those that occur in transition metal containing catalysts. Nanocrystalline zeolites and metal oxides with particle sizes less than about 100 nm, can be particularly useful in environmental applications due to the small crystal sizes and large internal and external surface areas. Urea or ammonia can be used as the reductant, for example. Urea can have broader applications than ammonia as urea is safer to handle and store. Ammonia can be utilized in stationary applications, but urea is more practical for mobile applications.

A nanocrystalline zeolite with adsorbed reductant (27) is exposed to reactant gases (29) sufficient to provide the nanocrystalline zeolite (23) and reaction products (31). The nanocrystalline zeolite (23) acts as the catalyst for reducing pollutant reactant gases to harmless reaction products such as nitrogen gas (N₂) and nitrous oxide (N₂O). The adsorbed reductant, such as urea, reduces the reactant gases according to the mechanism of selective catalytic reduction (SCR). Reaction products can also include water and by-products of hydrocarbon breakdown, such as carbon dioxide (CO₂).

A solution of about 32.5% urea in water can be an example of a precursor for ammonia. Urea thermally decomposes in two steps (reaction 1 and 2) to form ammonia and carbon dioxide.

\[
\text{(NH}_2\text{)}_2\text{CO} \rightarrow \text{NH}_3 + \text{H}_2\text{NCO} \quad (1)
\]

\[
\text{H}_2\text{NCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2 \quad (2)
\]

Silanol groups and Bronsted acid sites on the external surface of nanocrystalline NaY can be effective surface sites for the decomposition of urea to NH₃ and the subsequent SCR of NO₂.

Example 2

Zeolite Sample Preparation and Materials

Nanocrystalline NaY zeolite was synthesized using clear solutions as discussed above. Sodium hydroxide (NaOH), aluminum isopropoxide, tetramethylammonium hydroxide (TMAlOH) and distilled water were mixed and stirred until the resulting mixture became a clear solution. Then tetraethyl orthosilicate (TEOS) was added to the clear solution. The clear solution mixture was stirred overnight to ensure complete hydrolysis of the aluminum and silicon sources. The final clear synthesis gel had the following composition: 0.07Na₂:2.4TMAlOH:1.0Al₂OSi₄:132H₂O:3.0H₂O/PrOH:8.0EtOH (mol ratio), the latter two alcohols came about from the hydrolysis of the aluminum isopropoxide and TEOS, respectively. In order to optimize the formation of small NaY crystals, the sodium content was intentionally set too low relative to aluminum content in the synthesis gel. The clear solution was transferred into a 500 ml flask equipped with an air cooled condenser and was heated to T=368 K in an oil bath for 84 hours with stirring. Nanocrystalline Y powders were recovered from the milky, colloidal suspension of NaY after two cycles of centrifugation, washed with deionized water and dried at T=393 K in air. The nanocrystalline Y Na sample was calcined at T=773 K under oxygen flow for sixteen hours to remove organic templates.

The synthesized nanocrystalline NaY zeolite and the commercial NaY zeolite purchased from Aldrich were characterized by several different techniques including scanning electron microscopy (SEM), X-ray diffraction (XRD), nitrogen adsorption isotherms and solid state NMR. The average crystal size of nanocrystalline NaY zeolite was determined to be 23 nm. The commercial NaY zeolite is composed of large intergrowths NaY crystals with diameters of ~1 μm. The external, internal and total surface areas of nanocrystalline NaY zeolite were determined to be 178, 406 and 584 m²/g, respectively. The total surface area of commercial NaY zeolite was 477 m²/g and the external surface area of commercial NaY zeolite is estimated from the crystal size to be ~4 m²/g. The Si/Al ratios of nanocrystalline NaY and commercial NaY zeolite were determined to be 1.8 and 2.0, respectively.

Fourier Transform Infrared Spectroscopy

4 mg urea in aqueous solution (-0.3 M) and 7 mg NaY zeolite were mixed and sonicated for 30 minutes at room temperature. The resulting hydrogel was coated onto a 3 cm x 2 cm tungsten grid held in place by nickel jaws. The nickel jaws are attached to copper leads so that the sample can be resistively heated. A thermocouple wire attached to the tungsten grid is used to measure the temperature of the sample. The tungsten grid with zeolite sample is placed inside a stainless steel cube. The cube has two BaF₂ windows for infrared measurements and is connected to a vacuum/gas handling system.

The stainless steel IR cell is held in place by a linear translator inside the sample compartment of an infrared spectrometer equipped with a narrowband MCT detector. The linear translator allows each half of the sample grid to be moved into the infrared beam path. This allows the detection of gas phase and adsorbed species in zeolites to be obtained under identical reaction conditions. Each absorbance spec-
trum shown is obtained by referencing 64 scans at an instrument resolution of 4 cm⁻¹ to the appropriate background of the zeolite or the blank grid, unless otherwise noted.

The NaY zeolite sample with adsorbed urea was dried in air and evacuated at room temperature overnight to remove weakly adsorbed water. Reactant gases (NO₂, and O₂) were loaded into the NaY zeolite through the gas handling system. Two absolute pressure transducers were used to monitor the pressure. The extinction coefficient of individual gases was calibrated using the characteristic IR absorption band and measuring the pressure using an absolute pressure transducer. Typically, the NaY zeolite was equilibrated with gases prior to a spectrum being recorded. In SCR reactions, NO₂ was first introduced into the IR cell at room temperature. Thirty minutes were allowed for adsorption equilibrium before an excess amount of oxygen was added into the IR cell. Time course experiments were conducted by automatically recording infrared spectra of the gas phase every 60 seconds.

Example 3

Solid State MAS NMR Experiments

Approximately 0.2 g of zeolite was impregnated with an aqueous solution of labeled urea (¹³C and ¹⁵N). Samples with adsorbed urea were allowed to dry at room temperature and were placed into pyrex sample tubes that were degassed on a vacuum rack. To prepare samples containing labeled urea and nitric oxide and oxygen, the nitric oxide and oxygen were introduced to the zeolite sample while still attached to the vacuum rack. Then, the pyrex sample tube was sealed while the sample was immersed in liquid nitrogen. The sealed samples were heated for 1 hour at the desired temperature. Samples were allowed to cool to room temperature for the NMR measurements.

Magic angle spinning (MAS) NMR spectra were obtained using a 7 Tesla wide bore Bruker cryomagnet and a TecMag Discovery console. The Larmor frequencies for ¹³C and ¹⁵N were 75.40 MHz and 30.425 MHz, respectively. A Chemagnetics double-channel 7.5 mm nol4l MAS probe was used to spin rotors containing the sealed samples. The spinning speed was approximately 4.0 kHz. Single pulse direct excitation was used for ¹³C and ¹⁵N. The π/2 pulse width was 6.0 μs for ¹³C; the π/2 pulse width was 4.5 μs for ¹⁵N. Recycle delay was 2 s and a line broadening of 50 Hz was used for both ¹³C and ¹⁵N. The number of scans for ¹³C and ¹⁵N MAS NMR was 4,000 scans and 25,000 scans, respectively. Solid adamantane mixed with KBr (38.5 ppm) and saturated ¹⁵NH₄NO₃ solution (0 ppm for NO₂⁻) were used as external chemical shift standards for ¹³C and ¹⁵N, respectively. All of the chemical shifts for ¹³C and ¹⁵N are reported relative to TMS and CH₃NO₂, respectively. All ¹³C and ¹⁵N spectra were obtained at room temperature.

