Self-assembled hybrid metal oxide base catalysts prepared by simply mixing with organic modifiers

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Multidentate materials formed by simply mixing heterogeneous and homogeneous components are promising for construction of versatile active sites on the surface of heterogeneous compounds, however, to the best of our knowledge, there are no reports on such materials. Self-assembly of hetero-hybrid catalytic materials occurs when heterogeneous catalysts having adjacent Lewis acid-Lewis base sites are mixed with an organic modifier that contains at least two Lewis base functional groups. Here we demonstrate the strategy by combining cerium oxide and 2-cyanopyridine that self-assembles to form a charge-transfer complex in methanol that exhibits a 2,000-fold increase in reaction rate for hydromethoxylation of acrylonitrile with high selectivity compared with cerium oxide or 2-cyanopyridine alone. The catalytic system is applied to the transesterification and Knoevenagel condensation affording 14-fold and 11-fold higher activity, respectively, than cerium oxide alone. These results demonstrate the potential versatility of the catalytic system and the generality of the catalyst preparation strategy.

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Catalysts are essential materials for developing efficient and environmental friendly processes in the chemical industry. The cooperation among two or more different materials is one of the most promising methods for preparing novel catalysts that are effective because the catalytic system has the potential to have enhanced properties that may not be observed in the individual materials. Among various approaches, homogeneous–heterogeneous hybridization enables fine-tuning of the active site property at the molecular level by virtue of the flexibility and versatility of the organic components. Immobilization of homogeneous catalysts on solid materials is a well-known and often-used technique, however this approach requires cumbersome catalyst preparation procedures. In contrast, treatment of solid catalysts by addition of organic modifiers is an ideal method since it is simple and it has high versatility. Amines are widely used as organic modifiers for supported noble metal catalysts, while heterogeneous Pd catalysts with quinoline derivatives are traditionally used as Lindlar or Rosenmund catalysts. Baiker and co-workers have reported that CeO$_2$ exhibits high catalytic activity in liquid-phase organic reactions at low temperatures ($\leq$ 473 K), which is related to the unique acid–base property of CeO$_2$ (refs 36–41), particularly high basicity and moderate Lewis acidity. We focus on the unique acid–base property of CeO$_2$, and aim at constructing a heterogeneous/homogeneous hybrid catalyst through the interaction between Lewis acid sites on CeO$_2$ and Lewis base functional groups of various organic compounds (Fig. 1b). Herein, we demonstrate that the catalyst complex composed of CeO$_2$ and 2-cyanopyridine, readily self-assemblies by simply mixing the compounds, and the resulting catalytic material exhibits dramatic activity rate enhancement for hydromethoxylolation of acrylonitrile (reaction rate $>2,000$-fold compared with only CeO$_2$ or 2-cyanopyridine).

**Results**

Catalyst screening in hydromethoxylolation of acrylonitrile. As a first step toward developing the strategy, we investigated the combination of CeO$_2$ and pyridine derivatives bearing various functional groups at the 2-position of the pyridine ring in hydromethoxylolation of acrylonitrile to 3-methoxypropionitrile at 323 K (Table 1), which is known to be a typical addition reaction catalysed by a base and is useful for the synthesis of pharmaceutical intermediates, plasticizers and additives for synthetic rubber. Without pyridine derivatives, using only CeO$_2$ provided low yield (0.5%) even after 24 h reaction time (Table 1, entry 13).

