A unified intermediate and mechanism for soot combustion on potassium-supported oxides

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The soot combustion mechanism over potassium-supported oxides (MgO, CeO2 and ZrO2) was studied to clarify the active sites and discover unified reaction intermediates in this typical gas-solid-solid catalytic reaction. The catalytically active sites were identified as free K\(^1\) rather than K\(^2\)CO\(_3\), which can activate gaseous oxygen. The active oxygen spills over to soot and forms a common intermediate, ketene, before it was further oxidized into the end product CO\(_2\). The existence of ketene species was confirmed by density functional theory (DFT) calculations. The oxygen spillover mechanism is proposed, which is explained as an electron transfer from soot to gaseous oxygen through the active K\(^1\) sites. The latter mechanism is confirmed for the first time since it was put forward in 1950, not only by ultraviolet photoelectron spectroscopy (UPS) results but also by semi-empirical theoretical calculations.

Soot (black carbon) from diesel engines has become a highly hazardous pollutant which can cause serious environmental and health problems\(^1\). Catalytic soot combustion is an efficient after-treatment for soot clean-up and also a relatively complex gas-solid-solid reaction, which has always been thought to operate by an oxygen-transfer mechanism. However, truly conclusive examples are rare. In 1950 the so-called electron-transfer mechanism was put forward, unfortunately no firm proof was available\(^2,3\). Although this was mentioned in a review paper in 2001\(^3\), no further information is available. Therefore, it is important to clarify the two mechanisms and their relationship. In this context catalysts containing alkali metals and potassium (K) in particular were chosen due to their extremely high catalytic soot removal activity\(^4-7\).

In most cases K is present to promote catalytic soot combustion and improve the contact of catalysts with soot and/or enhance the oxidation activity of the catalysts\(^8\). In addition K-compounds, for instance, K\(_2\)O, KOH and K\(_2\)CO\(_3\), can serve as independent catalysts or active components of catalysts for soot combustion and have high activity\(^9\). It is well known that as opposed to precious metals and transition metals with variable valence states\(^10-15\), K is present as K\(^1\) in the catalyst, which cannot be reduced or oxidized during the redox reactions. How then can K-containing compounds catalyze an oxidation reaction like diesel soot combustion? Okubo et al. proposed carbonates on the surface of thermally treated K\(_2\)CO\(_3\)/Na-nepheline as the active species\(^16,17\), possibly following the reaction of K\(_2\)CO\(_3\) + C + O\(_2\) \(\rightarrow\) K\(_2\)O + 2CO\(_2\)\(^18\). However, this is not a catalytic cycle\(^19\). The role of K was suggested to effectively participate in a redox cycle between K\(_2\)O and K\(_x\)O\(_y\), though these K species did not correlate with activity\(^20\). Apart from the nature of the active sites, the reaction intermediates play an important role in the elucidation of the reaction mechanism. Ketene groups, a carbon–oxygen complex containing the structure of C\(=\)C\(=\)O, were first reported as intermediates for soot combustion on K/MgAlO catalysts in our previous work\(^21-23\). The question is whether ketene species are common reaction intermediates when K\(^1\) is present?

In this work, we prepared different K-related species (K\(_2\)CO\(_3\) and KO\(_x\)) on three typical oxides (MgO, CeO\(_2\) and ZrO\(_2\)) by a single method using K\(_2\)CO\(_3\) as the precursor. Not only the K\(^+\) active sites but also a common intermediate were confirmed experimentally and theoretically. Thus an oxygen spillover mechanism including activation of gaseous oxygen, the formation and fate of ketene intermediates, and electron transfer processes was proposed.
in Figure 1a in K/MgO, K/CeO₂ and K/ZrO₂ are almost the same as
and S₂. However, the normalized absorption spectra of K-edge of K
single oxide, suggesting that the K species was present as a highly
K₂CO₃ (Figure 1c). It can be concluded that the K₂CO₃ phase on K/
results, two kinds of K species, K₂CO₃ and KOₓ, have been successfully
on the three typical oxides and these can be inter-
convected by desorption/adsorption of CO₂.