Results

Adsorption of NO₂ in NaY Zeolite at T=298 K

As discussed above, an aqueous urea solution and the NaY zeolite powder were mixed at room temperature. Prior to adsorbing NO₂, the NaY zeolite sample was dried in air and evacuated at room temperature overnight to remove weakly adsorbed water. The FT-IR spectrum of commercial NaY zeolite with adsorbed urea is shown in FIG. 11. The FT-IR spectrum of a clean commercial NaY sample is also plotted in FIG. 11 (dotted line) for comparison.

Adsorbed urea in NaY zeolite can be identified by several absorption bands at 1456, 1584, 1610, 1650 and 1712 cm⁻¹ in the FT-IR spectrum shown in FIG. 11. The absorption at 1456 cm⁻¹ is assigned to the asymmetric N—C—N stretching mode of adsorbed urea. The absorptions at 1584 and 1610 cm⁻¹ are both due to the NH₃ bending mode of adsorbed urea. The bands at 1650 cm⁻¹ and 1712 cm⁻¹ (both C=O stretching mode) can be assigned to urea adsorbed at different sites or different coordination environments in NaY zeolite. Some additional bands in the spectral region 3100-3800 cm⁻¹ due to O—H—N—H stretching are also seen (not shown). The general features of the FT-IR spectrum of nanocrystalline NaY zeolite with adsorbed urea (not shown) are similar to those of commercial NaY zeolite, except that there is an increase in the spectral broadening of the peaks. This broadening has been previously attributed to an increase in site heterogeneity for nanocrystalline zeolite samples.

The NaY sample with adsorbed urea was then exposed to 0.5 Tor pressure of NO₂ at room temperature and was equilibrated for 30 min. The changes in the FT-IR spectra of NaY sample upon exposure to NO₂ are clearly seen in the difference spectra shown in FIG. 12. Each difference spectrum was obtained by subtracting the spectrum of NaY zeolite before adsorbing NO₂ from the corresponding spectrum after the adsorption equilibrium. As shown in the difference FT-IR spectrum of commercial NaY zeolite (FIG. 12), several absorption bands appeared at 1272, 1372, 1514 and 1770 cm⁻¹. The absorption bands at 1272 and 1372 cm⁻¹ are attributed to the formation of nitrite and nitrate on Na⁺ sites, respectively. The appearance of two absorption peaks at 1514 cm⁻¹ ( ν(ν(NH₃+δ(NH₄+))) and 1770 cm⁻¹ ( ν(C=O) indicates the formation of a surface species with a linear imido structure (e.g. —(C—O)−NH—(C—O)—). The simultaneous loss in intensity of the bands around 1456 and 1650 cm⁻¹ was observed, indicating that adsorbed urea reacted with NO₂ (or surface species generated in NO₂ adsorption).

The difference FT-IR spectrum of nanocrystalline NaY with adsorbed urea after being exposed to NO₂ is shown in FIG. 12 (bottom). Similar to the commercial NaY zeolite, the formation of nitrite (1272 cm⁻¹) and disappearance of adsorbed urea (1456 and 1650 cm⁻¹) were observed for nanocrystalline NaY zeolite. However, several differences were observed between the spectra of nanocrystalline NaY zeolite and commercial NaY zeolite. For example, the formation of the surface species with the linear imido structure (1514 and 1770 cm⁻¹) occurs to a much less extent in nanocrystalline NaY (FIG. 12). Furthermore, NO₂ adsorption in nanocrystalline NaY zeolite resulted in the formation of nitrate adsorbed on external (vide infra) EFAL sites (1336 cm⁻¹) as well as nitrate on internal Na⁺ sites (1372 cm⁻¹). Finally, the formation of isocyanic acid (HCONH₂) adsorbed on EFAL sites is observed in nanocrystalline NaY zeolite, as indicated by a broad absorption band around 2276 cm⁻¹. In NO₂ adsorption at room temperature, the formation of adsorbed isocyanic acid is not appreciable in commercial NaY zeolite (FIG. 12). Previous studies of pyridine adsorption coupled with infrared analysis indicate that EFAL sites are located on the external surface of nanocrystalline NaY zeolite and are not present to any great extent in the commercial NaY sample due to its low external surface area.

Unlabeled urea and ¹⁵N labeled urea were used in SCR reactions over both nanocrystalline NaY and commercial NaY zeolite. Compared to the FT-IR spectrum of NaY zeolite with unlabeled urea, several differences were observed when ¹⁵N-urea solution was mixed with the zeolite sample. For example, the absorption band for adsorbed H₂¹⁵NCO shifts from 2276 cm⁻¹ to 2258 cm⁻¹ when nanocrystalline NaY with adsorbed ¹⁵N-urea was exposed to NO₂ at room temperature (not shown). A similar isotopic shift was also observed for gas-phase HCONH₂. The FT-IR spectra of the gas
phase after NO₂ adsorption in commercial and nanocrystalline NaY zeolite with unlabeled urea and ¹⁵N-urea are shown in FIG. 13. Gas-phase NO₂, (1616 cm⁻¹), NO (1875 cm⁻¹), HNCO (2268 cm⁻¹) and CO₂ (2349 cm⁻¹) were observed when NaY zeolite with adsorbed urea was exposed to NO₂ at room temperature. For gas-phase HNCO, an isotopic shift of 8 cm⁻¹ was observed on substituting ¹⁵N for ¹⁴N. The complete list of isotopic shifts for nitrogen-containing gas-phase and adsorbed species is given in FIG. 6 and will be discussed in detail in later sections. In the spectra shown in FIG. 13, the absorption band for gas-phase NO₂ over nanocrystalline NaY zeolite is less intense than that over commercial NaY, indicating that more NO₂ was adsorbed/reacted with nanocrystalline NaY zeolite relative to commercial NaY. This is consistent with our previous observation that nanocrystalline NaY zeolite has a greater adsorption capacity for NO₂ relative to commercial NaY zeolite.

Urea-SCR of NO₂ in NaY Zeolite at T=473 K: Gas-Phase Products

An excess amount of O₂ was introduced into the IR cell after the NaY zeolite sample was equilibrated with NO₂ for 30 min at room temperature. Urea-SCR of NO₂ was then carried out at T=473 K. A control experiment was also done by heating the commercial NaY zeolite with adsorbed urea at T=473 K in the presence of oxygen.