![Figure 1](https://www.nature.com/naturecommunications/article/6/8580/figures/1)

**Figure 1 | Schematic images of strategy for design of organic compound-modified metal oxides.** (a) Self-assembled heterogeneous/homogeneous hybrid catalyst composed of a metal oxide and an organic modifier. (b) Self-assembled heterogeneous/homogeneous hybrid catalyst based on CeO$_2$ and pyridine derivatives.
Addition of pyridine gave slightly higher activity than that without pyridine derivatives (Table 1, entry 5), and the activity was similar to the activity of only pyridine (without CeO\textsubscript{2}) as a base catalyst (reaction rate of only pyridine: 0.04 mmol h\textsuperscript{-1} g\textsuperscript{-1}). Pyridine derivatives with OH, CH\textsubscript{3} or OCH\textsubscript{3} groups showed two to fourfold higher activity than that in the case of pyridine (Table 1, entries 2–4). In contrast, pyridine derivatives with COCH\textsubscript{3}, CH\textsubscript{2}OH, C\textsubscript{2}H\textsubscript{5}, CONH\textsubscript{2} or CH\textsubscript{2}OCH\textsubscript{3} showed low activity (Table 1, entries 2–4). In the case of pyridine (without CeO\textsubscript{2}), the reaction completely stopped (Supplementary Fig. 1). Inductive coupled plasma results confirmed that the Ce species in the solution was below the detection limit (<0.1 p.p.m.), which demonstrated that catalytically active species did not elute from CeO\textsubscript{2} under the reaction conditions and the observed catalysis was truly heterogeneous. The number of Ce cations on CeO\textsubscript{2} surface was calculated to be 1.13 mmol g\textsuperscript{-1} from the surface density of Ce atoms on CeO\textsubscript{2} (111) and from its surface area (86 m\textsuperscript{2} g\textsuperscript{-1}) (ref. 37). On the basis of the total amount of CeO\textsubscript{2} and the number of Ce cations on CeO\textsubscript{2} surface, the turnover numbers were calculated to be 9.8 and 50, respectively, so that CeO\textsubscript{2} + 2-cyanopyridine catalytically promoted the reaction. Finally, the effect of nitrile compounds, pyridine and furan was examined in the same reaction (Fig. 2c). Detailed results are shown in the Supplementary Table 4.


![Table 1 | Comparison of catalysts composed of CeO\textsubscript{2} and pyridine derivatives in hydromethoxylation of acrylonitrile.](image)

| Entry | X          | t(h) | Yield (%) | Selectivity (%) | V (mmol h\textsuperscript{-1} g\textsuperscript{-1}) |
|-------|------------|------|-----------|-----------------|-----------------------------------|
| 1     | CN         | 0.5  | 20        | >99             | 23                                |
| 2     | OH         | 4    | 4.2       | 29              | 0.50                              |
| 3     | CH\textsubscript{3} | 4    | 2.9       | >99             | 0.46                              |
| 4     | OCH\textsubscript{3} | 4    | 2.1       | >99             | 0.30                              |
| 5     | H          | 24   | 5.0       | 98              | 0.12                              |
| 6     | COCH\textsubscript{3} | 24   | 4.2       | >99             | 0.10                              |
| 7     | CH\textsubscript{2}OH | 24   | 0.8       | >99             | 0.02                              |
| 8     | C\textsubscript{2}H\textsubscript{4} | 24   | 0.6       | >99             | 0.02                              |
| 9     | CONH\textsubscript{2} | 24   | 0.2       | >99             | 0.00                              |
| 10    | CH\textsubscript{2}OCH\textsubscript{3} | 24   | 0.1       | >99             | 0.00                              |
| 11    | CH\textsubscript{2}CN | 24   | <0.1      | —               | 0.00                              |
| 12    | COOH       | 24   | <0.1      | —               | 0.00                              |
| 13    | Blank (only CeO\textsubscript{2}) | 24   | 0.5       | >99             | 0.01                              |

