Novel cerium-tungsten mixed oxide catalyst for the selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3}

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Electronic Supplementary Information

Preparation of Ce\textsubscript{a}W\textsubscript{b}O\textsubscript{x}, V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} and Fe-ZSM-5 catalysts

The serial Ce-W mixed oxide catalysts were prepared by homogeneous precipitation method using cerium nitrate and ammonium tungstate as precursors. (NH\textsubscript{4})\textsubscript{10}W\textsubscript{12}O\textsubscript{41} with equal weight H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}·2H\textsubscript{2}O were added to deionized water. After the dissolution of (NH\textsubscript{4})\textsubscript{10}W\textsubscript{12}O\textsubscript{41}, the aqueous solution of Ce(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O was added with required molar ratio (Ce/W = 2:1, 1:1 and 1:2). Excessive urea aqueous solution was then added into the mixed solution, with an urea/(Ce + W) molar ratio being 10:1. The mixed solution was then heated to 90 °C and held there for 12 h under vigorous stir. After filtration and washing with deionized water, the resulting precipitant was dried at 100 °C overnight and subsequently calcined at 500 °C for 5 h in air condition. The obtained catalysts were denoted as Ce\textsubscript{a}W\textsubscript{b}O\textsubscript{x}, where “a/b” denotes the Ce/W molar ratio, such as Ce\textsubscript{2}W\textsubscript{1}O\textsubscript{x}, CeWO\textsubscript{x} and Ce\textsubscript{1}W\textsubscript{2}O\textsubscript{x}. Pristine CeO\textsubscript{x} and WO\textsubscript{x} were also prepared using the same method as reference samples for activity test and characterizations. The CeWO\textsubscript{x} catalyst calcined at 800 °C for 1 h in air condition was also prepared to investigate its thermal stability for practical use, which was denoted as CeWO\textsubscript{x}-800. Before the NH\textsubscript{3}-SCR activity test, the power catalysts were pressed, crushed and sieved to 40-60 mesh.

In order to comprehensively evaluate the activity of Ce-W mixed oxide catalyst in this study, a conventional V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalyst with 4.5 wt.% V\textsubscript{2}O\textsubscript{5} and 10
wt.% WO$_3$ and a Fe-ZSM-5 catalyst with an iron loading of 7 wt.% were prepared as reference materials.

The V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst with 4.5 wt.% V$_2$O$_5$ and 10 wt.% WO$_3$ was prepared by conventional impregnation method using NH$_4$VO$_3$, (NH$_4$)$_{10}$W$_{12}$O$_{41}$, H$_2$C$_2$O$_4$·2H$_2$O as precursors and anatase TiO$_2$ as support. After impregnation, the excess water was removed in a rotary evaporator at 80 °C. The sample was dried at 100 °C overnight and then calcined at 550 °C for 3h in air condition.

The Fe-ZSM-5 catalyst with an iron loading of 7 wt.% was prepared by incipient wetness impregnation method using FeCl$_2$·4H$_2$O as precursor and H-ZSM-5 (Si/Al = 25) as support. FeCl$_2$·4H$_2$O was firstly dissolved in deionized water and then added to H-ZSM-5 to form a paste. The paste was aged for 24 h at room temperature and dried at 60 °C overnight. Finally, the sample was calcined in air condition at 550 °C for 6 h.

Characterizations

The surface areas of the catalysts were obtained from N$_2$ adsorption/desorption analysis at 77 K using a Quantachrome Quadrasorb SI-MP. Prior to the N$_2$ physisorption, the catalysts were degassed at 300 °C for 4 h. Surface areas were determined by BET equation in 0.05-0.35 partial pressure range.

Powder X-ray diffraction (XRD) measurements of Ce$_a$W$_b$O$_x$ serial catalysts were carried out on a computerized PANalytical X’Pert Pro diffractometer with Cu K$_\alpha$ (λ = 0.15406 nm) radiation. The data of 20 from 20 to 80 ° were collected at 8 °/min with the step size of 0.07 °.

Visible Raman spectra of Ce$_a$W$_b$O$_x$ serial catalysts were collected at room temperature on a Spex 1877 D triplemate spectrograph with spectral resolution of 2 cm$^{-1}$. A 532 nm DPSS diode-pump solid semiconductor laser was used as the excitation source and the power output was about 40 mW. Before measurements, the samples were well ground and mounted into a spinning holder to avoid thermal damage during the scanning. The Raman signals were collected with conventional 90 ° geometry and the time for recording each spectrum was about 1000 ms. All Raman spectra used in the paper were original and unsmoothed.
The XPS of CeO₃, WO₃ and CeWO₃ were recorded on a Scanning X-ray Microprobe (PHI Quantera, ULVAC-PHI, Inc.) using Al Ka radiation (1486.7 eV). Binding energies of Ce 3d and O 1s were calibrated using C 1s peak (BE = 284.8 eV) as standard.

