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N-alkylation of ammonia and amines with alcohols catalyzed by Ni-loaded $CaSiO_3$

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ABSTRACT

Nickel nanoparticles loaded onto calcium silicate ($Ni/CaSiO_3$) have been prepared by ion-exchange method followed by in situ H_2-reduction of the calcined precursor. $Ni/CaSiO_3$ was found to be effective for the catalytic direct synthesis of primary amines from alcohols and NH_3 under relatively mild conditions. Various aliphatic alcohols are tolerated, and the turnover number (TON) was higher than those of Ru-based homogeneous catalysts. The catalyst was recoverable and was reused. Effects of the surface oxidation states and particle size of Ni on the catalytic activity were studied by infrared (IR) investigation of the states of adsorbed CO and transmission electron microscopy (TEM). It is clarified that the surface Ni^0 sites on small (3 nm) sized Ni nanoparticles are the catalytically active species. $Ni/CaSiO_3$ was also effective for the alkylation of anilines and aliphatic amines with various alcohols (benzyl and aliphatic alcohols) under additive free conditions; primary amines were converted into secondary amines and secondary amines into tertiary amines.

1. Introduction

Amines are of significant importance for the bulk- and fine-chemical industry as building blocks for polymers, surfactants, dyes, pharmaceuticals and agrochemicals. Among the amines, the terminal primary amines are the most useful intermediates for further derivatization reactions [1]. Aliphatic primary amines can be synthesized by the reductive amination of the corresponding carbonyl compounds [2,3], but their selective synthesis is challenging due to their high reactivity. Although heterogeneous catalysts are used for reductive aminations of simple alcohols under H_2 [2–5], they suffer from drawbacks such as limited substrate scope, low selectivity for primary amines and needs of high temperature (>200 °C), high H_2 pressure, and high NH_3 pressure. Heterogeneous Ru [6] and Cu [7] catalysts reported by Mizuno and co-workers and homogeneous Ir catalysts reported by Fujita and co-workers [8] were effective and reusable catalysts for the direct synthesis of secondary and tertiary amines from alcohols and aqueous ammonia (or urea), but selective formation of primary amines were not reported. Milstein and co-worker [9] reported the first example of the selective synthesis of primary amines from primary alcohols and NH_3 using Ru PNP pincer complex, but the system was ineffective for the amination of secondary alcohols. Recently, Vogt and co-worker [10] and Beller and co-worker [11] independently discovered the selective amination of secondary alcohols with NH_3 to give primary amines. Although these systems, driven by a borrowing-hydrogen [12] (or hydrogen-autotransfer [2]) mechanism (Scheme 1), provided successful examples catalytic primary amines syntheses, the homogeneous Ru catalysts had problems such as necessity of expensive noble metals and difficulties in recovery and reuse of catalysts.

The N-alkylation of amines with alcohols to give higher order amines has been also attracted considerable attention as an environmentally friendly synthetic method of alkyl amines [1,2]. Recently, homogeneous Ru [13] and Ir [14] catalysts were shown to be highly effective for this one-pot reaction, but these systems have problems such as difficulty in the recovery and reuse of expensive catalysts and the use of co-catalysts such as base and stabilizing ligand. Recyclable heterogeneous noble metal catalysts (Pd [15], Ru [6,16], Au [17], Pt [18] and Ag [19,20]) have been also reported, but some of them suffer from low TON, low selectivity to mono-alkylation, and necessity of co-catalysts. From the environmental and economic viewpoints, it is desired to accomplish this reaction by an inexpensive catalyst. However, most of the heterogeneous base metal catalysts reported so far (Ni [21], Fe [22] and Cu [7]

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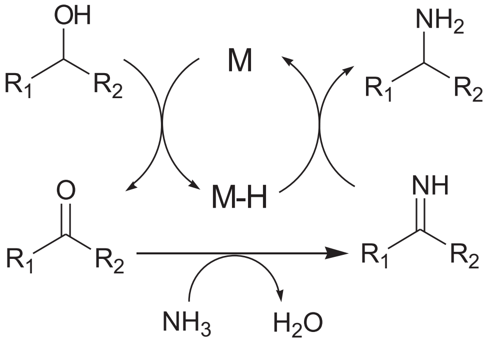

Scheme 1. Borrowing-hydrogen mechanism of transition metal-catalyzed amination of alcohols.

catalysts) generally suffer from low TON, limited scope and necessities of high temperatures or basic co-catalyst. For example, Ni/Cu co-loaded Al_2O_3 catalyst recently reported by Sun et al. exhibited TON of 1.9 for N-alkylation of aniline with benzylalcohol in the presence of 25 mol% NaOH and 12.5 mol% $CaCl_2$ [21].