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|-------|------------|------|-----------|-----------------|-----------------------------------|
| 1     | CN         | 0.5  | 20        | >99             | 23                                |
| 2     | OH         | 4    | 4.2       | 29              | 0.50                              |
| 3     | CH\textsubscript{3} | 4    | 2.9       | >99             | 0.46                              |
| 4     | OCH\textsubscript{3} | 4    | 2.1       | >99             | 0.30                              |
| 5     | H          | 24   | 5.0       | 98              | 0.12                              |
| 6     | COCH\textsubscript{3} | 24   | 4.2       | >99             | 0.10                              |
| 7     | CH\textsubscript{2}OH | 24   | 0.8       | >99             | 0.02                              |
| 8     | C\textsubscript{2}H\textsubscript{4} | 24   | 0.6       | >99             | 0.02                              |
| 9     | CONH\textsubscript{2} | 24   | 0.2       | >99             | 0.00                              |
| 10    | CH\textsubscript{2}OCH\textsubscript{3} | 24   | 0.1       | >99             | 0.00                              |
| 11    | CH\textsubscript{2}CN | 24   | <0.1      | —               | 0.00                              |
| 12    | COOH       | 24   | <0.1      | —               | 0.00                              |
| 13    | Blank (only CeO\textsubscript{2}) | 24   | 0.5       | >99             | 0.01                              |

Reaction conditions: acrylonitrile 0.53 g (10 mmol), methanol 0.48 g (15 mmol), CeO\textsubscript{2} 0.172 g (1 mmol), additive (1 mmol), 323 K, air.

*Reaction rate (V) = (amount of 3-methoxypyrrolidone (mmol))/reaction time (h)/CeO\textsubscript{2} amount (g).
base functional groups at the suitable position in the additive structure are necessary for effective nitrile additives. Focusing on the effective nitrile additives (2-cyanopyridine, cyanopyrazine, 5-fluoro-2-cyanopyridine, 2-cyanopyrimidine, 2-furonitrile and methoxylacetonitrile), moderate correlation between the reaction rate and the higher basicity among the base functional groups (lower $\Delta F$) was observed. However, the effective nitriles can be divided into two types, nitriles with another N atom (2-cyanopyridine, cyanopyrazine, 5-fluoro-2-cyanopyridine and 2-cyanopyrimidine) and nitriles with an O atom (2-furonitrile and methoxylacetonitrile). In the case of the former nitriles (2-cyanopyridine, cyanopyrazine, 5-fluoro-2-cyanopyridine and 2-cyanopyrimidine), the basicity of the N atom in the heteroaromatic ring is higher than that of the N atom of the cyano group, in contrast, in the case of the latter nitriles (2-furonitrile and methoxylacetonitrile), the basicity of the O atom is lower than that of the N atom in the cyano group. In addition, focusing on the basicity of the cyano group in each type of effective nitriles, the higher basicity of the cyano group seems to be effective for the catalytic system. However, the effect of the basicity of the base functional groups in organic modifiers will be pretty complex, and systematic studies on the effect of nitrile additives including substituent effects or steric effects will be explored in the future to clarify the effect of basicity.

The reusability of CeO$_2$ was investigated. CeO$_2$ was easily retrieved from the reaction mixture by filtration. After washing with acetone, followed by calcining at 873 K for 3 h, the recovered CeO$_2$ was used for the next reaction. CeO$_2$ could be reused at least three times without remarkable loss of activity and selectivity (Supplementary Fig. 2), and x-ray diffraction (XRD) analyses confirmed that the structure of CeO$_2$ remained intact during the reusability tests (Supplementary Fig. 3).

Investigation of adsorption state of 2-cyanopyridine on CeO$_2$. The colour of metal oxides such as CeO$_2$ and TiO$_2$ is largely influenced by the electronic state, and such a colour change is often observed for adsorption of organic compounds onto metal oxides$^{34-36}$. In the present reaction, the colour of CeO$_2$ in methanol solvent was yellowish (Blank, see the inset of Fig. 3a), while the colour of CeO$_2$ in methanol solvent became deep yellow almost instantaneously when 2-cyanopyridine was added to the