Discussion

Soot combustion in O₂ was carried out by temperature-programmed
oxidation (TPO) reactions to evaluate catalytic activity, which was
expressed in terms of Tₘ (Figure 2, Supplementary Figure S5 and
Supplementary Table S1). It was observed that both the fresh samples
and those after O₂ treatment exhibited almost the same Tₘ values.
Furthermore, a weak CO₂ desorption (insets in Supplementary
Figure S5) was observed at higher temperatures (> 700 °C) for the
fresh samples, which is attributed to the decomposition of K₂CO₃²⁴.
However, this is not the case for samples after O₂ treatment. This
shows that in the TPO experiments over catalysts after O₂ treatment,
the K-related phase is KOₓ rather than K₂CO₃. The TPO results
confirmed that the KOₓ and K₂CO₃ species displayed almost the
same catalytic activity. Specifically, in situ Laser Raman experiments
(Supplementary Figure S6) also demonstrated that both K₂CO₃ and
KOₓ can catalyze soot combustion reactions. In other words, no
matter which K species is present, either K₂CO₃ or KOₓ in catalysts,
the catalytically active sites are identified as K⁺. This is highly
important because K₂CO₃ was always thought to be responsible for
soot combustion¹⁶-²⁷. After water-washing, no catalytic activity is
observable due to dissolution of the K⁺ components (Supplementary
Table S2)²⁴, confirming that free (isolated) K⁺ is the active site. In
order to exclude the effects of the support on soot combustion activity,
SiO₂ as an inert substrate was chosen to demonstrate the role of
K⁺. It is showed that when K₂CO₃ was present (Supplementary
Figure S7 and Figure S8), K/SiO₂ showed relatively high catalytic
activity (Supplementary Figure S9), similar to that of K/MgO, K/
CeO₂, and K/ZrO₂ (Figure 2). Thus, it can be confirmed that K⁺ acts
as an active site rather than a promoter.

Now, it is important to determine the origin of the active oxygen
species in catalytic soot combustion when K⁺ is present. For K-con-
taining catalysts, the oxygen-transfer mechanism is the most import-
ant in which gaseous O₂ is activated by the alkali metal and then
transferred to the carbon surface²⁴. Both Janiak et al.²⁷ and Lamoen
and Persson²⁴ proposed that K can enhance the affinity and disso-
ciation of gaseous O₂ based on theoretical calculations. A similar view
was presented by Jiménez et al. who found that the active oxygen on
the catalyst for soot oxidation was increased by the presence of K⁺.
However, the active oxygen species cannot be detected by tempera-
ture-programmed reduction (TPR) with H₂²⁴. The existence of the
active oxygen species needs to be confirmed by carefully designed
experiments.

Soot–TPR results show that a certain amount of soot can be ox-
idized in the absence of O₂ (Figure 3a), suggesting the existence of
active lattice oxygen in K/MgO, K/CeO₂ and K/ZrO₂. The activity of
active lattice oxygen, as seen in Figure 3a inset, follows the order of K/
ZrO₂ > K/CeO₂ > K/MgO, which is in the same order as the Sanderson
electron- negativity of the corresponding supports (Supplemen-
tary Table S1). Because strong electron- negativity means strong elec-
tron attraction, strengthened chemical bonds of pure oxides with K⁺
were formed, leading to weakening of the K–O bond in the catalysts.
The Soot–TPR result is in good agreement with that of Tₘ from TPO
(Supplementary Table S1, Figure 2 and Supplementary Figure S5).
Additionally, it is noted that the strong CO₂ signal below 700 °C and
CO signal above 600 °C for the bulk K₂CO₃ are ascribed to the

Results

X-ray powder diffraction (XRD) patterns of K-supported oxides after
calcination at 850 °C for 2 h and exposure in air (K/MgO, K/CeO₂
and K/ZrO₂) show typical diffraction peaks of the corresponding
single oxide, suggesting that the K species was present as a highly
dispersed phase (Supplementary Figure S1, Supplementary Table S1
and S2). However, the normalized absorption spectra of K-edge of K
in Figure 1a in K/MgO, K/CeO₂ and K/ZrO₂ are almost the same as
that of K₂CO₃, showing two prominent peaks at 3612 and 3619 eV,
similar to the results reported by Gomilšek et al.²⁷, which indicates
that the K species was present as K₂CO₃. A small shift of the peak at
3619 eV for K/MgO may be associated with the formation of a small
amount of K₂Mg(CO₃)₂·4H₂O, as observed for the same sample
before calcinations (Supplementary Figure S2)²⁴. No changes of ox-
des were observed after impregnation with K (Supplementary
Figure S3). The presence of carbonate species can also be shown by IR
spectra. As observed in Figure 1b, peaks at 1370 and 1460 cm⁻¹ were
observed, which are assigned to ν₁ and ν₄ of undentate carbonate
(O–C=O)²⁴. Furthermore, X-ray photoelectron spectroscopy (XPS)
spectra show two peaks at 295.6 and 292.8 eV, identical with that of
K₂CO₃ (Figure 1c). It can be concluded that the K₂CO₃ phase on K/
MgO, K/CeO₂ and K/ZrO₂ has been confirmed using the described
preparation conditions.