FIG. 14 shows the FT-IR spectra of gas-phase species formed during the first 30 minutes of ¹⁵N-urea SCR over nanocrystalline NaY zeolite at T=473 K. In the beginning of the SCR reaction (t=0), gas-phase NO₂, NO, HNCO, CO₂, and a small amount of H₂O were observed in the FT-IR spectrum. At t=1 min, more H₂O and HNCO appeared in the gas phase as shown by the spectra (FIG. 14). Gas-phase HNCO decayed quickly after t=2 minutes. Several additional changes in the gas phase composition can be seen in these time course experiments, including the rapid production of ¹⁵NH₃ (927, 960, 1623 and 3331 cm⁻¹) and CO₂ at t=2 min. Gas-phase ¹⁵N-urea appeared and is identified by several characteristic absorptions, including three broad bands between 3100 and 3520 cm⁻¹ and several absorptions between 1290 and 1720 cm⁻¹ in the FT-IR spectra shown in FIG. 14. Furthermore, gas-phase NO₂ disappeared quickly relative to the concentration of NO. ¹⁵NNO (2201 and 1270 cm⁻¹) appeared in these spectra as the only isomer of N₂O (FIG. 6). Other isomers of N₂O such as N¹⁵NO and N¹⁴N₂O have different absorption frequencies (2178/1280 cm⁻¹ for N¹⁵NO and 2155/1265 cm⁻¹ for N¹⁴N₂O) and were not detected in our experiments. The formation of ¹⁵NNO in the gas phase indicates that N—N bond formation occurred at room temperature between a ¹⁵N-atom from urea and a ¹⁴N-atom from NO₂, and that the N—O bond in NO₂ remains intact during the formation of ¹⁵NNO. There was no significant change in the gas phase after 30 minutes of SCR reactions over nanocrystalline NaY zeolite.

Compared to the SCR reaction in nanocrystalline NaY zeolite, the urea-SCR of NO₂ in commercial NaY zeolite was much slower. The FT-IR spectra of the gas phase species present during the 2 hours of urea-SCR over commercial NaY zeolite are shown in FIG. 15. Similar to the spectra over the nanocrystalline NaY, NO₂, NO, HNCO, CO₂ and a small amount of H₂O were among the detectable gas-phase species present before the SCR reaction started (t=0). NO₂ disappeared quickly, but NO persisted in the gas phase during the two-hour reaction period. More gas-phase HNCO and H₂O appeared immediately after the heating began. The concentration of HNCO reached a maximum at t=5 min and HNCO remained detectable in the IR cell for at least 60 minutes during the SCR reaction process (FIG. 15). Compared to nanocrystalline NaY, a larger amount of gas-phase urea appeared over commercial NaY zeolite. There was an induction period (~3 min) for the production of NH₃ and CO₂ which did not appear in the gas phase with significant concentrations until t=4 min (FIG. 15). N₂O appeared as one of the final products in gas phase. It should be noted that a gas-phase species with an absorption around 2185 cm⁻¹ was present in the FT-IR spectra from t=4 min to 10 min. Since another absorption band at 1255 cm⁻¹ was also observed, this species is assigned to formonitrile oxide (HCN=O). Further supporting the assignment is the fact that HNCO (2190 and 1255 cm⁻¹) was produced in the presence of a large amount of HNCO during the thermal decomposition of urea at T=473 K in commercial NaY zeolite (not shown).

The time course concentrations of the gases in the infrared cell can be determined from the integrated absorbance of the corresponding bands using calibrated extinction coefficients, as described in previous work. The time course concentrations of gas-phase NH₃, CO₂ and H₂O in urea-SCR of NO₂ are shown in FIG. 16(a), (b) and (c), respectively. The time course concentrations for the urea thermal decomposition over commercial NaY zeolite are also included in FIG. 16.

In urea-SCR of NO₂ using nanocrystalline NaY zeolite as the catalyst, the concentration of NH₃ in the gas phase initially increased until a maximum was reached at approximately t=15 min (FIG. 16(a)). The concentration of NH₃ then gradually decreased and the remained at a constant level of approximately 55 μmol L⁻¹. The concentration of CO₂ also increased quickly during the first 15 minutes after the urea-SCR of NO₂ in nanocrystalline started (FIG. 16(b)). The concentration of gas-phase H₂O rapidly increased to a maximum at t=2 min, then decreased sharply until a minimum was reached at approximately t=15 min and started increasing again thereafter (FIG. 16(c)). Most likely, strongly adsorbed water that remained in nanocrystalline NaY zeolite was released initially upon heating to T=473 K, followed by the consumption and production of H₂O in SCR reactions.

In urea-SCR of NO₂ over commercial NaY zeolite, the changes in concentrations of NH₃, CO₂ and H₂O are quite different relative to the corresponding ones in nanocrystalline NaY zeolite (FIG. 16). For example, the concentration of NH₃ during urea-SCR over commercial NaY zeolite increased slightly, remained at a concentration lower than 30 μmol L⁻¹ and decreased after t=60 min (FIG. 16(a)). The final concentration of CO₂ over commercial NaY zeolite was about half of the final concentration over nanocrystalline NaY zeolite (FIG. 16(b)). The concentration of H₂O in gas phase during urea-SCR over commercial NaY zeolite increased initially and changed slightly after t=10 min (FIG. 16(c)). In the thermal decomposition of urea over commercial NaY zeolite, the concentration of NH₃ increased until a maximum was reached at t=40 min and then slightly changed thereafter (FIG. 16(a)). The time course concentrations of CO₂ and H₂O in the thermal decomposition of urea are just slightly lower than those in urea-SCR of NO₂ over commercial NaY zeolite (FIGS. 16(b) and 16(c)).

The time course concentrations of NO and N₂O in the gas phase are shown in FIGS. 17(a) and 17(b), respectively. In urea-SCR of NO₂ over nanocrystalline NaY zeolite, the concentration of NO decreased monotonically and gas-phase NO completely disappeared around t=40 min (FIG. 17(a)). When commercial NaY zeolite was used as the SCR catalyst, the concentration of NO initially increased until a maximum and decreased slowly thereafter. The time course concentration of N₂O demonstrates that N₂O was produced more quickly and
in much higher concentration in nanocrystalline NaY zeolite than in commercial NaY zeolite (Fig. 17(b)). The initial rates for formation of gas-phase NH₃, CO₂ and N₂O and loss of gas-phase NO can be obtained by linear fitting of the concentrations of individual gas-phase species in the beginning of the reactions, as listed in Fig. 7. In urea-SCR of NOₓ over nanocrystalline NaY zeolite, the initial rate of NH₃ formation is slightly higher than the initial formation rate of CO₂. Time course concentrations of NH₃ (Fig. 16(a)) and CO₂ (Fig. 16(b)) in the first 15 minutes of SCR reactions also indicate that the amount of NH₃ released into the gas phase is almost the same as the amount of CO₂. In the thermal reaction of urea over commercial NaY zeolite, the ratio of NH₃ formation rate to CO₂ formation rate is close to 2:1, which matches the fact that 1 mole of urea thermally decomposes into 2 moles of NH₃ and 1 mole of CO₂ (reactions 1 and 2). Furthermore, the initial rates for NH₃ and CO₂ formation are much higher in nanocrystalline NaY than in commercial NaY. Fig. 7 also includes the initial rates of NO formation and NO loss. It can be concluded from the data listed in Fig. 7 that urea-SCR of NOₓ occurred more quickly in nanocrystalline NaY than in commercial NaY zeolite.