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**Figure 2** | **Metal oxides and nitriles screening and the time course.** (a) Comparison of the combination of metal oxide catalysts and 2-cyanopyridine. Reaction conditions without 2-cyanopyridine (grey bar): acrylonitrile (10 mmol), methanol (20 mmol), metal oxide (172 mg), 323 K, air, 12–48 h. Reaction conditions with 2-cyanopyridine (black bar): acrylonitrile (10 mmol), methanol (20 mmol), metal oxide (1 mmol), 2-cyanopyridine (2 mmol), 323 K, air, 0.5–48 h. Detailed data are described in Supplementary Tables 1 and 2. (b) Time course of the reaction over CeO$_2$ + 2-cyanopyridine hybrid catalyst. Reaction conditions: acrylonitrile (10 mmol), methanol (15 mmol), CeO$_2$ (1 mmol), 2-cyanopyridine (1 mmol), 323 K, air. Detailed data are described in Supplementary Table 3. (c) Effect of organic compounds on the activity. Reaction conditions: acrylonitrile (10 mmol), methanol (20 mmol), CeO$_2$ (1 mmol), organic additive (2 mmol), 323 K, air. Detailed data are described in Supplementary Table 4.
CeO₂ + methanol solution. The corresponding change of UV–vis spectra was observed to have a maximum absorption peak at 402 nm (Fig. 3a). When CeO₂ was removed from the solution by filtration, the residual liquid solution was clear and colourless. The absorption intensity increased with increasing amounts of 2-cyanopyridine (Fig. 3b). The difference spectra, which are obtained by subtracting the blank spectrum, showed that the band intensity increased with increasing amounts of 2-cyanopyridine. Neither CeO₂ nor 2-cyanopyridine has absorption peaks in this range (Fig. 3a and Supplementary Fig. 4). Therefore, the colour change is derived from strong interaction between CeO₂ and 2-cyanopyridine, and can be assigned to the ligand-to-metal charge transfer (C-T) between CeO₂ and 2-cyanopyridine according to the reported literature on C-T complex formation between CeO₂ or TiO₂ and phenolic compounds. The maximum position of the absorption band was almost unchanged (Fig. 3c), which indicates that the same adsorption species were formed on CeO₂ regardless of the amount of 2-cyanopyridine present. The interpretation of this phenomenon is that the surface species formed by the interaction between CeO₂ and 2-cyanopyridine are uniform in the range from low-to-high concentration. No colour change was observed by using benzonitrile or pyridine instead of 2-cyanopyridine, although benzonitrile or pyridine can be adsorbed onto Lewis acid sites of CeO₂ at the N atom of the cyano group or at the pyridine ring, respectively. The 2-cyanopyridine was easily removed from CeO₂ by washing with large amounts of methanol (determined by TG-DTA (Supplementary Fig. 5), which means that 2-cyanopyridine does not react with the surface of CeO₂. These results are evidence that 2-cyanopyridine is adsorbed onto CeO₂ at both the N atoms of the cyano group and the pyridine ring without transformation of the cyano group in 2-cyanopyridine. The band intensity at 402 nm is plotted as a function of 2-cyanopyridine concentration (Fig. 3d). The band intensity increased linearly with an increase in the 2-cyanopyridine concentration, and leveled off at high concentrations (≥0.24 M). Good linear correlation between 1/(2-cyanopyridine concentration) and 1/(KM-KMblank) was obtained (Fig. 3e), indicating that the complexation between 2-cyanopyridine and CeO₂ follows Langmuir isotherm kinetics. The CeO₂ and 2-cyanopyridine are in equilibrium with CeO₂-2-cyanopyridine C-T complex (see inset of Fig. 3e), resulting in the observed colour change of CeO₂. The UV–vis spectra were measured by varying 2-cyanopyridine/methanol ratios from 1/15 to ∞ (no methanol) (Supplementary Fig. 6). Although the spectrum with the ratio of ∞ (no methanol) had a wide absorption band that was different from that under standard reaction conditions, the other spectra were almost the same (2-cyanopyridine/methanol ratio = 0.067, 0.1, 0.2, 1 and 2). Thus, the amount and electronic state of the formed CeO₂-2-cyanopyridine C-T complex were almost the same provided that methanol was present, meaning that CeO₂ and 2-cyanopyridine self-assembled in the methanol solvent to form the same C-T complex.