As shown above, the development of non-noble-metal-based heterogeneous catalyst for the direct amination reactions is an important research target. We report herein that calcium silicate ($CaSiO_3$)-supported nickel metal nanoparticle catalyst readily prepared from inexpensive commercial materials [23] acts as a versatile heterogeneous catalyst for the selective synthesis of primary amines from alcohols and ammonia N-alkylation of amines with alcohols to give higher order amines under relatively mild conditions without any additives. In order to clarify the controlling factors of the catalytic system, the effects of the particle size and surface oxidation states of Ni on the activity is discussed based on the results of catalyst characterization.

2. Experimental

Commercially available organic and inorganic compounds (from Tokyo Chemical Industry, Wako Pure Chemical Industries, or Kanto Chemical) were used without further purification. The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out with Ultra ALLOY capillary column UA$^+$-5 (Frontier Laboratories Ltd.) capillary column (Shimadzu) using nitrogen as the carrier gas.

$CaSiO_3$ was kindly supplied from Konoshima Chemical. Ni^{2+}-exchanged $CaSiO_3$ was prepared by treating the support with aqueous solution of Ni nitrate for 12 h at room temperature, followed by centrifuging and washing with deionized water (three times), and by drying at 90 °C for 12 h. NiO-loaded $CaSiO_3$ (NiO/$CaSiO_3$) was prepared by calcining Ni^{2+}-exchanged $CaSiO_3$ in air for 4 h at 350 °C. Ni-loaded $CaSiO_3$ (Ni/$CaSiO_3$) was prepared by in situ pre-reduction of NiO/$CaSiO_3$ under H_2 flow (20 $cm^3\,min^{-1}$) at 600 °C for 0.5 h. ICP analysis showed that Ni content in the sample was 10 wt%. SiO_2 (Q-10) was supplied from Fuji Silysia Chemical Ltd. CaO was prepared by calcination of $Ca(OH)_2$ at 500 °C for 3 h. CaO or SiO_2-supported Ni (10 wt%) were prepared by the impregnation method, followed by drying at 90 °C for 12 h, and by in situ pre-reduction of the precursor under H_2 at 600 °C. Raney Ni (B113 W, Ni >90%) was supplied from Evonik Industries.

Ni/$CaSiO_3$ pre-reduced at 600 °C was used as a standard catalyst. For the reaction of alcohols with NH_3, the pre-reduced catalyst in the closed glass tube sealed with a septum inlet was cooled to room temperature under H_2 atmosphere. The mixture of *o*-xylene (4.0 g), alcohol (3.0 mmol), and *n*-dodecane (0.5 mmol) was injected to the pre-reduced catalyst inside the glass tube through the septum inlet. Then, the septum was removed under air, and a magnetic stirrer was put in the tube, followed by inserting the tube inside stainless autoclave with a dead space of 33 cm^3. Soon after being sealed, the reactor was flushed with NH_3 from a high pressure gas cylinder and charged with 0.4 MPa NH_3 at room temperature. The amount of NH_3 present in the reactor before heating was 6.7 mmol (2.2 equiv. with respect to the alcohol). Then, the reactor was heated typically at 160 °C under stirring (150 rpm).

For the reaction of alcohols with amines, the mixture of alcohol (1.0 mmol) and amine (1.2 mmol) in *o*-xylene (1 g) was injected to the pre-reduced catalyst inside a reactor (cylindrical glass tube) through a septum inlet, followed by filling with N_2. Then, the resulting mixture was stirred under reflux; bath temperature was 155 °C and reaction temperature was ca. 144 °C. For both reactions, conversion and yields of products were determined by GC using n-dodecane as an internal standard. The products were identified by GC–MS equipped with the same column as GC and by comparison with commercially pure products.