Fig. 8 summarizes the product distribution in the gas phase after urea-SCR of NOₓ and thermal reaction of urea. In nanocrystalline NaY zeolite, the concentrations of NH₃ and CO₂ after SCR reaction are much higher than in commercial NaY zeolite. In addition, urea-SCR of NOₓ over nanocrystalline NaY zeolite resulted in 100% NO (NO₂ and NO) conversion and higher selectivity toward N₂O formation relative to commercial NaY zeolite. Based on mass balance for nitrogen, more than 80% of NOₓ was converted into N₂ in urea-SCR over nanocrystalline NaY zeolite at T=473 K (Fig. 8). Although about 17% of NO₂ was converted into N₂O in urea-SCR reactions over nanocrystalline NaY zeolite, it was observed that N₂O could be reduced into N₂ in nanocrystalline NaY zeolite at higher temperatures, which are more practical for typical engine operation.

Adsorbed Products Following Urea-SCR of NOₓ in NaY Zeolite at T=473 K

Besides kinetics studies, infrared analysis of surface adsorbed intermediates or products can assist in understanding the mechanism for urea-SCR of NOₓ. Difference FT-IR spectra of nanocrystalline NaY and commercial NaY zeolite after urea-SCR of NOₓ are shown in Fig. 18. The difference FT-IR spectrum of nanocrystalline NaY zeolite after urea-SCR of NOₓ and commercial NaY zeolite after thermal reaction of urea are also shown. The zeolite samples were cooled back to room temperature prior to recording the spectra. It was observed that most gas-phase NH₃, H₂O and urea disappeared from the gas phase after cooling the zeolites back to room temperature due to adsorption in the zeolite samples.

In urea-SCR of NOₓ over nanocrystalline NaY zeolite, the formation of adsorbed HNCO and OCN⁻ can be identified by the absorption bands at 2276 cm⁻¹ and 2169 cm⁻¹, respectively, in the FT-IR spectra shown in Fig. 18(b). The loss of adsorbed urea, characterized by the negative absorptions at 1271, 1527, 1712 cm⁻¹ (vCO), 3424 and 3514 cm⁻¹ (both vCN), can be seen as well in the spectrum. The absorption band at 1527 cm⁻¹ is assigned to the CNH bend-stretch mode where the nitrogen and hydrogen move in opposite directions relative to the carbon, while the absorption band at 1271 cm⁻¹ is assigned to the CNH open-stretch mode where NH and atoms move in the same direction relative to the carbon. In addition, the recovery of silanol groups (3742 cm⁻¹) and OH groups attached to Na⁺ (3695 cm⁻¹) are evident in the spectrum of nanocrystalline NaY zeolite shown in Fig. 18(b). This indicates that adsorption and SCR reactions occurred to a significant extent on the external surface since silanol groups are mainly present on the external surface of the nanocrystalline NaY zeolite.

The difference FT-IR spectrum of nanocrystalline after ¹⁵N-urea SCR of NOₓ for 30 min (Fig. 18(a)) is similar to that after urea-SCR for 2 h (Fig. 18(b)). The formation of adsorbed HNCO (2258 cm⁻¹) and OCN⁻ (2153 cm⁻¹) as well as the loss of adsorbed ¹⁵N-urea (1522 and 1266 cm⁻¹) are apparent in the spectrum. The isotopic shifts for these nitrogen-containing species are apparent in the spectra and are listed in Fig. 6. In the spectrum shown in Fig. 18(a), a dotted baseline is drawn in the range between 1200 and 1800 cm⁻¹, revealing that a small amount of nitrate remained in nanocrystalline NaY zeolite after 30 min of SCR reactions at T=473 K.

When commercial NaY zeolite was used as the SCR catalyst, the loss of adsorbed urea was observed, as indicated by the negative absorption bands at 1286 cm⁻¹ (vCO), 1651, 1712 cm⁻¹ (both vCO), 3436 and 3555 cm⁻¹ (both vCN) in the spectrum of commercial NaY zeolite after urea-SCR reactions (Fig. 18(c)). The other CNH vibration which should fall between 1400 and 1600 cm⁻¹ can be less pronounced in the spectrum due to the formation of two absorption bands at 1455 and 1495 cm⁻¹ (Fig. 18(c)). The two absorption bands at 1455 and 1495 cm⁻¹ are assigned to the bending mode of adsorbed ammonium ion and stretching mode of surface species containing imine groups (C=NIH), respectively. In the spectrum shown in Fig. 18(c), the corrected baseline (dotted line) in the range between 1200 and 1800 cm⁻¹ clearly demonstrates the formation of adsorbed biuret (1759 cm⁻¹) and cyannic acid (1735 cm⁻¹) in commercial NaY zeolite after SCR reactions. Furthermore, surface OCN⁻ (2175 cm⁻¹) and nitrate (1376 cm⁻¹) were observed after urea-SCR of NOₓ for 2 hours in commercial NaY zeolite. In the O/H/NIH stretching region (Fig. 18(c)), the absorptions in the spectrum of commercial NaY zeolite indicate the formation of OCN⁻ on Na⁺ (3695 cm⁻¹), surface adsorbed H₂O (3623 cm⁻¹) and NH-containing species (3220, 3380, 3489 cm⁻¹) as well as the loss of adsorbed urea (3436 and 3555 cm⁻¹). The FT-IR spectrum of commercial NaY zeolite after thermal reaction of urea is almost the same as the spectrum after urea-SCR of NOₓ, except that the formation of nitrate, biuret or cyannic acid are not observed in the thermal decomposition of urea (Fig. 18(d)).

The comparison between the difference FT-IR spectra of the zeolite samples after urea-SCR of NOₓ for 2 hours indicates that higher conversion of nitrate was achieved in nanocrystalline NaY zeolite than in commercial NaY zeolite. This is consistent with the fact that urea-SCR of NOₓ is much slower in commercial NaY than in nanocrystalline NaY, as mentioned previously (Fig. 7). Furthermore, undesired surface products (biuret and cyannic acid) were observed in commercial NaY zeolite after urea-SCR of NOₓ, but not in nanocrystalline NaY zeolite.

The assignments of absorption bands in FT-IR spectra shown in Fig. 18 are further supported by isotopic studies (Fig. 6). The absorption frequencies for HNCO and OCN⁻ in nanocrystalline NaY zeolite are different from those in commercial NaY zeolite. In nanocrystalline NaY, HNCO (2276 cm⁻¹) and OCN⁻ (2169 cm⁻¹) most likely adsorbed on EFAL sites. In commercial NaY zeolite, OCN⁻ is characterized by the relatively intense absorption band at 2175 cm⁻¹ in the FT-IR spectrum shown in Fig. 18(c) and most likely attached to Na⁺ sites. In nanocrystalline NaY zeolite, the isotopic shift for the CNH vibration mode of adsorbed urea (5 cm⁻¹) is exactly the same as that for the NH₃ deformation mode of
gas-phase NH$_3$. This suggests that urea adsorbed in nanocrystalline NaY zeolite in a way that at least one NH$_3$ group was almost unperturbed. In commercial NaY zeolite, the isotopic shift for the C=O stretching mode of adsorbed biuret and cyanuric acid (8 cm$^{-1}$) is the same as that for the NCO stretching mode of gas-phase HNCO. This can be due to the configuration, exchange —(C=O)—NH$_2$—S—(C=O)—N — in adsorbed biuret and cyanuric acid in commercial NaY zeolite.