To confirm the adsorption state of 2-cyanopyridine and methanol on CeO₂, FTIR analyses were carried out by the introduction of methanol to CeO₂, that was followed by the introduction of 2-cyanopyridine at 323 K (Supplementary Fig. 7). The bands at 2,235 and 2,287 cm⁻¹ were observed in the...
region between 2,000 and 2,350 cm\(^{-1}\), which can be assigned to non-interactive \(\nu(CN)\) and hydrogen-bonding \(\nu(CN)\), respectively. Therefore, considering that the band at 2,287 cm\(^{-1}\) was not observed without methanol (Supplementary Fig. 7), introduction of methanol brings about hydrogen bond between the CN group in 2-cyanopyridine and the H atom.

To ascertain whether the formed CeO\(_2\)-2-cyanopyridine C-T complex truly acts as a catalyst for hydromethoxylation of acrylonitrile, reactions were carried out at various concentrations of 2-cyanopyridine (0–0.34 M), and reaction rates (mmol h\(^{-1}\) g\(^{-1}\)) were determined under conditions where the conversion was below 30%. Figure 4a shows the reaction rate as a function of the concentration of 2-cyanopyridine. The reaction rate increased with increasing 2-cyanopyridine concentration and became asymptotic at high concentrations (\(\geq 0.24\) M), which was similar in tendency to that of the band intensity in UV–vis spectra against the 2-cyanopyridine concentration (Fig. 3d). The reaction rates were plotted as a function of the band intensity at the same 2-cyanopyridine concentration (Fig. 4b), which provided good correlation between the parameters. The formed complex was concluded to be strongly connected to the active sites. From these results, the uniform CeO\(_2\)-2-cyanopyridine CT complex is most likely formed by the equilibrium adsorption of 2-cyanopyridine on CeO\(_2\), which serves as the active sites for the reaction.

To determine the surface ratio of 2-cyanopyridine amount \((C_{2\text{-cyanopyridine}}\text{ (mol)})\) to Ce cation amount on CeO\(_2\) surface \((C_{\text{surf}}\text{ (mol)})\)\(^{37}\), the reaction rates were measured by maintaining the total amount of CeO\(_2\)-2-cyanopyridine and Ce\(_{\text{surf}}\) constant (\(\sim 2.0\) mmol). Job’s plot showed a volcano curve and a maximum yield at the molar ratio of \(C_{\text{surf}}/(C_{\text{surf}} + C_{2\text{-cyanopyridine}}) = 0.8\) (Fig. 5a and Supplementary Table 6), indicating that a 1:4 complex between 2-cyanopyridine and surface Ce cations is preferably formed. Considering that CeO\(_2\) has only Lewis acid sites as acid sites and Lewis base sites on the surface\(^{42}\) and that the basicity of the N atom of pyridine ring is higher than that of the cyano group in 2-cyanopyridine (Supplementary Table 5), the N atom of the pyridine ring in 2-cyanopyridine will be preferentially adsorbed onto the Lewis acid site of the Ce cations of CeO\(_2\), and the N atom of the cyano group will be close to the O atom of CeO\(_2\) surface. From the results of the nitrile screening, UV–vis analysis and TG-DTA (Figs 2c and 3, and Supplementary Fig. 5), it is possible that 2-cyanopyridine interacts with CeO\(_2\) at both the N atoms of the pyridine ring and the cyano group. Further, FTIR analyses demonstrated that the cyano group in 2-cyanopyridine formed a hydrogen bond with the H atom (Supplementary Fig. 7). The precise adsorption structure of the heterogeneous/homogeneous hybrid material is unknown at this point of the research. However, considering that methanol can be dissociated on the acid–base sites on CeO\(_2\) (ref. 47) and the evidence of the related results presented, such as structural feature of the effective additives (Table 1 and Fig. 2c), UV–vis analyses and TG-DTA of the CeO\(_2\)+2-cyanopyridine (Fig. 3 and Supplementary Fig. 5), and kinetics showing the relationship between the 2-cyanopyridine concentration and reaction rate (Fig. 4), we speculate that an adsorption structure composed of CeO\(_2\), 2-cyanopyridine and methanol is present, where a N-H\(^{+}\)-O hydrogen bond exists between the N atom of the cyano group and the O atom of CeO\(_2\) (Fig. 5b). If such an adsorption structure is formed, expression of strong basicity can be expected due to high stabilization of H\(^{+}\) by the neighbouring two heteroatoms (N and O), which may be related to results that effective nitriles with high basicity of the cyano group have high reaction rates (Supplementary Table 5).

