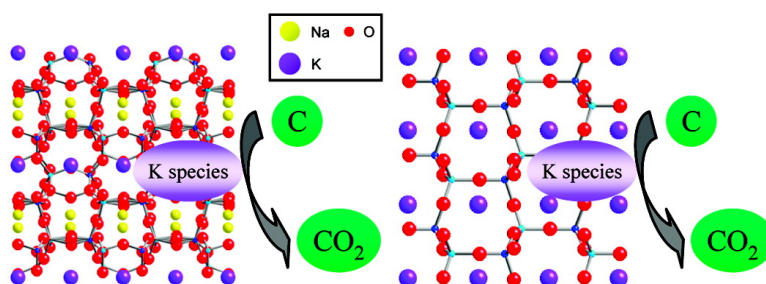


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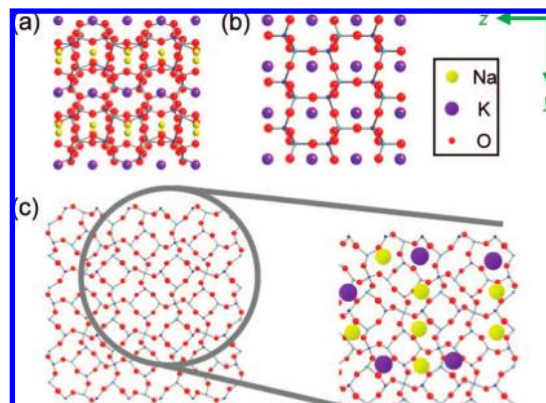
## Nepheline from $K_2CO_3$ /Nanosized Sodalite as a Prospective Candidate for Diesel Soot Combustion

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Diesel technology has tremendously advanced over the past decade owing to the efficient energy conversion of the diesel engine.<sup>1</sup> However, emission of a particulate matter (PM) from diesel vehicles, which consists mostly of carbonaceous soot as a major pollutant, causes acute health problems to humans. Consequently, a Diesel Particulate Filter (DPF) has been employed to reduce PM; it can collect more than 90% of diesel soot.<sup>2</sup> The most challenging task is the in situ simultaneous regeneration of the DPF by combusting trapped PM. Active regeneration is a fast process and represents a promising strategy for filter regeneration but requires a higher temperature (ca. 550–600 °C) than that of exhaust gas (200–400 °C) from a diesel engine.<sup>3</sup> Hence, there is a strong incentive to develop a catalyst for continuous regeneration of the DPF that displays good activity at lower temperature, better stability and durability, and relatively low cost and, most of all is environmentally benign; i.e. the diesel soot combustion catalyst should be economical and eco-friendly. Potassium compounds show considerable activity toward diesel soot combustion.<sup>4–8</sup> However, alkali metals can sublime under the reaction conditions, and the prolonged usage results in catalyst loss in the exhaust stream. In addition, highly alkaline solution induced by hydrated potassium gives rise to physical damage on DPF materials. Thus the usage of alkali metal based catalysts for DPF applications is minimizing.<sup>9,10</sup> In view of resource as well as economic and environmental concerns, it is advisable to utilize the most abundant elements on the earth such as O, Si, Al, Na, and K, which are listed at the top of the Clarke numbers.<sup>11</sup> We have already reported that  $K_2CO_3$ -supported sodalite exhibited activity toward diesel soot combustion that can partially retain potassium ions on the structure attributed to the ionic interaction between the negative framework of sodalite and potassium ions.<sup>12</sup> It was found that the activity was further enhanced after hydrothermal treatment of  $K_2CO_3$ /sodalite at 800 °C with the appearance of a dense phase. Hence, the objective of this study is to identify the phase transformation and to investigate their activity toward continuous combustion of carbonaceous matter. To obtain the phenomenon from a homogeneous reaction and moreover to facilitate coating the precursor on a DPF, we use nanosized sodalite as a starting material. Here, we will report the transformation of  $K_2CO_3$ /nanosized sodalite into potassium-enriched nepheline group materials, viz. nepheline, kalsilite, and kaliophilite, and show the superior activity of nepheline group materials compared to  $K_2CO_3$ /nanosized sodalite toward economic and eco-friendly (by avoiding the use of noble and transition metals) continuous combustion of carbonaceous matter.