The *in situ* DRIFTS experiments were performed on an FTIR spectrometer (Nicolet Nexus 670) equipped with a smart collector and an MCT/A detector cooled by liquid nitrogen. The reaction temperature was controlled precisely by an Omega programmable temperature controller. Prior to each experiment, the sample was pretreated at 400 °C for 0.5 h in a flow of 20 vol.% O₂/N₂ and then cooled down to 200 °C. The background spectrum was collected in flowing N₂ and automatically subtracted from the sample spectrum. The reaction conditions were controlled as follows: 300 ml/min total flow rate, 500 ppm NH₃, 500 ppm NO, 5 vol.% O₂ and N₂ balance. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹.

**Influence of H₂O + CO₂ on the SCR activity of CeWO₃ catalyst**

![Fig. S1](image)

**Fig. S1** NH₃-SCR activity of CeWO₃ catalyst in the presence of H₂O + CO₂. Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5 vol.%, 5 vol.% H₂O, 5 vol.% CO₂, N₂ balance and GHSV = 250,000 h⁻¹.

The description of Fig. S1 was already shown in the main text.
BET surface area derived from N\textsubscript{2} physisorption and CeO\textsubscript{2} crystallite size calculated by Scherrer equation from XRD results

Table S1 BET surface area and CeO\textsubscript{2} crystallite size of the catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
<th>CeO\textsubscript{2} crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO\textsubscript{x}</td>
<td>46.1</td>
<td>17.6</td>
</tr>
<tr>
<td>Ce\textsubscript{2}W\textsubscript{1}O\textsubscript{x}</td>
<td>44.4</td>
<td>8.8</td>
</tr>
<tr>
<td>CeWO\textsubscript{x}</td>
<td>70.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Ce\textsubscript{1}W\textsubscript{2}O\textsubscript{x}</td>
<td>74.1</td>
<td>11.8</td>
</tr>
<tr>
<td>WO\textsubscript{x}</td>
<td>6.1</td>
<td>−</td>
</tr>
</tbody>
</table>

Raman spectra

**Fig. S2** Raman spectra of Ce\textsubscript{a}W\textsubscript{b}O\textsubscript{x} serial catalysts (\textit{\lambda}_{\text{ex}} = 532 nm). The peak at 465 cm\textsuperscript{-1} is assigned to CeO\textsubscript{2}, and the peaks at 280, 332, 720 and 811 cm\textsuperscript{-1} are assigned to WO\textsubscript{3}.

The visible Raman spectra of Ce\textsubscript{a}W\textsubscript{b}O\textsubscript{x} serial catalysts are presented in Fig. S2. The band at 465 cm\textsuperscript{-1} is assigned to the Raman active $F_{2g}$ mode of CeO\textsubscript{2}, the typical band of a fluorite structural material.\textsuperscript{S1} The bands at 280 and 332 cm\textsuperscript{-1} are assigned to the W-O-W bending modes ($F_{2g}$) of the bridging oxygen, and the bands at 720 and
811 cm\(^{-1}\) are assigned to the W-O stretching mode \((A_{1g})\) and W-O bending mode \((E_g)\), respectively.\(^{S2-S4}\) The lower band intensity of CeO\(_2\) on Ce\(_n\)W\(_b\)O\(_x\) serial catalysts showed that the particle size of CeO\(_2\) on the catalyst surface was rather small due to the inhibition of crystallization by W doping. In addition, no WO\(_3\) species was detected at all, which was in well accordance with the XRD results in Fig. 4.

**Normalized NH\(_3\)-SCR activity by BET surface area**

![Normalized NH\(_3\)-SCR activity by BET surface area](image)

**Fig. S3** NH\(_3\)-SCR activity of the Ce-W mixed oxide catalysts normalized by BET surface area. Reaction conditions: [NO] = [NH\(_3\)] = 500 ppm, [O\(_2\)] = 5 vol.\%, N\(_2\) balance and GHSV = 250,000 h\(^{-1}\).