**Application to other base-catalysed reactions.** To explore the versatility of the catalytic system of CeO\(_2\)+2-cyanopyridine, the catalytic material was applied to transesterification of methyl benzoate with 1-hexanol and Knoevenagel condensation from benzaldehyde and ethyl cyanoacetate, which are known to be catalysed by a base catalyst. The material showed >10-fold higher activity in these reaction systems over that of only CeO\(_2\) (14-fold for the transesterification and 11-fold for the Knoevenagel condensation, Supplementary Fig. 8). Thus the catalytic system can act as a strong base catalyst, which demonstrates that the catalyst can have widely applied to base-catalysed reactions.

**Discussion**

A method for preparing self-assembled heterogeneous/homogeneous hybrid catalysts has been developed. For CeO\(_2\) and 2-cyanopyridine, by only mixing these materials, the catalytic system has >2,000-fold higher activity for hydromethoxylation of acrylonitrile than when only CeO\(_2\) or 2-cyanopyridine is used. Formation of the hydrogen bond between the cyano group in 2-cyanopyridine and the H atom derived from methanol was observed. The hydrogen bond between the cyano group in 2-cyanopyridine and the H atom derived from methanol can...
increase the basicity, which most likely leads to the high activity of the catalytic system. However, the mechanism of the rate enhancement remains unclear because the decisive evidence for the adsorption structure of 2-cyanopyridine, such as whether 2-cyanopyridine is truly adsorbed on the CeO2 surface at the N atom in the pyridine ring or whether the hydrogen bond is truly formed in the methanol solvent, could not be determined. Further investigations including DFT calculations of the adsorption state of various nitriles on CeO2 and kinetics about nitriles or substrates will be required to clarify the mechanism and the probable adsorption species. Nevertheless, the concept of the self-assembly of metal oxides having acid–base sites and an organic modifier having two functional groups with different basicities or acidities, provides an effective strategy for preparing metal oxide materials that have enhanced catalytic properties.

Methods

Materials. All the chemicals for organic reactions were purchased from chemical products corporations and were used without further purification. Acrylonitrile (Tokyo Chemical Industry, >99.9%), 2-cyanopyridine (Tokyo Chemical Industry, >99.9%), methanol (Super dehydrated, Wako Pure Chemical Industries, >99.8%), 3-methoxypropanitrile (Tokyo Chemical Industry, >99.0%), 1,4-dioxane (Wako Pure Chemical Industries, >99.5%), 2-hydroxypyridine (Tokyo Chemical Industry, >98.0%), 2-methylpyridine (Wako Pure Chemical Industries, >98.0%), 2-methoxypyridine (Wako Pure Chemical Industries, >97.0%), 2-acetylpyridine (Wako Pure Chemical Industries, >98.0%), 2-pyrindinemethanol (Tokyo Chemical Industry, >98.0%), 2-ethylpyridine (Tokyo Chemical Industry, >98.0%), 2-(methoxymethyl)-pyridine (Aldrich, >97.0%), 2-pyridineacetone (Tokyo Chemical Industry, >98.0%), pyridine-2-carboxylic acid (Wako Pure Chemical Industries, >98.0%), cyanoazine (Tokyo Chemical Industry, >97.0%), 2-cyanopyridimine (Tokyo Chemical Industry, >98.0%), 2-furonitrile (Wako Pure Chemical Industries, >98.0%), pyridine (Tokyo Chemical Industry, >99.0%), butyrotritile (Wako Pure Chemical Industries, >98.0%), furan (Tokyo Pure Chemical Industries, >98.0%), benzonitrile (Wako Pure Chemical Industries, >98.0%), 3-cyanopyridine (Wako Pure Chemical Industries, >98.0%), 4-cyanopyridine (Wako Pure Chemical Industries, >98.0%), 2,6-lutidine (Tokyo Chemical Industry, >98.0%), methoxyacetone (Tokyo Chemical Industry, >98.0%), acetone (Wako Pure Chemical Industries, >99.5%), 1-hexanol (Tokyo Chemical Industry, >98.0%), methyl benzoate (Wako Pure Chemical Industries, >98.0%), benzaldehyde (Wako Pure Chemical Industries, >98.0%), ethyl cyanoacetate (Wako Pure Chemical Industries, >98.0%), ethyl 2-cyanocinnamate (Tokyo Chemical Industry, >98.0%), ethanol (super dehydrated, Wako Pure Chemical Industries, >99.5%), dodecan (Tokyo Chemical Industry, >99.5%).

