

Graphite oxide activated zeolite NaY: applications in alcohol dehydration†

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2013, **3**, 135Alexander D. Todd^a and Christopher W. Bielawski^{*ab}

A mixture of graphite oxide (GO) and the zeolite NaY (Si/Al = 5.1) was used to dehydrate various alcohols to their respective olefinic products. Using conditions optimized for 4-heptanol (15 wt% GO–NaY (1 : 1 wt/wt), 150 °C, 30 min), a series of secondary and tertiary aliphatic alcohols were cleanly dehydrated in moderate to excellent conversions (27.5–97.2%). Several primary alcohols were also dehydrated, although higher catalyst loadings (200 wt% GO–NaY (1 : 1) and longer reaction times (3 h) were required. The enhanced dehydration activity was attributed to the ability of GO to convert NaY to an acidic form and without the need for ammonium cation exchange and/or high temperature calcination.

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Introduction

The use of solid acid catalysts (SACs) has become increasingly important for applications in industry as well as academia. The benign nature of SACs has been shown to be an effective alternative to conventional mineral acids such as H₂SO₄, HCl, HF, and H₃PO₄.¹ Moreover, SACs possess advantages over their homogeneous counterparts, particularly in terms of separation, adaptation to flow reactor systems, and negating the need for corrosion resistant equipment.^{1,2} The composition and structure of SACs is diverse and includes alumina and modified alumina,^{3,4} modified zirconia,⁵ reactive clays,⁶ sulfonated polymer resins,^{7–9} carbon-based materials,^{10–15} and zeolites.^{16–19} Zeolites, which are high-surface area aluminosilicates with a well-defined structure, are among the most widely used SACs largely because they are employed in the petroleum industry as fluid cracking catalysts.²⁰ Although zeolites can assume a variety of structures and compositions, the protic form (*i.e.*, H⁺ as the counter cation) has shown remarkable utility in the dehydration of alcohols as well as other organic transformations that require acid catalysts (*e.g.*, deprotections,²¹ transesterifications,²² macrolactonizations of hydroxyacids,²³ and cyclizations²⁴).

There are two widely used methods for preparing the protic form of zeolites: (1) ion exchange or (2) high temperature (>400 °C) calcination of an NH₄⁺ exchanged precursor. For the former process, only high silica zeolites effectively undergo ion exchange with protons *via* mineral acid washing. Zeolites with low silica content (*e.g.*, NaY) are prone to structural damage *via* dealumination when exposed to strong mineral acids.²⁵

Carbon-based SACs have also been used in various catalytic applications. For example, activated carbons treated with different chemical reagents (HNO₃, Cl₂, NH₃, air, *etc.*) have been examined for their abilities to dehydrate/dehydrogenate isopropanol.¹³ Although good conversions were observed in these reactions, high catalyst loadings (>1000 wt%) were required. Sulfonated pyrolyzed carbon sources such as olive stone, sucrose and starch have also been utilized as SACs for the dehydration of ethanol, the esterification of glycerol, and the hydration of 2,3-dimethyl-2-butene, respectively.^{11,12,14} These sulfonated carbon materials maintain a high level of acidity even in the presence of water which offers advantages over traditional inorganic oxides such as zeolites, whose acidity can be compromised under aqueous conditions.¹¹ Unfortunately, the pyrolysis step required to prepare these sulfonated catalysts utilizes temperatures that commonly exceed 400 °C.

Recently, graphite oxide (GO), an acidic, insoluble carbon-based material known for more than 150 years,²⁶ was found to mediate a variety of acid catalyzed transformations,^{27–29} including the ring opening polymerization of lactones and the dehydration polymerization of benzyl alcohol.^{28,29} GO is an ideal candidate for use in solid acid catalysis due to its relatively low cost, heterogeneous state, and ease of preparation.³⁰ The material is typically synthesized in one step by treating natural flake graphite with KMnO₄ in H₂SO₄ at room temperature followed by filtration.