Complementary Solid State NMR ($^{13}$C and $^{15}$N) Spectra of Labeled Urea, NO and O$_2$ on Nanocrystalline NaY The $^{13}$C MAS NMR spectra for urea ($^{13}$C and $^{15}$N labeled), NO, and O$_2$ on nanocrystalline NaY, shown in Fig. 18(a), has a $^{13}$C peak at 165 ppm prior to heating. This peak is assigned to the carbonyl group of adsorbed urea. After heating to T=423 K, there is a narrow intense peak present at 125 ppm that can be assigned to CO$_2$. After heating to T=623 K, there is a substantial increase in peak intensity for CO$_2$ at 125 ppm while the peak at 165 ppm is no longer present. Fig. 19(b) shows the $^{15}$N MAS NMR of urea ($^{13}$C and $^{15}$N labeled), NO, and O$_2$ on nanocrystalline NaY. Before heating, the $^{15}$N peak at ~301 ppm is present and is assigned to the adsorbed urea. After heating to T=423 K, ammonia is produced as indicated by the peak at ~356 ppm. After heating to T=523 K, a peak at ~74 ppm is present and is assigned to N$_2$. After heating to T=623 K, there is substantial increase in N$_2$ peak and loss of intensity for the ammonia peak.

The solid state NMR spectra were acquired under conditions of thermal equilibrium due to the long periods of time required for signal averaging. In the presence of oxygen, the adsorption of NO in zeolite Y occurs in a similar manner as the adsorption of NO$_2$ due to the oxidation of NO into NO$_2$. Thus these NMR results can be readily compared to the FT-IR data in this study. The NMR results are also found to be consistent with the FT-IR results in that urea thermally decomposes to form NH$_3$ and CO$_2$ at elevated temperatures in the presence of NO and O$_2$. The most important aspect of the NMR results is the observation of the formation of N$_2$ which cannot be directly observed by FT-IR spectroscopy. As discussed previously, more than 80% of NO$_2$ was converted into N$_2$ in urea-SCR over nanocrystalline NaY zeolite based on mass balance for nitrogen (Fig. 8).

Reactions Between Gas-Phase NO$_2$ and Adsorbed Urea in NaY Zeolite at T=298 K

In this study, NO$_2$ adsorption in NaY zeolite occurs preferentially according to reaction 3 or 4 since there was a considerable amount of water remaining in the zeolite after evacuating the zeolite samples at room temperature.

\[ \text{N}_2 \text{O} + \text{H}_2 \text{O} \rightarrow \text{HNO}_2 + \text{HONO} \]  
\[ \text{N}_2 \text{O}_3 + \text{H}_2 \text{O} \rightarrow 2\text{HONO} + \text{NO} \]  
(3)  
(4)

The nitric acid and nitrous acid further deprotonate and adsorb on surface cationic sites to form surface nitrate and nitrite. This explains the formation of surface nitrate, nitrite (Fig. 12) and gas-phase NO$_2$ adsorption in NaY zeolite (Fig. 13). The formation of nitrate on EFAL sites in nanocrystalline NaY zeolite was also observed (Fig. 12). In nanocrystalline NaY zeolite, NO$_2$ adsorption in part occurs on cationic sites of EFAL species (M$^{n+}$O$^{2-}$), according to reaction 5.

\[ M^{n+} + NO_2 \rightarrow M^{n+} + NO_2^- \]  
(5)

The formation of NO, HNCO and a small amount of CO$_2$ and H$_2$O was observed when NO$_2$ was adsorbed in NaY zeolite with adsorbed urea at room temperature (Figs. 13, 14) and 15). Isotopic labeling shows that the N-atom in HNCO originates from urea (Fig. 14). The loss of adsorbed urea was observed as well upon the adsorption of NO$_2$ (Fig. 13). Since the decomposition of urea into HNCO and NH$_3$ is not significant at room temperature, HNCO most likely formed in the reactions between urea and HNCO$_2$ (reaction 6). The reaction between urea and HNCO can lead to the formation of CO$_2$ and H$_2$O at room temperature.

\[ \text{NH}_2\text{CO} + \text{HNCO} \rightarrow \text{HNCO} + \text{NH}_3 \]  
\[ \text{NH}_2\text{CO} + 2\text{HNCO} \rightarrow 2\text{H}_2\text{O} + 2\text{NH}_3 \]  
\[ \text{HNCO} \rightarrow \text{N}_2 + \text{CO} + \text{H}_2 \text{O} \]  
(6)  
(7)

NH$_2$NO$_2$ can thermally decompose into N$_2$O$_2$+2H$_2$O providing a minor route for N-N bond formation in urea-SCR of NO$_2$ in NaY zeolite. Reaction 7 is used in destroying excess nitrous acid in diizotization.

When commercial NaY zeolite was exposed to NO$_2$ at room temperature, surface species with a linear imido structure such as biuret appeared, most likely generated in the reactions between HNCO and adsorbed urea (Fig. 12). It is reported that amide carbonyls of bi- and tri-uretes have characteristic absorbance bands around 1750-1770 cm$^{-1}$. Biuret can be produced via reaction 8.

\[ \text{HN}_2\text{CO} - \text{NH}_2\text{CO} \rightarrow \text{HNCO} + \text{NH}_2\text{CO} \]  
\[ \text{HN}_2\text{CO} - \text{NH}_2\text{CO} + \text{HNCO} \rightarrow \text{HNCO} + \text{HNCO} + \text{NH}_2\text{CO} \]  
\[ \text{HNCO} \rightarrow \text{N}_2 + \text{CO} + \text{H}_2 \text{O} \]  
(8)

The above analysis suggests that EFAL species in nanocrystalline NaY zeolite provide additional surface sites for NO$_2$ adsorption and its further reactions at room temperature. Previous studies show that EFAL sites on the external surface of nanocrystalline NaY zeolite are important for the formation of reactive nitrate and for the following SCR reactions. In this study, EFAL sites in nanocrystalline NaY zeolite also provide important surface adsorption sites for HNCO and inhibit the formation of undesired products such as biuret or triuret.