TEM measurements were carried out by using a JEOL JEM-2100F TEM operated at 200 kV. Ni K-edge extended X-ray absorption fine structure (EXAFS) was measured in transmission mode at the BL01B1 in the SPring-8 (Proposal No. 2011B1137). The storage ring was operated at 8 GeV. A Si(1 1 1) single crystal was used to obtain a monochromatic X-ray beam. The EXAFS analysis was performed using the REX version 2.5 program (RIGAKU). The Fourier transformation of the k^3-weighted EXAFS oscillation from k space to R space was performed over the range 3.0–16.0 $Å^{-1}$ to obtain a radial distribution function. The inversely Fourier filtered data were analyzed with a usual curve fitting method in the k range of 3.0–16.0 $Å^{-1}$. The parameters for the Ni—O and Ni—Ni shells were provided by the FEFF6.

The surface characterization of the Ni/$CaSiO_3$ was carried out by the infrared (IR) spectroscopic investigation of adsorbed CO over the catalyst. The Ni/$CaSiO_3$ catalyst (40 mg) was pressed into self-supporting pellet of 20 mm in diameter, and was placed in an infrared cell, which was connected to a closed gas circulation system equipped with vacuum line. The Ni/$CaSiO_3$ catalyst pre-reduced at 600 °C was placed in the IR cell and reduced again by H_2 at 500 °C for 10 h, followed by evacuation at the same temperature for 1 h before use. Adsorption of CO was carried out at 25 °C. Infrared spectra were recorded by an FT-IR (Jasco. FT/IR 7300) equipped with an MCT detector. The spectra were obtained by 100 scans at 4 cm^{-1} resolution. The spectra of adsorbed CO were obtained from rationing the background spectra of the catalyst to those of adsorbed CO.

3. Results and discussion

The XRD spectrum of Ni/$CaSiO_3$ (recorded under ambient conditions) showed broad lines due to metallic Ni. Fig. 1 shows the EXAFS spectrum of Ni/$CaSiO_3$. The catalyst pre-reduced in a flow of H_2 for 0.5 h at 600 °C was cooled to room temperature in the flow of H_2 and was sealed in a cell made of polyethylene under N_2, and then the EXAFS spectrum was taken at room temperature. Table 1 shows the results of curve-fitting analyses of the EXAFS. The EXAFS of Ni/$CaSiO_3$ consists of a Ni-Ni shell (at 2.48 Å with coordination number of 4.3) and a Ni—O shell (at 2.00 Å and coordination number of 2.6). By comparison with the crystallographic data of Ni metal, the Ni—Ni shell was assigned to metallic Ni. The weak contribution of the Ni—O shell indicates the presence of NiO or Ni^{2+} species as minor Ni species. Fig. 2 shows Ni particle size distributions of Ni/$CaSiO_3$ pre-reduced at different temperatures (600 °C and 700 °C). The average particle sizes of the catalysts reduced at 600 °C and 700 °C were 3.0 ± 0.8 nm and 12.6 ± 2.9 nm, respectively. The average size of Ni crystallites in Ni/$CaSiO_3$ (reduced at 600 °C) estimated by XRD (Fig. 1) using Scherrer equation is

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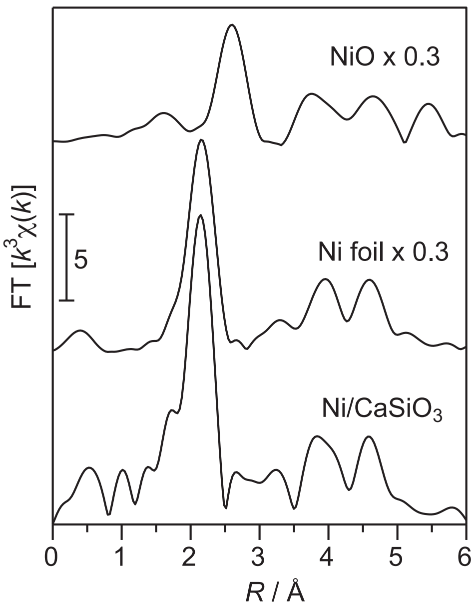

Fig. 1. Ni K-edge EXAFS Fourier transforms of Ni/CaSiO$_3$ (T_{H_2} = 600 °C) and reference compounds.