Catalyst. Preparation of CeO2 catalyst was carried out by calcining cerium oxide HS (Daichi Kigenso Kogyo) in 3 h under air at 873 K. The specific surface area (BET method) of pure CeO2 was 86 m2 g⁻¹. Some metal oxides were commercially available or supplied from the Catalysis Society of Japan: ZrO2 (Daichi Kigenso Kogyo, Zr[OH]4 was calcined under air at 673 K for 3 h.), MgO (Ube Industries, MgO 500 A, MgO was used after calcining under air at 873 K for 3 h.), TiO2 (Nippon Aerosil, P-25), γ-Al2O3 (Sumitomo Chemical Company, γ-Al2O3 was used after calcining under air at 873 K for 3 h), SiO2, (Wako Pure Chemical Industries, H2O was calcined at 773 K for 3 h). Y2O3 was prepared by the precipitation method. Y(NO3)3·nH2O (Pure Chemical Industries, >99.5%) was used as a precursor. A precipitant (25 g) was dissolved in water (100 ml) and NaOH (1 M) was dropped with stirring. The pH of the solution was set to 10, resulting in a precipitate. The precipitate was filtered and washed with water, following a drying at 383 K overnight (12 h) and calcined under air at 873 K for 3 h. The specific surface area of the metal oxides is summarized in Supplementary Table 7.

Typical procedure for hydromethylation of acrylonitrile. A typical procedure for nucleophilic addition of methanol to acrylonitrile is as follows: CeO2 (cerium oxide HS, Daichi Kigenso Kogyo, calcined at 873 K for 3 h) 172 mg (1 mmol) and methanol 0.64 g (20 mmol) were added to a reaction vessel capped by a rubber plug under air, and the mixture was vigorously stirred at 500 r.p.m. at 323 K under air for 1 h. After the treatment, acrylonitrile 0.53 g (10 mmol) was added into the mixture, and the mixture was constantly stirred during the reaction. The time when acrylonitrile was added in the reactor was defined as zero reaction time. After the reaction, the reaction mixture was filtrated, diluted with acetone, and transferred to a vial. Details of the reaction conditions are described in each result. The products were analysed by gas chromatography (GC) equipped with a FID detector and CP-Sil5 capillary column (length 50 m, i.d. 0.25 mm, film thickness 0.25 μm). Conversion and yield of products were determined based on acrylonitrile by GC using 1,4-dioxane as an internal standard. Products were also identified using standard compounds and GC–MS equipped with the same detector and capillary column. The typical GC chart was shown in Supplementary Fig. 9.

Typical procedure for transesterification of methyl benzoate with 1-hexanol to hexyl benzoate. CeO2 172 mg (1 mmol), 2-cyanopyridine (1 mmol), methyl benzoate (10 mmol) and 1-hexanol (10 mmol) were added to a reaction vessel, and the mixture was rigorously stirred at 500 r.p.m. at 393 K under air. After the reaction, the reaction mixture was filtrated, diluted with acetone and transferred to a vial. Details of the reaction conditions are described in each result. The products were analysed using GC equipped with a FID detector and CP-Sil5 capillary column (length 50 m, i.d. 0.25 mm, film thickness 0.25 μm). Conversion and yield of products were determined based on methyl benzoate by GC using dodecan as an internal standard. Products were also identified using standard compounds and GC–MS equipped with the same detector and capillary column.