In order to deduce the main active component in the Ce-W mixed oxide catalyst, we normalized the NO\(_x\) conversion over the catalysts with different Ce/W molar ratios using BET surface area (see Fig. S3). With the increase of Ce/W molar ratio, the normalized NO\(_x\) conversion showed a monotonic increase, indicating that small CeO\(_2\) crystallite might be the main active component. Though the normalized NH\(_3\)-SCR activity of CeWO\(_x\) is lower than that of Ce\(_2\)W\(_1\)O\(_x\), from the viewpoint of application we still chose CeWO\(_x\) as the model catalyst for further study due to its high apparent NH\(_3\)-SCR activity.
NO and NH₃ oxidation activity

In order to investigate the synergistic effect of Ce and W species in CeWOₓ catalyst, the separate NO oxidation (NO + O₂) and separate NH₃ oxidation (NH₃ + O₂) experiments were carried out.

The NO₂ production during separate NO oxidation reaction over CeOₓ, WOₓ and CeWOₓ are shown in Fig. S4. The NO₂ production over CeWOₓ is obviously higher than those over pristine CeOₓ and WOₓ in the low temperature range. Many studies have shown that, if the SCR catalyst can oxidize NO to NO₂ in situ, its low temperature SCR activity will be significantly enhanced due to the occurrence of “fast SCR” reaction.⁵⁵,⁵⁶ Therefore, the synergistic effect of CeOₓ and WOₓ could enhance the low temperature activity of CeWOₓ, by promoting NO oxidation to NO₂ to facilitate the “fast SCR” reaction.

![Graph showing NO₂ production during separate NO oxidation reaction](image)

**Fig. S4** NO₂ production during separate NO oxidation reaction over CeOₓ, WOₓ and CeWOₓ. Reaction conditions: [NO] = 500 ppm, [O₂] = 5 vol.%, N₂ balance and GHSV = 250,000 h⁻¹.

The NH₃ oxidation activities of CeOₓ, WOₓ and CeWOₓ are presented in Fig. S5. The NH₃ oxidation ability of CeWOₓ is obviously higher than those of pristine CeOₓ and WOₓ, which means that synergistic effect of CeOₓ and WOₓ makes the CeWOₓ catalyst more effective in NH₃ activation. Besides, the N₂ selectivity in NH₃ oxidation
reaction over CeWO₃ catalyst was much higher than that over CeOₓ, suggesting that the introduction of W species into CeWO₃ catalyst greatly suppressed the unselective oxidation of NH₃ to N₂O or NOₓ, which is also beneficial to the enhancement of N₂ selectivity in NH₃-SCR reaction.

![Graph showing NH₃ conversion and N₂ selectivity over CeOₓ, WOₓ, and CeWO₃ catalysts.](image)

**Fig. S5** Separate NH₃ oxidation activity and corresponding N₂ selectivity (inserted) over CeOₓ, WOₓ and CeWO₃. Reaction conditions: [NH₃] = 500 ppm, [O₂] = 5 vol.%, N₂ balance and GHSV = 250,000 h⁻¹.

**XPS results**

![XPS spectra showing Ce 3d peaks for CeOₓ and CeWO₃.](image)

**Fig. S6** XPS results of Ce 3d of CeOₓ and CeWO₃.
The XPS results of Ce 3d on CeO\textsubscript{x} and CeWO\textsubscript{x} are shown in Fig. S6. The Ce 3d peaks were fitted by searching for the optimum combination of Gaussian bands with the correlation coefficients ($r^2$) above 0.99. The sub-bands labeled u' and v' represent the 3d\textsuperscript{10}4f\textsuperscript{1} initial electronic state corresponding to Ce\textsuperscript{3+}, and the sub-bands labeled u, u'', v, v'', and v''' represent the 3d\textsuperscript{10}4f\textsuperscript{0} state of Ce\textsuperscript{4+}.\textsuperscript{7,8} The Ce\textsuperscript{3+} ratio on CeWO\textsubscript{x} (37.2\%) calculated by Ce\textsuperscript{3+}/(Ce\textsuperscript{3+} + Ce\textsuperscript{4+}) is much higher than that on CeO\textsubscript{x} (7.8\%). The higher Ce\textsuperscript{3+} ratio in CeWO\textsubscript{x} indicates the presence of more surface oxygen vacancies, which will facilitate the adsorption of oxygen species or activate reactants in SCR reaction.