^a Department of Chemistry and Biochemistry, The University of Texas at Austin,
1 University Station, A1590, Austin, TX, 78712, USA.
E-mail: bielawski@cm.utexas.edu

^b World Class University (WCU) Program of Chemical Convergence for Energy & Environment (C₂E₂), School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Korea

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As a result of the oxidation process, various functional groups are installed (*e.g.*, hydroxyl, epoxide, carboxylic acid, *etc.*) and enable the material with catalytic properties.³¹

Although heterogenous composites comprised of carbons and zeolites have gained attention for their applications in separation, gas absorption, templating agents, and photocatalysis,^{32–36} the catalytic activities of such composites are relatively unexplored. Considering the complementary acidic characteristics displayed by zeolites and GO, we hypothesized that the two materials may function in a synergistic manner to promote their intrinsic catalytic activities. Herein we explore the abilities of mixtures of NaY and GO to facilitate the dehydration of alcohols, a reaction of significant industrial importance.³⁷ We show that the GO exchanges its protons with the zeolite's sodium ions and that the resulting mixture facilitates the dehydration of primary, secondary, and tertiary alcohols under mild conditions.

Results and discussion

As summarized in Table 1, initial studies focused on the dehydration of 1-octanol using a mixture of either GO–NaY or GO–NH₄Y. In a preliminary experiment, 1-octanol (50.0 mg), GO (50 mg), zeolite (50 mg) and CDCl₃ (0.5 mL) were added to a pressure tube which was sealed and then mixed with constant stirring at 150 °C for 3 h. Upon cooling to room temperature, the contents of the reaction vessel were filtered through a 0.2 μm PTFE syringe filter into a NMR tube containing a standard (mesitylene, 10 μL) and the conversion of starting material to product were measured by quantitative ¹H NMR spectroscopy. The highest conversion of 1-octanol to its dehydration products (46.9% to a mixture of olefins and 32.3% to di-*n*-octyl ether) was achieved using a combination of GO and NaY (entry 1).

Table 1 Preliminary studies for the dehydration of 1-octanol using various GO–zeolite mixtures^a

Entry	Catalyst ^b	Olefins ^c (% conv.)	Ether (% conv.)	Total (% conv.)
1	GO–NaY	46.9	32.3	83.9
2	GO–NH ₄ Y	4.4	<1.0	15.8
3 ^d	GO	3.7	5.0	77.2
4	NaY	6.1	<1.0	10.0

^a Commercial Y zeolites were obtained from Zeolyst International (Si/Al = 5.1) and used as received. The products consisted of a mixture of C₈ olefins and di-*n*-octyl ether which were identified by ¹H and ¹³C NMR spectroscopy. Because the products were not separable by gas chromatography (GC), the catalyst selectivities were not quantified.

^b The catalyst loading was based on the mass of 1-octanol and the GO and zeolite were used in 1 : 1 (wt/wt) ratio (200 wt% total). ^c The conversions were determined by ¹H NMR spectroscopy using mesitylene as an internal standard. ^d A series of unidentified products were obtained. Mass spectrometry showed the presence of a species with an *m/z* = 287 consistent with the MH⁺ for di-*n*-octyl carbonate and a species with an *m/z* = 159 consistent with protonated methyl octanoate. An unidentified species possessing a *m/z* = 314 was also present.

A similar reaction that utilized GO and NH₄Y as the catalyst was also performed but only a small amount of the desired products was obtained under otherwise identical conditions (entry 2). Likewise, neither GO nor NaY independently afforded appreciable quantities of desired dehydration products (entries 3 and 4). Although the treatment of 1-octanol with 200 wt% GO (entry 3) resulted in a relatively high substrate conversion, the majority of the products were intractable, possibly due to the oxidation of the 1-octanol starting material.† Based on these preliminary results, we surmised that GO and the NaY operated in a synergistic manner to facilitate the aforementioned alcohol dehydration reaction.

To optimize the dehydration conditions, 4-heptanol was chosen as a model substrate and numerous reaction parameters were varied, including: catalyst loading (5–50 wt% with respect to the alcohol), time (10–60 min), temperature (100–180 °C), and catalyst composition (*e.g.*, 1 : 1 GO–NaY wt/wt). The results of the optimization study are summarized in Table 2. The conversion of the alcohol dehydration reaction as well as the total alcohol conversion were measured using ¹H NMR spectroscopy. Entry 1 in Table 2 showed that GO (15 wt%) was capable of dehydrating 4-heptanol to its heptene isomers in high conversions (88.5%); however, further investigation revealed that loadings could be decreased (7.5 wt% GO) when paired with NaY (7.5 wt%) without detriment to the outcome of the reaction (entry 10). As previously observed with 1-octanol, NaY was ineffective for facilitating the dehydration of 4-heptanol (entry 2) as was graphite–NaY (entry 18), which indicated the functionality and acidity of the GO were critical for the observed dehydrations. Entries 13 and 14, which summarize experiments that involved varying the weight ratio of GO and NaY, revealed evidence for an interaction between the two materials. For instance, when the weight ratio of GO–NaY was 3 : 1 (entry 13), only a 15.8% conversion to product was measured. Conversely, when a 1 : 3 weight ratio mixture of GO–NaY was used, the conversion to product was 86.6% (entry 14). Collectively, these results demonstrated that the zeolite had a relatively greater influence than the GO on the catalytic activity of the GO–NaY mixture.