Typical procedure for Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate to ethyl α-cyanoacetamide. CeO2 172 mg (1 mmol), 2-cyanopyridine (1 mmol), ethanol 3.0 g (65 mmol), benzaldehyde (3 mmol) and ethyl cyanoacetate (4 mmol) were added to a reaction vessel, and the mixture was vigorously stirred at 500 r.p.m. at 303 K under air. After the reaction, the reaction mixture was filtrated, diluted with acetone and transferred to a vial. The products were analysed using GC equipped with a FID detector and CP-Sil5 capillary column (length 50 m, i.d. 0.25 mm, film thickness 0.25 μm). Conversion and yield of products were determined based on benzaldehyde by GC using 1,4-dioxane as an internal standard. Products were also identified using standard compounds and GC–MS equipped with the same detector and capillary column.

Figure 5 | Job’s plot and adsorption models of 2-cyanopyridine on CeO2. (a) Job’s plot in complexation of 2-cyanopyridine and CeO2. Cesurf: surface Ce amount of CeO2 (mol), C2-cyanopyridine: 2-cyanopyridine amount (mol). Reaction conditions: acrylonitrile (40 mmol), methanol (60 mmol), CeO2 (0–10.3 mmol), 2-cyanopyridine (2.0–3.6 mmol), 323 K, air, 0.25 h. Detailed data are described in Supplementary Table 6. (b) Adsorption image of 2-cyanopyridine and methanol on CeO2.
Spectroscopic and XRD analyses. UV–vis diffuse reflectance spectra were measured with Shimadzu UV 2450 spectrophotometer with the integration sphere diffuse reflectance attachment (ISP-2200 Shimadzu) and a photomultiplier detector. Pure BaSO₄ was used as a reference sample. The solution samples were added in a transparent quartz cell and the cell was located at the integration sphere diffuse reflectance attachment. The spectra were measured in the region of 350–800 nm at room temperature. The scan speed is middle and the resolution of spectra is 0.1 nm, the sample without CeO₂ sample was measured by the conventional transmission method on the same spectrophotometer using the 1-cm path length transparent quartz cell. XRD patterns were recorded by Rigaku MiniFlex600 with Cu Kα (40 kV, 15 mA) radiation and D/teX Ultra2 detector. The diffractometer were measured for 20 values between 20 and 70° at a scanning rate of 1°·min⁻¹ at a resolution of 0.02°.

FTIR spectra were recorded with a NICOLET 6700 spectrometer (Thermo Scientific) equipped with a liquid nitrogen-cooled MCT (HgCdTe) detector (resolution 4 cm⁻¹), using an in situ IR cell with CaF₂ windows, which was connected to a conventional gas flow system. CeO₂ sample (~80 mg) was pressed into a self-supporting wafer (20 mm diameter) and mounted into the IR cell. Adsorption of methanol and 2-cyanopyridine was carried out in the following method: The catalyst was preheated at 873 K under He at 350 ml·min⁻¹/ O₂ at 10 ml·min⁻¹ flow for 10 min. Then the catalyst was cooled down to 323 K under a He flow. Methanol (4 μl) was injected into the gas line heated at 523 K under a He flow, which was fed to the in situ IR cell. After the spectrum was stable, 2-cyanopyridine was introduced under He into the IR cell, and the spectrum change was monitored. Spectra were obtained by subtraction of the reference spectrum of CeO₂ measured at 323 K under He flow.

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**Author contributions**

M.T. and K.T. conceived the concept and directed the project. R.K. and M.T. conducted experiments. M.T. and Y.N. discussed the experiments and results, and prepared the manuscript.

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