Temperature-programmed desorption of CO₂ (CO₂–TPD)
experiments (Figure 1d and Supplementary Figure S4) show that
the supported K₂CO₃ on MgO, CeO₂ and ZrO₂ has been completely
decomposed after heat-treatment at 850 °C for 2 h. As observed in
Figure 1b, the IR peaks for the samples after O₂ treatment at 850 °C
for 2 h at 1370 and 1460 cm⁻¹, due to carbonates, disappeared. This
would result in the formation of another K species, KOₓ, following
the decomposition of supported K₂CO₃. Combining the above
results, two kinds of K species, K₂CO₃ and KOₓ, have been successfully
produced on the three typical oxides and these can be inter-

Figure 1 | (a) K K-edge normalized absorption, (b) IR spectra of fresh
samples and the samples after O₂ treatment at 850 °C for 2 h, (c) XPS
spectra of K 2p for K/MgO, K/CeO₂, K/ZrO₂ and K₂CO₃, (d) CO₂–TPD
patterns of K/MgO, K/CeO₂ and K/ZrO₂ heating from 150 to 850 °C in He
and holding at 850 °C for 2 h.
reactions of $K_2CO_3 + C \rightarrow K_2O + CO_2$ and $K_2CO_3 + 2C \rightarrow 2K + 3CO$ or $K_2O + C \rightarrow 2K + CO$, respectively.

In situ IR of NO adsorption was also performed, in which NO is used as a probing molecule, because NO can be efficiently stored on K$^+$ cation sites only after NO has been oxidized to NO$_2$. First, the catalysts were pre-oxidized and then exposed to NO (Figure 3b and Supplementary Figure S10). A strong and stable peak at 1248 cm$^{-1}$ is observed, which can be attributed to nitrite species derived from the oxidation of NO by the active oxygen in the catalysts. However, over the corresponding potassium-free supports, only negligible peaks were present, possibly due to weak NO oxidation and adsorption. This is evidence of activation of gaseous O$_2$ on the active K$^+$ sites.

The role of activated O$_2$ was further confirmed by isothermal anaerobic titrations, in which the O$_2$ flow was turned on at first and then turned off during the catalytic soot combustion process (Supplementary Figure S11, Supplementary Table S1). The results showed that once the O$_2$ flow was stopped, the soot combustion activity gradually decreased, confirming the participation of active oxygen (O*) derived from gaseous O$_2$ in real reaction conditions (the O* amounts are listed in Table S1). Similar results have been demonstrated on Li-doped MgO, on which the [LiO$_2$] active sites were formed from the interaction of Li$^+$ with molecular oxygen, which were responsible for the activity of methyl radical formation.

Moulijn and Kapteijn proposed that oxygen-containing reactant molecules were incorporated in or dissociated by a K-oxide cluster to produce an O* species with a relatively high reactivity for carbon and this oxygen species could be exchanged extremely quickly by gaseous oxygen-containing reactants, which is an example of oxygen spillover.

In situ IR experiments for soot combustion were carried out over K/MgO, K/CeO$_2$, K/ZrO$_2$ and K$_2$CO$_3$ (Figure 4a and Supplementary Figure S12). A characteristic IR band at 2162 cm$^{-1}$ can be clearly observed, accompanied by the band at 2358 cm$^{-1}$ and a series of bands in the

Figure 2 | TPO patterns of CO$_2$ for soot combustion on pure oxides, K-supported oxides, K-supported samples after treatment in O$_2$ at 850°C for 2 h, and K-supported samples after water-washing treatment for 24 h: (a) MgO, (b) CeO$_2$ and (c) ZrO$_2$.