Thermal Decomposition of Urea in Nanocrystalline NaY Zeolite at T=473 K

The FT-IR spectra of the gas phase shown in Fig. 14 demonstrate that the thermal decomposition of urea occurred at T=473 K in nanocrystalline NaY zeolite. As described previously, gas-phase HNCO was produced initially and decayed rapidly after t=2 min (Fig. 14). The initial change in H$_2$O concentration (Fig. 16(a)) is similar to that of HNCO. Not until t=2 min did the concentration of NH$_3$ in gas phase start to increase sharply (Fig. 16(a)). According to reaction 1, the first step in thermal decomposition of urea produces equal amounts of HNCO and NH$_3$. This suggests that most of the NH$_3$ produced in thermal decomposition of urea remained in the nanocrystalline NaY zeolite. In addition, the concentrations of NH$_3$ and CO$_2$ in gas phase increased sharply after t=2 min (Figs. 16(a) and 16(b)). The kinetic data in Fig. 7 show that the initial formation rates of NH$_3$ and CO$_2$ in gas phase are 10.3 and 8.9 pmol L$^{-1}$ min$^{-1}$, respectively. This correlates well with the stoichiometry shown by reaction 2, in which 1 mole of HNCO hydrolyzes to form 1 mole of NH$_3$ and 1 mole of CO$_2$. Most likely, NH$_3$ formed in hydrolysis of HNCO in the zeolite immediately goes into the gas-phase at T=473 K.

Furthermore, both the loss of adsorbed urea and regeneration of surface silanol groups were observed in nanocrystalline NaY zeolite after urea-SCR of NO$_2$ (Fig. 18). The absorption frequencies for the urea bands (1527 and 1271 cm$^{-1}$) in the FT-IR spectrum of nanocrystalline NaY zeolite are different from those (1286 cm$^{-1}$) in the spectrum of commercial NaY zeolite which contains few silanol groups (Fig. 6). It can be concluded that in nanocrystalline NaY zeolite the
adsorption and the thermal decomposition of urea involved the silanol groups on the external surface. Finally, HINC produced in thermal decomposition of urea adsorbed and hydrolyzed on EFA sites in nanocrystalline NaY zeolite. This is supported by the fact that HINC adsorbed on EFA sites was observed before (Fig. 12) and after urea-SCR of NO₂ (Fig. 18) in nanocrystalline NaY zeolite.

Based on the above discussion, a mechanism can be proposed for the thermal decomposition of urea in nanocrystalline NaY zeolite (Fig. 9). Initially, urea adsorbed in nanocrystalline NaY zeolite by hydrogen bonding to silanol groups on the external surface. At elevated temperature (T = 473 K), urea decomposed into HINC and NH₂. While NH₂ remained on the silanol groups of nanocrystalline NaY zeolite via hydrogen bonding, HINC adsorbed on EFA sites and continued to hydrolyze and produce NH₃ and CO₂.

It is generally accepted that NH₃ is the actual reducing agent in urea-SCR of NO₂. In Fig. 9, urea adsorbed in nanocrystalline NaY zeolite by hydrogen bonding to silanol groups via one N-atom, leaving the other NH₂ almost unperturbed. This is consistent with the isotopic studies showing that the isotopic shift for the CNH vibration mode is the same as the isotopic shift for the NH₂ deformation mode of gas-phase NH₃ (Fig. 6). In addition, we suggest that NH₃ molecules produced in thermal decomposition of urea remained in nanocrystalline NaY zeolite by hydrogen bonding with silanol groups on the external surface. When NH₂ was adsorbed in nanocrystalline NaY zeolite at room temperature, the loss of silanol groups was observed. NH₃ adsorbed on EFA sites in nanocrystalline NaY zeolite was observed, too. In urea-SCR of NO₂ over nanocrystalline NaY, however, EFA sites are more likely associated with the adsorption/reactions of nitrate and HINC as discussed previously.

Deposition of urea occurred when the nanocrystalline NaY zeolite with adsorbed urea was heated at T = 473 K, as shown by the presence of urea in the gas phase (Fig. 14). The spectra shown in Fig. 14 also indicate that most gas-phase urea stayed as stable species during the SCR reactions at T = 473 K.

Formation of N—N Bond in Urea-SCR of NO₂ Over Nanocrystalline NaY Zeolite at T = 473 K

When nanocrystalline NaY zeolite was used in urea-SCR of NO₂, more than 80% of the total loaded NO₂ was converted into N₂, based on nitrogen mass balance. In this work, N₂ cannot be monitored directly by infrared spectroscopy, but was observed in complementary solid state NMR experiments. Isotopic studies show that only 15NNO among four isotomers of N₂O was produced when 15N-urea was used in the SCR reactions (Fig. 14). Previous studies in literature suggest that N—N bond formation occurs in the reaction between NO₂ and NH₂ produced in thermal decomposition of urea. Based on isotopic labeling studies, it can be concluded that the formation of dinitrogen in urea-SCR of NO₂ over NaY zeolite involves both a N-atom from NO₂ and a N-atom from urea. As for the production of N₂O, the bond formation occurs when a N-atom from urea binds with NO from NO₂ through the N-atom.

In selective catalytic reduction of NO₂ using hydrocarbons, isotopic studies have shown that the N—N bond formation occurs between NO₂ from the gas phase and a surface N-containing adsorbate. In urea-SCR of NO₂ over nanocrystalline NaY zeolite, the N—N bond formation is complex since reaction might involve (i) surface adsorbed NH₂ and/or gas-phase NH₂ and/or gas-phase NO₂ and/or surface NO₂⁻ (NO₂⁻ and NO₃⁻).

Previous studies on thermal reduction of NO₂ in nanocrystalline NaY zeolite demonstrated that NO was initially generated in thermal reactions of nitrate and nitrite at elevated temperatures according to reactions 9–11. M⁺ represents Na⁺ or EFA sites.

\[ \text{M}^+\text{NO}_3^- \rightarrow \text{M}^+\text{O}^+ + \text{NO}_2 \]  \hspace{1cm} (9)

\[ \text{M}^+ + 2\text{NO}_2 \rightarrow \text{M}^+\text{NO}_3^- + \text{NO} \]  \hspace{1cm} (10)

\[ \text{M}^+\text{NO}_3^- + \text{NO}_2 \rightarrow \text{M}^+\text{NO}_3^- + \text{NO} \]  \hspace{1cm} (11)

Although the concentration of NO decreased monotonically in urea-SCR of NO₂ over nanocrystalline NaY zeolite (Fig. 17(a)), further analysis suggests that the formation of NO in reactions 9–11 could reflect the initial rate of NO₂ formation was much greater than the initial rate of NO loss in urea-SCR of NO₂ over nanocrystalline NaY zeolite (Fig. 7). The actual initial rate for N—N bond formation should be even greater since more than 80% of NO₂ was converted into N₂ in urea-SCR of NO₂ over nanocrystalline NaY zeolite. In urea-SCR of NO₂ over commercial NaY zeolite, the concentration of NO initially increased and then decreased after a maximum at t = 9 min (Fig. 17(a)), indicating that both production and consumption of NO occurred at elevated temperature. Similar time course concentration of NO has been observed in propylene-SCR of NO₂ in nanocrystalline NaY zeolite.