To further investigate the nature of the interaction between GO and NaY during the aforementioned dehydration reactions, a series of experiments were performed; the results summarized in Table 3. The protic form of zeolite Y (HY) displayed good conversion (79.2%) of 4-heptanol to the desired mixture of olefinic products at low loadings (entry 1). This result led us to postulate that a protic form of NaY was the active catalyst in the GO–NaY mixture. Thus, studies were undertaken to determine if Na⁺–H⁺ exchange was occurring between the two materials. Entries 4–7 summarizes a series of experiments where GO (7.5 wt%) was placed in a reaction vessel then heated at 40 or 80 °C in the presence of CDCl₃ and 4-heptanol for 10 or 30 min, respectively. The supernatant was then filtered into a different reaction vessel containing NaY (7.5 wt%); entries 4 and 6) or no zeolite

† To determine if the olefinic product underwent oxidation, 1-octene was heated at 150 °C in the presence of GO (200 wt%) for 3 h. ¹H NMR spectroscopy revealed that 1-octene was isomerized to the disubstituted C₈ olefinic isomers (>99%); no oxidized products were observed.

Table 2 Optimization study for the dehydration of 4-heptanol using GO–NaY

Entry	Catalyst	Loading (wt%)	Temperature (°C)	Time (min)	Olefins ^a (% conv.)	Total ^b (% conv.)
1	GO	15	150	30	88.5	>99.0
2	NaY	15	150	30	3.8	12.0
3	GO–NaY (1 : 1)	5	150	40	50.6	60.8
4	GO–NaY (1 : 1)	10	150	40	78.1	84.4
5	GO–NaY (1 : 1)	15	150	40	88.9	>99.0
6	GO–NaY (1 : 1)	20	150	40	60.3	>99.0
7	GO–NaY (1 : 1)	50	150	40	68.3	>99.0
8	GO–NaY (1 : 1)	15	150	10	72.9	73.4
9	GO–NaY (1 : 1)	15	150	20	81.4	82.8
10	GO–NaY (1 : 1)	15	150	30	97.0	>99.0
11	GO–NaY (1 : 1)	15	150	45	77.8	>99.0
12	GO–NaY (1 : 1)	15	150	60	87.3	>99.0
13	GO–NaY (3 : 1)	15	150	30	15.8	20.8
14	GO–NaY (1 : 3)	15	150	30	86.6	89.8
15	GO–NaY (1 : 1)	15	100	30	2.7	13.5
16	GO–NaY (1 : 1)	15	130	30	40.3	50.9
17	GO–NaY (1 : 1)	15	180	30	73.5	>99.0
18 ^c	Graphite–NaY (1 : 1)	15	150	30	<1.0	8.2

^a The product selectivities were determined by GC and the substrate conversions were determined by quantitative ¹H NMR spectroscopy using mesitylene as the internal standard. ^b The total conversion reflects the disappearance of the 4-heptanol pentet at 3.58 ppm in the ¹H NMR spectrum of the reaction mixture after being subjected to the indicated conditions. ^c Used as received from Bay Carbon SP-1.

Table 3 Control studies with GO and/or zeolite Y derivatives

Entry	Catalyst	Loading (wt%)	Temperature (°C)	Time (min)	Olefins (% conv.)	Total (% conv.)
1	HY	5	150	30	79.2	>99.0
2	GO–HY	15	150	30	94.3	>99.0
3	GO–NH ₄ Y	15	150	30	25.2	30.1
4 ^a	GO then NaY	7.5	150	30	26.3	35.6
5 ^b	–	N/A	150	30	<1.0	3.6
6 ^c	GO then NaY	7.5	150	30	79.8	>99.0
7 ^d	–	N/A	150	30	1.7	3.3

^a GO (7.5 wt% with respect to 4-heptanol) was heated in a CDCl₃–4-heptanol solution for 10 min at 40 °C, and the supernatant was filtered through a 0.2 μm PTFE syringe filter into a separate reaction vessel containing 7.5 wt% NaY. The resulting mixture was then heated at 150 °C for 30 min.