The XPS results of Ce\textsuperscript{3+} on CeO\textsubscript{x} and CeWO\textsubscript{x} are shown in Fig. S6. The Ce 3d peaks were fitted by searching for the optimum combination of Gaussian bands with the correlation coefficients ($r^2$) above 0.99. The sub-bands labeled u' and v' represent the 3d\textsuperscript{10}4f\textsuperscript{1} initial electronic state corresponding to Ce\textsuperscript{3+}, and the sub-bands labeled u, u'', v, v'', and v''' represent the 3d\textsuperscript{10}4f\textsuperscript{0} state of Ce\textsuperscript{4+}.\textsuperscript{7,8} The Ce\textsuperscript{3+} ratio on CeWO\textsubscript{x} (37.2\%) calculated by Ce\textsuperscript{3+}/(Ce\textsuperscript{3+} + Ce\textsuperscript{4+}) is much higher than that on CeO\textsubscript{x} (7.8\%). The higher Ce\textsuperscript{3+} ratio in CeWO\textsubscript{x} indicates the presence of more surface oxygen vacancies, which will facilitate the adsorption of oxygen species or activate reactants in SCR reaction.

![Fig. S7 XPS results of O 1s of CeO\textsubscript{x}, WO\textsubscript{x} and CeWO\textsubscript{x}.](image)

The XPS results of O 1s on CeO\textsubscript{x}, WO\textsubscript{x} and CeWO\textsubscript{x} are shown in Fig. S7. The O 1s peak was fitted into two sub-bands by searching for the optimum combination of Gaussian bands with the correlation coefficients ($r^2$) above 0.99. The sub-bands at lower binding energy (528.7-530.9 eV) corresponded to the lattice oxygen O\textsuperscript{2−} (denoted as O\textsubscript{β}), and the sub-bands at higher binding energy (531.4-532.5 eV) corresponded to the surface adsorbed oxygen (denoted as O\textsubscript{α}), such as O\textsuperscript{2−} or O\textsuperscript{−} belonging to defect-oxide or hydroxyl-like group.\textsuperscript{9} The O\textsubscript{α} ratio on CeWO\textsubscript{x} (37.2\%) calculated by O\textsubscript{α}/(O\textsubscript{α} + O\textsubscript{β}) is much higher than those on CeO\textsubscript{x} (7.8\%) and WO\textsubscript{x} (8.4\%), which means that the synergistic effect between Ce and W species indeed resulted in more surface oxygen vacancies. Usually, O\textsubscript{α} is more reactive in oxidation
reactions due to its higher mobility than O$_\beta$.$^{10}$ Therefore, the higher O$_\alpha$ ratio on CeWO$_x$ is beneficial for the NO oxidation to NO$_2$ in the SCR reaction and thereafter facilitate the “fast SCR” reaction.

**In situ DRIFTS study**

![Graphs showing DRIFTS data](image)

**Fig. S8** *In situ* DRIFTS of (A) NH$_3$ adsorption, (B) NO + O$_2$ adsorption, (C) NO + O$_2$ reacted with pre-adsorbed NH$_3$ species, and (D) NH$_3$ reacted with pre-adsorbed NO$_x$ species at 200 °C on CeWO$_x$ catalyst.

Band assignments.$^{9,11-18}$

(A) 1668 cm$^{-1}$ and 1419/1421 cm$^{-1}$: symmetric and asymmetric bending vibrations of ionic NH$_4^+$; 1591/1593 cm$^{-1}$ and 1190/1155 cm$^{-1}$: asymmetric and symmetric bending vibrations of coordinated NH$_3$; 1539/1549 cm$^{-1}$: scissoring vibration mode of NH$_2$ species; 3257 and 3350 cm$^{-1}$: N-H stretching vibration modes; 1620 cm$^{-1}$ and 3637, 3670 cm$^{-1}$: hydroxyl consumption due to the interaction with NH$_3$ to form NH$_4^+$.

(B) 1601/1558 cm$^{-1}$ and 1232/1219 cm$^{-1}$: bridging nitrate; 1578/1539 cm$^{-1}$: bidentate nitrate; 1549/1527 cm$^{-1}$: monodentate nitrate; 1508 cm$^{-1}$: unknown species.
(C) 1603 and 1232 cm\(^{-1}\): bridging nitrate; 1578 cm\(^{-1}\): bidentate nitrate; 1549 cm\(^{-1}\): monodentate nitrate; 1508 cm\(^{-1}\): unknown species.

(D) 1668 and 1419 cm\(^{-1}\): symmetric and asymmetric bending vibrations of ionic NH\(_4^+\); 1591 and 1188 cm\(^{-1}\): asymmetric and symmetric bending vibrations of coordinated NH\(_3\); 1620 cm\(^{-1}\): hydroxyl consumption due to the interaction with NH\(_3\) to form NH\(_4^+\); 1556 cm\(^{-1}\): bidentate nitrate with red shift; 1250 cm\(^{-1}\): surface ammonium nitrate species.

The description of Fig. S8 was already shown in the main text.

**References**