It has been suggested that OH groups and Bronsted acid sites on the catalyst surface can coordinate with and further activate NH₂. Fig. 10 describes a possible pathway for N—N bond formation in urea-SCR of NO₂ over nanocrystalline NaY zeolite. In the mechanism shown by Fig. 10, NO is released during the thermal reactions of nitrate and nitrite attached to Na⁺ or EFA sites and reacts with hydrogen bonded NH₂ to produce N₂ (or N₂O) and H₂O. Reaction 12 is the standard SCR reaction using NH₃.

\[ 4\text{NH}_{3} + 4\text{NO} + 3\text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \]  \hspace{1cm} (12)

From the above discussion, a mechanism in which N—N bond formation in urea-SCR over nanocrystalline NaY zeolite occurs on the external surface and involves surface adsorbed NH₂ and NO from the gas phase is proposed. Minor pathways for N—N bond formation in nanocrystalline NaY zeolite include the thermal decomposition of NH₂NO₃ and NH₂NO₂ produced in the reaction between HNO₃ and urea (reaction 6). As it has been previously suggested that urea initially decomposes into CO and an NH₂ radical which consequently reacts with NO₂ to form N₂. However, this pathway is unlikely in urea-SCR over nanocrystalline NaY zeolite since CO was not observed in this study.

Origin of Size Effect in Urea-SCR of NO₂ Over NaY Zeolite

Reducing the zeolite crystal size can increase the external surface area and dramatically alter the diffusional properties of the zeolite materials. Infrared characterization revealed that silanol groups and EFA sites on the external surface are present in greater concentration in nanocrystalline NaY zeolite than in commercial NaY zeolite due to the difference in external surface areas. The external surface areas of nanocrystalline NaY and commercial NaY zeolite are 178 and 4 m²/g, respectively. Silanol groups and EFA sites on the external surface were found to be responsible for the improved performance of nanocrystalline NaY zeolite in propylene-SCR of NO₂. In the present study, urea-SCR of NO₂ using nanocrystalline NaY zeolite as the catalyst led to a significantly greater SCR reaction rate and less formation of undesired products than urea-SCR in commercial NaY.

The SCR reactions in nanocrystalline NaY zeolite occurred more quickly than in commercial NaY zeolite, as indicated by the initial rates for NO loss and N₂O production.
listed in FIG. 7. Consequently, higher NOx conversion was achieved in nanocrystalline NaY than in commercial NaY zeolite after urea-SCR for 2 hours (FIG. 8). A significant amount of nitrate remained in commercial NaY zeolite after urea-SCR of NO2 for 2 hours, but nitrate was barely observed in nanocrystalline NaY zeolite after 30 min (FIG. 18(a)). The enhanced SCR reaction rate in urea-SCR over nanocrystalline NaY zeolite can be explained by the presence of both silanol groups and EFAL sites. As described by FIG. 10, urea-SCR of NO2 in nanocrystalline NaY zeolite involves both the production of NO from nitrate and the N—N bond formation between NO and NH3 adsorbed on silanol groups. First, the silanol groups and EFAL species possess diffusional advantages since they are both located on the external surface of the nanocrystalline NaY zeolite. Furthermore, they are considered as chemically distinct surface sites. A major conclusion of this study and previous studies is that nitrate adsorbed on EFAL sites on the external surface of nanocrystalline NaY zeolite is more reactive than nitrate in the internal pores adsorbed to Na+. The activation of NH3 by silanol groups is also important for N—N bond formation.

As shown in FIG. 9, EFAL species in nanocrystalline NaY zeolite also provides important sites for the adsorption and fast hydrolysis of HNCO, which is essential for avoiding isocyanic acid emission and inhibiting the formation of undesired products. The kinetic data listed in FIG. 7 indicate that the hydrolysis of HNCO in nanocrystalline NaY zeolite occurred at a much faster rate compared to that in commercial NaY zeolite. This is consistent with the observation that gas-phase HNCO persists for a much longer period of time (~60 min, FIG. 15) in the presence of commercial NaY zeolite compared to nanocrystalline NaY zeolite (~20 min, FIG. 14). The time course measurements for H2O also indicate that hydrolysis happens much faster in nanocrystalline NaY zeolite than in commercial NaY zeolite (FIG. 16(c)).

To conclude, silanol groups and EFAL species are physically and chemically distinct surface sites, which are present on the external surface of nanocrystalline NaY zeolite. These sites are responsible for the improved performance of nanocrystalline NaY zeolite relative to commercial NaY since the majority of urea-SCR reactions occur on the external surface. The role of the internal surface is to store the NO2 prior to SCR reactions on the external surface. Thus nanocrystalline alkali zeolites can be classified as new materials for SCR catalysts with potentially significantly better performance.

Urea-SCR vs. Propylene-SCR of NO2 in Nanocrystalline NaY Zeolite

In a previous study, nanocrystalline NaY zeolite was examined in deNOx reactions at T=473 K using propylene as the reducing agent. It was found that nanocrystalline NaY zeolite was very sensitive to pre-adsorbed water in propylene-SCR of NO2. Compared to urea-SCR, propylene-SCR appears to be a less realistic deNOx technology under typical conditions of humid, oxygen rich exhaust streams.

Although the effect of adsorbed water on urea-SCR is not studied in this work, water should not be detrimental to deNOx with urea over nanocrystalline NaY zeolite. First, water is necessary for the hydrolysis of HNCO in urea-SCR reactions (reaction 2). Second, it is suggested from the above discussion that at elevated temperature H2O did not inhibit the adsorption of NH3 in nanocrystalline NaY zeolite. In urea-SCR of NO2 over nanocrystalline NaY zeolite, the concentration of H2O in gas phase kept increasing after the urea-SCR reactions were finished around t=40 min (FIG. 16(c)). FIG. 16(c) indicates that the concentration of NH3 in gas phase further decreased after t=40 min. Since the oxidation of NH3 by O2 was not significant under the experimental conditions described in this work, NH3 most likely adsorbed on available silanol groups and/or EFAL sites in nanocrystalline NaY zeolite in the presence of water.

Compared to urea-SCR, a significant amount of nitrate and carbonaceous deposit remained in nanocrystalline NaY zeolite after propylene-SCR of NO2 at 473 K for 6 hours. The carbonaceous deposit in nanocrystalline NaY zeolite was found to hinder the adsorption of propylene and NO2 and further SCR reactions. In urea-SCR of NO2 over nanocrystalline NaY zeolite, surface nitrate was not observed after 2 hours of SCR reactions. Surface HNCO and OCN- were the only undesired products formed in urea-SCR over nanocrystalline NaY zeolite (FIG. 18). Furthermore, more than 80% of NO2 was converted into N2 in urea-SCR relative to ~20% selectivity to N2 formation in propylene-SCR of NO2 over nanocrystalline NaY zeolite. As mentioned previously, NOx emissions emerge at high velocity under typical lean burn conditions. At low temperatures, urea-SCR over nanocrystalline NaY zeolite appears to be an even more promising deNOx technology than propylene-SCR.