^b A procedure similar to the one used in entry 4 was used with the exception that the CDCl₃–4-heptanol supernatant was filtered into an empty reaction vessel and heated to 150 °C for 30 min. ^c GO (7.5 wt% with respect to 4-heptanol) was heated in a CDCl₃–4-heptanol solution for 30 min at 80 °C, and the supernatant was filtered into a separate reaction vessel containing NaY (7.5 wt%). The resulting mixture was then heated to 150 °C for 30 min. Heating a mixture of 7.5 wt% GO and 4-heptanol at 80 °C for 30 min resulted in no conversion to C₇ olefins as determined by quantitative ¹H NMR spectroscopy. ^d The reaction was performed in a manner similar to the one that described in entry 6 with the exception that the CDCl₃–4-heptanol supernatant was filtered into an empty reaction vessel and heated to 150 °C for 30 min.

(entries 5 and 7), then heated to 150 °C for 30 min. The experiments summarized in entries 4 and 6 show that 26.3% and 79.8% of the alcohol converted to an olefinic product, respectively. In contrast, when the zeolite was not included in the reaction mixture (entries 5 and 7), less than 2% of the alcohol underwent dehydration. Collectively, the results suggested to us that upon dispersion of GO in the alcohol and solvent, H⁺ was released from GO which then exchanged with Na⁺ to convert the zeolite into a protic form. § Additionally, the

protic form of the zeolite proved to be a more effective dehydration catalyst than a mineral acid (*cf.*, entry 6 vs. entry 1). ¶

The recyclability of the catalyst mixture was also examined under the optimized conditions (15 wt% GO–NaY (1 : 1), 150 °C, 30 min) using 4-heptanol as the starting material; the results are summarized in Fig. 1. The total conversion of alcohol to product steadily decreased with each subsequent cycle by approximately 20%, and may be due the deactivation of

§ It was previously shown⁴⁵ that aqueous GO dispersions at 1 mg mL⁻¹ have a pH of *ca.* 4.5. Under the optimized dehydration reactions (25 mg mL⁻¹), the pH of an aqueous dispersion was measured to be 3.3.

¶ 4-heptanol was dehydrated using a catalytic amount (5 drops) of conc. H₂SO₄ at 150 °C, and within 10 min the reaction mixture turned black in color. ¹H NMR analysis of the product mixture showed heptene isomers (59.0%) as well as several unidentified byproducts.

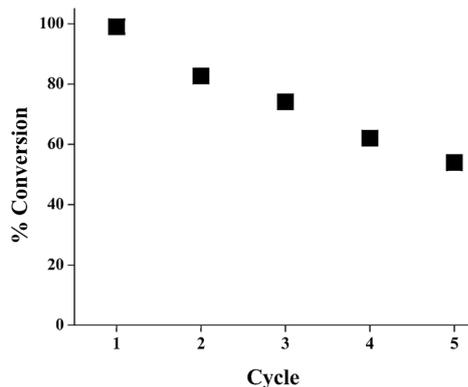


Fig. 1 Plot of the percent conversion of starting material to product versus reaction cycle for the dehydration of 4-heptanol using GO-NaY as the catalyst. Conditions: 15 wt% GO-NaY (1 : 1 wt/wt), 150 °C. Each reaction cycle was performed for a total of 30 min.

GO or NaY, or a combination thereof. GO has been shown to undergo thermal deoxygenation/reduction^{38–40} as well as chemical reduction in the presence of alcohols^{41–43} at elevated temperatures. Likewise, the deactivation of zeolites for alcohol dehydration has been attributed to the accumulation of byproducts as a result of side reactions which blocks the substrate from active sites within the pores of the material.⁴⁴

To examine the deactivation process in more detail, the surface area of the GO-NaY mixture was analyzed *via* the Brunauer-Emmett-Teller (BET) method before and after introduction of 4-heptanol. The BET surface areas of the pre and post-treated mixture of GO-NaY (1 : 1 wt/wt) were measured to be 130.6 m² g⁻¹ and 118.0 m² g⁻¹ respectively. The fresh and spent GO-NaY were also subjected to powder X-ray diffraction (XRD) to determine if the NaY structure was altered (see Fig. S2 in the ESI†). XRD analysis of the spent GO-NaY mixture showed that the zeolite retained its crystallinity after the reaction with 4-heptanol, while the characteristic peak of GO (2θ = 11.8°) was greatly diminished. However, based on the absence of the graphitic peak (2θ = 26.5°), the data revealed that the carbon did not undergo graphitization, even though the GO underwent deoxygenation/reduction. From the BET and XRD analyses, it was reasoned that the presence of reduced GO, which could prevent the alcohol from reaching the active sites in the zeolite, was the primary cause of activity loss.