Table 1
Curve-fitting analysis of Ni K-edge EXAFS of Ni/CaSiO$_3$.

Sample	Shell	N[a]	R/Å[b]	σ/Å[c]	R_f/%[d]
Ni/CaSiO$_3$	O	2.6	2.00	0.088	0.9
	Ni	4.3	2.48	0.065	
NiO[e]	O	6	2.02	–	–
	Ni	12	2.94	–	–
Ni foil[e]	Ni	12	2.49	–	–

[a] Coordination numbers.
[b] Bond distance.
[c] Debye–Waller factor.
[d] Residual factor.
[e] Crystallographic data of Ni oxide and Ni metal.

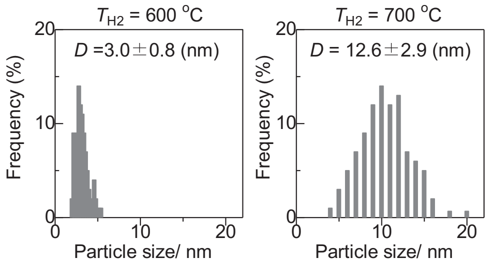

Fig. 2. Particle size distribution of Ni/CaSiO$_3$ catalysts (TEM analyses).

2.5 nm, which is nearly consistent with the size from TEM analysis.

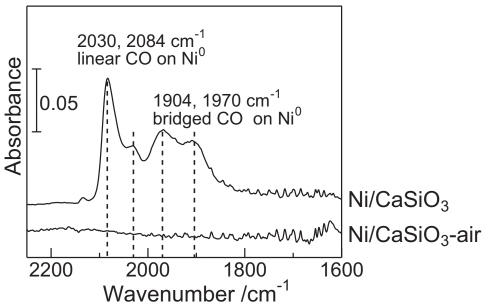

Fig. 3. IR spectra of CO adsorbed on in situ reduced Ni/CaSiO$_3$ and air-exposed catalyst, Ni/CaSiO$_3$–air.

Table 2 summarizes the catalytic results of various catalysts for the amination of 2-octanol (3 mmol) with NH_3 (P = 0.4 MPa, 6.7 mmol) to the corresponding primary amine, 2-octylamine, under the same conditions (Ni = 1 mol% with respect to alcohol, T = 160 °C, t = 20 h). Ni/CaSiO$_3$ reduced at 600 °C showed 86% yield of the corresponding primary amine, while Ni/CaO, Ni/SiO$_2$ and a conventional Ni catalyst (as received Raney Ni) were nearly inactive for the synthesis of the primary amine. Ni/CaSiO$_3$ with various Ni loadings (1, 3, 10, 20 wt%) were also tested, and the catalyst with 10 wt% Ni was found to be optimal (result not shown). Ni/CaSiO$_3$ catalysts pre-reduced at different temperatures (T_{H_2}) were also tested, and the catalyst reduced at 600 °C showed higher yield than that reduced at 700 °C. Combined with the TEM result that the average Ni particle size of the former catalyst (3.0 nm) was smaller than the latter catalyst (12.6 nm), it is suggested that smaller Ni metal particles is the catalytically important species. The catalyst named Ni/CaSiO$_3$–air was prepared by exposing the as-reduced Ni/CaSiO$_3$ to the ambient conditions for 0.5 h. Ni/CaSiO$_3$–air as well as the un-reduced precursor (NiO/CaSiO$_3$) showed no activity, suggesting that the metallic Ni^0 species on the surface of Ni nanoparticles are the active species and re-oxidation of them by O_2 under ambient conditions results in the catalyst deactivation. This hypothesis is confirmed by the following results. The oxidation states of surface Ni species were studied by the examination of the states of adsorbed CO by IR spectroscopy at 25 °C. IR spectra of adsorbed CO species are shown in Fig. 3. The spectrum for the as-reduced Ni/CaSiO$_3$ showed four main bands centered at 2084, 2030, 1970, and 1904 cm^{-1}. According to the literature, the bands at 1970 and 1904 cm^{-1} are assignable to ν(CO) of bridged CO on two Ni^0 atoms. A weak band at 2135 cm^{-1} is assignable to the CO adsorbed on Ni$^+$ species (CO—Ni$^+$). Bands at 2084 and 2030 cm^{-1} are assignable to ν(CO) of the linear CO on a Ni^0 site [23,24]. Upon exposure to air at 25 °C, the bands attributable to CO adsorbed on the Ni^0 sites completely disappeared. Combined with the result of catalytic test, the result indicates that the surface metallic Ni^0 sites are the catalytically active species. Under ambient conditions, the surface metallic Ni^0 species are completely converted to the inactive Ni^{2+} species. From these results, it is concluded that the metallic Ni^0 species on the surface of small Ni metal particles are the active species.