**Figure 1.** Structure of (a) nepheline, (b) kalsilite, and (c) sodalite.

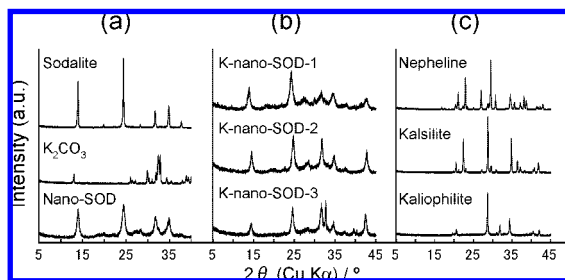
Nepheline group materials, viz. nepheline ( $KNa_3Al_4Si_4O_{16}$ ), kalsilite ( $K_4Al_4Si_4O_{16}$ ), and kaliophilite ( $K_4Al_4Si_4O_{16}$ ), are tectoaluminosilicates derived mostly from  $\beta$ -tridymite silica. The hexagonal six-tetrahedron rings of tridymite are distorted lower-symmetry ditrigonal and/or oval rings where alkali cations occupy the various voids.<sup>13–15</sup> Figure 1a,b show the structures of nepheline and kalsilite; the structure of kaliophilite is not shown here as the crystal data are yet unknown.<sup>16</sup> They belong to the same mineral group feldspathoid<sup>17</sup> as sodalite (Figure 1c). Nepheline group materials were obtained from thermal treatment of  $K_2CO_3$ -supported nanosized sodalite. Nanosized sodalite (nano-SOD) was synthesized according to the procedure reported in the literature.<sup>18</sup> An increasing concentration of  $K_2CO_3$ , 40 mL of 0.03 M, 40 mL of 0.2 M, and 100 mL of 1 M  $K_2CO_3$ , supported on nano-SOD denoted as K-nano-SOD-1, K-nano-SOD-2, and K-nano-SOD-3, on thermal treatment (800 °C; 5 h in air) is transformed to nepheline, kalsilite, and kaliophilite, respectively. The preparation method along with a cartoon has been depicted in Figure S1 of the Supporting Information. The catalytic activity for combustion of carbonaceous materials was evaluated by a temperature-programmed oxidation (TPO) method using a thermogravimetric-differential thermal analyzer connected directly to a mass spectrometer.<sup>12</sup>

Figure 2 exhibits the XRD patterns of nepheline group materials, K-nano-SOD-1, K-nano-SOD-2, and K-nano-SOD-3 along with nano-SOD, sodalite, and  $K_2CO_3$ . The pattern presented in Figure 2b reveals that the sodalite structure is retained after the impregnation of potassium carbonate. A trace of  $K_2CO_3$  phase has been detected in the case of K-nano-SOD-3. After thermal treatment (Figure 2c), nepheline (contains a trace of kalsilite phase), kalsilite, and kaliophilite were obtained from K-nano-SOD-1, K-nano-SOD-2, and K-nano-SOD-3, respectively. The XRD patterns of nepheline group materials closely resemble the patterns reported in the literature.<sup>19</sup> SEM images (cf. Figure S2) show that the nanosized