Finally, as summarized in Table 4, the substrate scope of the aforementioned catalyst under optimized conditions was explored. Overall, the GO-NaY catalyst displayed good activity for secondary (entries 1 and 9) and tertiary alcohols (entries 2–4, 6, and 8) as moderate to excellent conversions of the corresponding

† The surface area of GO and NaY were determined independently to be 2.5 m² g⁻¹ and 286.7 m² g⁻¹ respectively. The surface area of the carbon material obtained after the dehydration reaction was measured to be 4.2 m² g⁻¹, and the surface area of the NaY from entry 6 in Table 3 was measured to be 217.9 m² g⁻¹.

** GO was used as the catalyst and 4-heptanol as the starting material (15 wt% GO, 150 °C, 30 min). The FT-IR spectrum (Fig. S1, ESI†) recorded for the recovered carbonaceous material revealed that a substantial number of the oxygen containing groups were removed.

Table 4 Summary of the results obtained by dehydrating various alcohols using GO-NaY^a

Entry	Starting material	Product(s)	Olefin ^b (% conv.)	Selectivity (%)
1		(<i>E</i>)-2-Heptene (<i>E</i>)-3-Heptene (<i>Z</i>)-2-Heptene (<i>Z</i>)-3-Heptene 1-Heptene	82.7	36.5 ^c 32.0 14.6 13.8 3.1
2			56.7	N/A
3			97.2	90.5 9.5
4			81.2	N/A
5			34.1 ^d	N/A
6			68.1	84.9 15.1
7			27.5	N/A
8			44.5	N/A
9	7-Tridecanol	(<i>E</i>)-6-Tridecene (<i>Z</i>)-6-Tridecene	80.1	69.1 30.9

^a Conditions: 15 wt% GO-NaY (1 : 1), 150 °C, 30 min. ^b Unless otherwise noted, the conversions and selectivities were by determined by ¹H NMR spectroscopy and/or GC using mesitylene as the internal standard. For entries 1–4 and 6–9, a >99.0% conversion of starting material was observed. For entry 5, a 90.9% conversion of starting material was observed. ^c The product selectivities were determined by GC. ^d The low conversion to product (tetrahydrofuran) was the result of oligomerization as broad signals consistent with polytetrahydrofuran were observed in the ¹H NMR spectrum of the product mixture.

dehydration products were obtained. The reactions summarized in entries 1–4, 6 and 9 all proceeded cleanly under the optimized conditions with minimal byproducts according to the ¹H NMR spectra recorded for the products. The dehydration of 2-heptanol (entry 1) resulted in a mixture of C₇ olefins whereas the dehydration of 7-tridecanol (entry 9) resulted in only two isomers (*cis/trans*-6-tridecene). In general, aliphatic primary alcohols showed low conversions under the optimized conditions; however, the previously described preliminary studies with 1-octanol indicate that higher conversions may be obtained by increasing the catalyst loading and reaction time.†† Based on ¹H NMR spectroscopic data collected, the low conversion of 3-methylbut-2-en-1-ol and 2-methylbut-3-en-2-ol (entries 7 and 8) was a likely result of oligomerization. Similarly, α-aryl alcohols, such as 1-phenylethanol and 2-phenyl-2-propanol (not shown),

†† 1-Octanol showed <1% conversion to the corresponding olefinic products under the reaction conditions optimized for 4-heptanol.

suffered low conversion to the corresponding olefins despite high total conversion; oligomerization was observed by ^1H NMR spectroscopy for these substrates.

Conclusions

In summary, GO was used in tandem with the zeolite NaY to effectively dehydrate a variety of alcohols to their corresponding olefinic or ethereal products. The dehydration of alcohols which do not readily dimerize or oligomerize under acidic conditions proceeded cleanly and rapidly (30 min) in moderate to excellent conversions (27.5–97.2%) to their corresponding products. The acidic nature of the GO transformed the zeolite to a protic form without the need for ammonium exchange or high temperature calcination. Moreover, the structure of the zeolite was largely retained, as determined by powder XRD analysis. Collectively, these results demonstrate that GO may be used in a synergistic manner with other heterogenous materials, such as zeolites, to promote the intrinsic catalytic properties displayed by the latter.

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