The above results show that 10 wt% Ni/CaSiO$_3$ catalyst reduced at 600 °C is the optimal catalysts. Using this catalyst, we examined the catalytic properties of Ni/CaSiO$_3$ under the conditions shown in Table 3 (1 mol%, 20 h). The amination of 2-octanol by Ni/CaSiO$_3$ resulted in 86% yield of the primary amine, and the yields of secondary and tertiary amines were below the detection limits of GC analyses. The reaction was completely terminated by a removal of the catalyst from the reaction mixture after 23% conversion of 2-octanol (t = 1 h); further heating of the filtrate for 19 h under NH_3 (0.4 MPa) at 160 °C did not increase the yield. This confirms that the reaction is attributed to the heterogeneous catalysis of Ni/CaSiO$_3$. After amination of 2-octanol by Ni/CaSiO$_3$ for 20 h, the catalyst was separated from the reaction mixture by a centrifugation. Then, the catalyst was washed with acetone, followed by drying in air at 90 °C for 12 h, and by reducing in H_2 at 600 °C for 0.5 h. The recovered catalyst showed 26% yield of the product. This indicates that Ni/CaSiO$_3$ is not a reusable catalyst for this reaction. The amination of 2-octanol at lower temperature (120 °C) resulted in lower yield of the primary amine (15%) than the standard condition (86% yield at 160 °C). Ni/CaSiO$_3$-catalyzed amination reactions of various alcohols are also shown in Table 3. Various alcohols, including aliphatic and aromatic alcohols were selectively converted to the corresponding primary amines with good to high yield (70–88%), while the yields of the secondary amines were below 6%.

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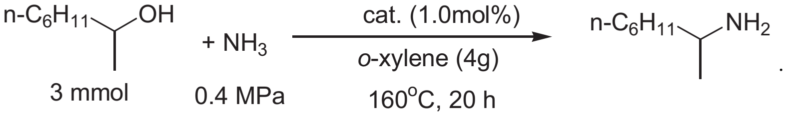
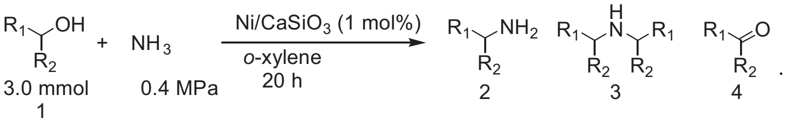
Table 2
Amination of 2-octanol with NH_3.[a]

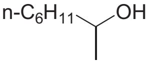
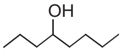
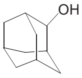
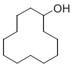
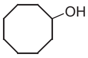
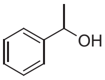
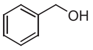


Catalyst	T_{H_2}/°C	Conv. (%)	Yield (%)
$NiO/CaSiO_3$	–	0	0
$Ni/CaSiO_3$	600	95	86
$Ni/CaSiO_3$–air[b]	600	0	0
$Ni/CaSiO_3$[c]	700	75	3
Ni/CaO[d]	600	45	<1
Ni/SiO_2	600	1	<1
Raney Ni	–	12	<1

[a] Conversion and yield were determined by GC based on alcohol.
[b] Pre-reduced $Ni/CaSiO_3$ was exposed to air at room temperature for 0.5 h.
[c] 2-Octanone (6%) and self-coupling products of 2-octanol (11%) were the byproducts.
[d] 2-Octanone (0.1%) was the byproduct.