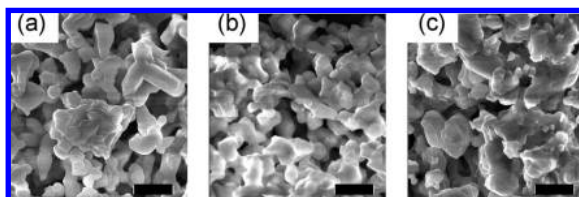
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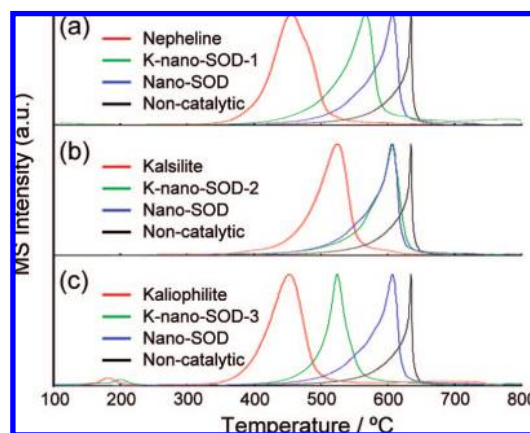
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**Figure 2.** XRD patterns of (a) sodalite,  $K_2CO_3$ , Nano-SOD, (b) K-nano-SODs, and (c) nepheline group materials.



**Figure 3.** SEM images of Nepheline group materials: (a) nepheline, (b) kalsilite, and (c) kaliophilite. Scale bar: 1  $\mu\text{m}$ .



**Figure 4.** Mass spectra of  $CO_2$  derived from combustion of carbon; (a) K-nano-SOD-1 and nepheline, (b) K-nano-SOD-2 and kalsilite, and (c) K-nano-SOD-3 and kaliophilite, along with noncatalytic and nano-SOD as a function of temperature.

sodalite crystallizes with a crystal size of  $\sim 26$  nm that aggregated to form particles 200–300 nm in size. The SEM images shown in Figure 3 reveal that the nepheline (trace of kalsilite) forms with spherical and rod shaped particles  $\sim 200$  nm to 1  $\mu\text{m}$  (Figure 3a) and tiny crystals of  $\sim 100$  nm of kalsilite and kaliophilite (Figure 3b and c) aggregated to form 1–2  $\mu\text{m}$  particles.

For the comparison of diesel soot combustion activity, mass spectra of  $CO_2$  derived from oxidation of carbon (mass to charge ratio,  $m/z = 44$ ) on nepheline, kalsilite, and kaliophilite phases and their corresponding precursors K-nano-SOD-1, K-nano-SOD-2, and K-nano-SOD-3 are shown in Figure 4 including the results of nano-SOD and noncatalytic combustion. For comparison, TPO of carbon on  $K_2CO_3$  supported on silica after thermal treatment as that of K-nano-SOD-1 (precursor for nepheline) is included in the Supporting Information (Figure S3). Nepheline, kalsilite, and kaliophilite exhibited a much improved activity compared to their corresponding  $K_2CO_3$ -supported nanosized sodalites and as-synthesized nano-SOD. Oxidation of carbon starts at  $\sim 330$  °C on nepheline and kaliophilite with a peak maximum of ca. 450 °C, while in the case of  $K_2CO_3$ -supported nanosized sodalite (K-nano-SOD-1 and K-nano-SOD-3) and nano-SOD the corresponding

temperatures are ca. 400 and 510 °C and 440 and 600 °C, respectively (cf. Figure 4). For kalsilite, oxidation starts at ca. 350 °C with peak maximum of ca. 510 °C, while in the case of  $K_2CO_3$ -supported nanosized sodalite (K-nano-SOD-2) the corresponding temperatures are ca. 440 and 600 °C, respectively. It is known that  $K_2CO_3$  itself contributes toward the combustion activity of diesel soot (ref 10; Figure S3). To find the activity contribution of surface K species, the nepheline group materials were washed with hot water, to remove the surface K species. TPO of carbon on the nepheline group materials after washing along with sodalite is presented in Figure S4. It reveals that the activity is reduced to some extent against the corresponding materials before washing (cf. Figure 4). However, the nepheline group materials even after washing possess a relatively better activity toward soot combustion in comparison with silica (cf. ref 12) and sodalite.