Location of EFAL Species

FIG. 20 shows the FT-IR spectra of nanocrystalline NaY zeolite and commercial sample after being heated overnight under vacuum at T=623 K. In the spectrum of nanocrystalline NaY zeolite, three absorptions are observed in the spectral region between 3765 and 3630 cm⁻¹. The most intense and highest frequency band at 3744 cm⁻¹ is assigned to terminal silanol groups that are on the external surface of the zeolite crystals. This feature is of much weaker intensity in the commercial NaY sample as expected since the external surface area is ~40 times smaller than the nanocrystalline NaY sample. The absorption band at 3695 cm⁻¹ is assigned to hydroxyl groups attached to Na+. The band at 3656 cm⁻¹ is associated with hydroxyl groups attached to extra framework alumina (EFAL) species. Pyridine adsorption experiments coupled with FT-IR analysis have revealed the existence of Bronsted acid sites as well as Lewis acid sites associated with EFAL species only present in nanocrystalline NaY zeolite.

In order to determine the location of the EFAL species, adsorption of pyridine and 2,6-Di-tet-butylpyridine (DBTBP) in nanocrystalline NaY zeolite was conducted. It has been suggested that most EFAL species are located on the external surface of zeolite Y. While pyridine can adsorb into the zeolite pores, DBTBP can only interact with the hydroxyl groups on the external surface (and in the pore mouth region) of the zeolites since its kinetic diameter is larger than the pore opening of Y zeolites. Thus DBTBP was used as a probe molecule to characterize acid sites located on the external surface of the zeolites. The difference FT-IR spectra after pyridine and DBTBP adsorption on nanocrystalline NaY zeolite are shown in FIG. 20 (inset). The integrated absorbance of the negative peak at 3656 cm⁻¹ is approximately proportional to the amount of EFAL species with Bronsted acidity in nanocrystalline NaY zeolite. After DBTBP and pyridine adsorption on nanocrystalline NaY zeolite, the integrated absorbance of the negative peak at 3656 cm⁻¹ are ~0.51 and ~0.62, respectively. Therefore, it can be concluded that more than 80% of the EFAL species with Bronsted acidity are located on the external surface of nanocrystalline NaY zeolite.

Discussion

Nanocrystalline NaY zeolite exhibits enhanced de-NOx at low temperature (T=473 K) compared to commercial NaY zeolite, as shown by the present study on the selective catalytic reduction of NO2 with urea. Silanol groups and EFAL
species on the external surface of nanocrystalline NaY were found to be responsible for the higher SCR reaction rate and decreased formation of undesired products relative to commercial NaY zeolite. Isotopic labeling coupled with infrared analysis indicates that N—N bond formation involves both a N-atom from NO\textsubscript{2} and a N-atom from urea. In nanocrystalline NaY zeolite, kinetic studies indicated that NH\textsubscript{3} formed in thermal decomposition of urea was activated by hydrogen bonding with silanol groups and NO was initially produced in the thermal reaction of nitrate on EFAL sites. Consequently N—N bond formation occurred between NH\textsubscript{3} adsorbed on silanol groups and NO from the gas phase.

Nanocrystalline alkali zeolites can be visualized as new catalytic materials that have NO\textsubscript{2} storage capacity in the internal pores and high reactivity on the external surface. This provides multifunctional capabilities beyond that found for zeolites with a larger crystal size and smaller external surface area. Although for shape selective catalysis, the reactivity of the external surface can be undesirable, in reactions such as deNO\textsubscript{2} or hydrocarbon cracking, nanocrystalline zeolite catalysts can have greatly enhanced reactivity due to reactions on the external surface. This is the first example in the literature demonstrating that the increased external surface area (up to ~40% of the total surface area) of nanocrystalline zeolites can be utilized as a reactive surface with unique active sites for catalysis.

What is claimed is:

1. A method for the reduction of reactant gases comprising:
   (a) contacting a nanocrystalline zeolite with a reductant, sufficient to produce a nanocrystalline zeolite with adsorbed reductant thereon; and
   (b) exposing the nanocrystalline zeolite with adsorbed reductant thereon to reactant gases, for a sufficient time and at a sufficient temperature to obtain reduction of the reactant gases;

2. The method of claim 1, wherein the nanocrystalline zeolite has a particle size of less than about 100 nm;

3. The method of claim 1, wherein the reactant gases comprise nitric oxide (NO).

4. The method of claim 1, wherein the reactant gases comprise nitrogen dioxide (NO\textsubscript{2}).

5. The method of claim 1, wherein the reactant gases comprise oxides of nitrogen (NO\textsubscript{x}).

6. A method for the reduction of reactant gases comprising:
   (a) contacting a nanocrystalline zeolite with a reductant, sufficient to produce a nanocrystalline zeolite with adsorbed reductant thereon; and
   (b) exposing the nanocrystalline zeolite with adsorbed reductant thereon to reactant gases, for a sufficient time and at a sufficient temperature to obtain reduction of the reactant gases;

7. The method of claim 6, wherein the nanocrystalline zeolite comprises a transition metal, alkali, or alkaline earth nanocrystalline zeolite Y.

8. The method of claim 6, wherein the nanocrystalline zeolite comprises zeolite NaY.

9. The method of claim 6, wherein the reactant gases comprise nitric oxide (NO).

10. The method of claim 6, wherein the reactant gases comprise nitrogen dioxide (NO\textsubscript{2}).

11. The method of claim 6, wherein the reaction products comprise water, nitrogen gas (N\textsubscript{2}), nitrous oxide (N\textsubscript{2}O), or any combination thereof.

12. The method of claim 6, wherein the reactant gases comprise oxides of nitrogen (NO\textsubscript{x}).

13. A method for the reduction of reactant gases comprising:
   (a) contacting a nanocrystalline zeolite with a reductant, sufficient to produce a nanocrystalline zeolite with adsorbed reductant thereon; and
   (b) exposing the nanocrystalline zeolite with adsorbed reductant thereon to reactant gases, for a sufficient time and at a sufficient temperature to obtain reduction of the reactant gases;

14. The method of claim 13, wherein the reactant gases comprise oxides of nitrogen (NO\textsubscript{x}).

15. The method of claim 13, wherein the reductant comprises ammonia.

16. The method of claim 13, wherein the reactant gases comprise nitric oxide (NO).

17. The method of claim 13, wherein the reactant gases comprise nitrogen dioxide (NO\textsubscript{2}).

18. The method of claim 13, wherein the reaction products comprise water, nitrogen gas (N\textsubscript{2}), nitrous oxide (N\textsubscript{2}O), or any combination thereof.

19. The method of claim 13, wherein the reactant gases comprise oxides of nitrogen (NO\textsubscript{x}).
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In column 17, line 61, delete "(M"\textsuperscript{2+}-O\textsuperscript{2-})" and insert -- (M"\textsuperscript{2+}-O\textsuperscript{2-}), --, therefor.

In column 17, line 63, delete " M"\textsuperscript{2+}·O\textsuperscript{-}+NO\textsubscript{2}→M"\textsuperscript{2+}·NO\textsubscript{3}\textsuperscript{-} " and insert -- M"\textsuperscript{2+}·O\textsuperscript{-} + NO\textsubscript{2} → M"\textsuperscript{2+}·NO\textsubscript{3}\textsuperscript{-} --, therefor.

Signed and Sealed this
Twenty-second Day of March, 2011

David J. Kappos
Director of the United States Patent and Trademark Office