Table 3
Amination of various alcohols with NH_3.[a]



Entry	Alcohol	T (°C)	Yield [%]		
			2	3	4
1		160	86	0	0
2		170	70	0	12
3		170	88	0	0
4		170	74	0	21
5[b]		140	71	0	18
6[b]		140	74	6	0
7[b]		160	70	0	0

[a] Conversion and yields were determined by GC based on alcohol.
[b] catalyst = 5 mol%.

The amination of 2-adamantanol resulted in 88% yield of the corresponding amine, corresponding to turnover number (TON) of 88. This value is larger than those of the state-of-the-art homogeneous Ru catalyst for the amination of secondary alcohols (TON of 46) [11] and comparable to that of Ni/Al_2O_3 (TON of 96) recently reported by our group [25]. Note that our heterogeneous system requires an order of magnitude lower amount of ammonia (2.23 equiv.) with respect to alcohols than the Ru catalysts (35–59 equiv.) [10,11].

$Ni/CaSiO_3$ was also effective for the N-alkylation of amines with various primary alcohols. Table 4 shows the scope of the N-alkylation reactions of various amines with various alcohols using 2 mol% of as-reduced $Ni/CaSiO_3$ catalyst in N_2 under reflux conditions in *o*-xylene solvent. For all the reactions, mono N-alkylated amine products were selectively produced. Aniline was converted into mono N-alkylated anilines (entries 1–4) and secondary amines were converted to tertiary amines (entries 5, 6) with good to excellent yields (72–96%). Both aromatic (entries 3, 4) and aliphatic alcohols (entries 1, 2, 5, 6) were tolerated. After the reaction of aniline and 1-octanol (entry 1), the catalyst was separated from the reaction mixture by a centrifugation. Then, the catalyst was washed with acetone, followed by drying in air at 90 °C for 12 h, and by reducing in H_2 at 600 °C for 0.5 h. The recovered catalyst showed 95% yield of the product. These catalytic results show that $Ni/CaSiO_3$ catalyst is an effective heterogeneous catalyst for the direst alkylation of ammonia and amines with alcohols.

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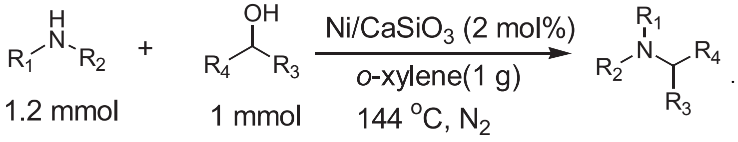
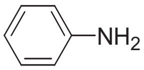
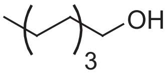
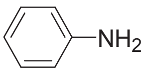
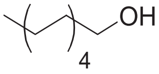
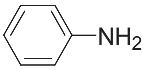
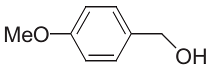
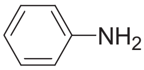
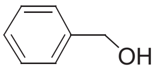
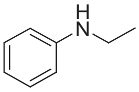
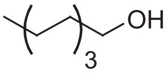
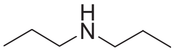
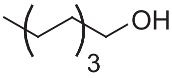
Table 4
N-alkylation of various amines with alcohols.[a]



Entry	Amine	Alcohol	*t* (h)	*T* (°C)	Conv. (%)	Yield (%)
1			20	155	99 (98)[b]	96 (95)[b]
2			12	155	100	91
3			6	140	100	93
4			17	155	100	78
5			36	155	100	72
6			15	155	100	77

[a] Conversion and yield were determined by GC based on alcohol.
[b] Reuse of Ni/$CaSiO_3$.

4. Conclusions

We have demonstrated that $CaSiO_3$-supported Ni metal nanoparticles act as effective heterogeneous catalysts for the alkylation of ammonia with alcohols to primary amines without additional hydrogen sources. This method provides an atom-efficient and economic method for the synthesis of primary amines. The same catalyst was effective for the N-alkylation of anilines and aliphatic amines with alcohols; primary amines are converted into secondary amines and secondary amines into tertiary amines. Structure-activity relationship showed that surface metallic Ni^0 species on smaller Ni nanoparticles are responsible for the high activity.

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