From the results shown here, it is clear that nepheline group materials show better activity than  $K_2CO_3$ -supported nanosized sodalite. In general, combustion activity is assumed to be dependent on the amount of potassium and the surface area of the support. In spite of the reduction in surface area (Table S2) and increase in crystal size after the formation of nepheline group materials from nanosized sodalite, the combustion activity becomes much higher. The superior activity of nepheline group materials against their corresponding  $K_2CO_3$ -supported nanosized sodalite is presumably attributed to the major contribution of K species existing on the surface of nepheline group materials. A relatively lower activity of kalsilite in comparison to nepheline and kaliophilite is still unclear. The materials employed for PM combustion should be stable for a sufficiently long time. To study the durability, TPO of carbon on nepheline obtained from K-nanoSOD-1 was carried out for five cycles of experiments.  $T_{\text{start}}$ ,  $T_{50}$ , and  $T_{\text{end}}$  depicted in Figure S5 indicate that nepheline possesses good reproducibility on repeated usage.

In conclusion, we showed preparation of potassium-enriched nepheline group materials, viz. nepheline, kalsilite, and kaliophilite, by thermal treatment of  $K_2CO_3$ -supported nanosized sodalite; thus prepared materials exhibit an excellent and highly improved oxidation activity of carbon toward diesel soot combustion.

**Supporting Information Available:** Chemical analysis, textural properties, experimental procedures, TPO of carbon, SEM images of nano-SOD, and reproducibility data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) van Setten, B. A. A. L.; Makkee, M.; Moulijn, J. A. *Catal. Rev.* **2001**, *43*, 489.
- (2) Walker, A. P. *Top. Catal.* **2004**, *28*, 165.
- (3) Görsmann, C. *Monatsh. Chem.* **2005**, *136*, 91.
- (4) Janiak, C.; Hoffmann, R.; Sjøvall, P.; Kasemo, B. *Langmuir* **1993**, *9*, 3427.
- (5) Jelles, S. J.; van Setten, B.; Makkee, M.; Moulijn, J. A. *Appl. Catal., B* **1999**, *21*, 35.
- (6) Fino, D.; Russo, N.; Saracco, G.; Spechia, V. *J. Catal.* **2003**, *217*, 367.
- (7) McKee, D. W. *Fuel* **1983**, *62*, 170.
- (8) Shanguan, W. F.; Teraoka, Y.; Kagawa, S. *Appl. Catal., B* **1998**, *16*, 149.
- (9) Wu, X.; Radovic, L. R. *Carbon* **2005**, *43*, 333.
- (10) An, H.; McGinn, P. J. *Appl. Catal., B* **2006**, *62*, 46.
- (11) Clarke, F. W.; Washington, H. S. U. S. *Geol. Survey, Prof. Paper* **1924**, 127.
- (12) Ogura, M.; Morozumi, K.; Elangovan, S. P.; Tanada, H.; Ando, H.; Okubo, T. *Appl. Catal., B* **2008**, *77*, 294.
- (13) Gaines, R. V.; Catherine, H.; Skinner, W.; Foord, E. E.; Mason, B.; Rosenzweig, A. *Dana's New Mineralogy*, 8th ed.; John Wiley & Sons, Inc.: New York, 1997; Chapter 8, pp 1617–1619.
- (14) Hassan, I.; Antao, S. M.; Hersi, A. A. M. *Can. Mineral.* **2003**, *41*, 759.
- (15) Cellai, D.; Gesting, T. M.; Wruck, B.; Carpenter, M. A. *Am. Mineral.* **1999**, *84*, 1950.
- (16) Hackwell, T. P.; Angel, R. J. *Eur. J. Mineral.* **1992**, *4*, 1221.
- (17) Merlino, S. In *Feldspars and feldspathoids*; Brown, W. L., Ed.; D. Reidel Publishing Company: Dordrecht, 1984; Chapter 12, pp 435–470.
- (18) Fan, W.; Morozumi, K.; Kimura, R.; Yokoi, T.; Okubo, T. *Langmuir* **2008**, *24*, 6952.
- (19) Smith, J. V.; Tuttle, O. F. *Am. J. Sci.* **1957**, *255*, 282.

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