Figure 3 | (a) Soot–TPR for K/MgO, K/CeO$_2$, K/ZrO$_2$ and K$_2$CO$_3$ after O$_2$ treatment at 850°C for 2 h. The inset in (a) is the partially enlarged figure at low temperature range; (b) In situ IR spectra of NO adsorption (1000 ppm NO + He) on MgO and K/MgO at 100°C after O$_2$ treatment in 5 vol.-% O$_2$ + He at 500°C for 30 min.
V6.438 and the IR vibration frequencies were thus calculated. The corrected DFT level using the quantum program package Turbomole was stopped (Supplementary Figure S13). In the 1st stage, soot range of 1000–1800 cm⁻¹, which can be attributed to ketene species, was oxidized to CO₂ in O₂ while the temperature was increased to 350°C (a and b). In the 2nd stage the flow of O₂ was stopped at 350°C and the CO concentration sharply dropped to zero while the CO₂ concentration declined slowly, implying that some surface active oxygen on the catalyst transferred to the ketene group. As the evolution of CO₂ decreased to a negligible level, the ketene group disappeared, which can be shown from the vanishing of its characteristic peak at 2162 cm⁻¹ in the inset in Figure S13 (c). These facts strongly support the transformation of the ketene species to CO₂ by active oxygen. Since the appearance of the ketene species is independent of the catalyst support, it should be a unified reaction intermediate for K-supported catalysts. As shown (Figure 4c), the K⁺ pulls O₂ from the gas phase and active oxygen species were obtained by the formation of KO₁ ([K'O−]). The activated oxygen transfers to free carbon sites where the ketene intermediate is formed. This is further oxidized, by active oxygen, to form the end product CO₂. This is a typical oxygen spillover mechanism proposed by us⁴⁴ and others⁴⁵, in which the catalyst, as an oxygen carrier, can promote the transfer of oxygen from the gas phase to the carbon surface, by means of the formation of an intermediate compound.

Most importantly in this work, the electron-transfer mechanism was proved for the first time both by ultraviolet photoelectron spectroscopy (UPS) experiments and by theoretical calculations. The UPS spectra gave direct evidence of the changes in the electronic structures of soot due to the presence of the K⁺ ions. As shown in Figure 5a, pure soot shows a broad UPS peak at approximately 9.0 eV, which is assigned to valence electrons of the p-σ bands on graphite soot⁴⁶. This peak became weaker when soot was mixed with K/ZrO₂ (Figure 5a) or K/CeO₂ (Supplementary Figure S14a). However, the peak intensity of the mixtures of soot with supports (ZrO₂ or CeO₂) was nearly unchanged, indicating that the perturbations in the electronic properties of soot occur only in the presence of K⁺ ions⁴⁷. The absence of photoemission signals of soot for the mixtures of soot + K/MgO and soot + MgO is possibly due to the relatively low electrical conductivity properties of MgO (Supplementary Figure S14b). The perturbations in the electronic properties of soot mixed with K-supported samples can be illustrated by semi-empirical theoretical calculations. The contour plots of net charges for the soot model (graphene) and the mixtures of soot + catalyst are given in Figure 5b and c, respectively, which clearly describe the changes in the electronic structures due to the presence of K⁺. The distribution of charges on pure soot is relatively homogeneous and the net charge is near to zero. When the K⁺ ions are present, the net charge of the edge carbons is substantially changed. As shown in Figure 5c, the edge charges on soot become negative while the inner charges are mainly positive, regardless of the locations of the K⁺ ions. This demonstrates an important role of the K⁺ ions that attract the electrons from the inner carbon atoms to the edge carbon atoms and this is in agreement with the calculations of Yang et al.⁴⁸ The electron-rich carbon atoms favour donating electrons to the electrophilic species such as oxygen molecules to form active oxygen species such as O₂⁻ and O¹⁻. In other words, the K⁺ ions facilitate the concentration of electrons on the soot surface with higher energy states, strengthening the driving force for efficient electron transfer from soot to O₂⁴⁹. The electron transfer and the oxygen spillover mechanisms can be effectively integrated by the interaction of soot with the K⁺ ions on K-supported catalysts⁴⁹. On the one hand, the K⁺ ions act on π electrons of soot and covalent K–C bonds may be present, leading to electron transfer from soot to the electronegative oxygen, thus decreasing the aromatic character of soot and activating gaseous oxygen. On the other hand, the activated oxygen spills over from K⁺ sites to soot and ketene species are formed, which weaken the neighbouring C–C bonds⁵⁰, and the product CO₂ is evolved. The transfer of electrons from soot to K⁺ was realized by way of oxygen species transferred from KO₁ ([K'O−]) to soot.

**Figure 4** | (a) In situ IR spectra for soot combustion in a flow of 5 vol.% O₂ + He on K/MgO; (b) The optimized complex geometry of the quinonoid-ketene molecular complex with K⁺; (c) Illustration of the unified oxygen spillover and the electron transfer process for soot combustion on potassium-supported oxides.
Catalyst preparation. The catalysts were prepared by impregnating single oxides (MgO, CeO₂ and ZrO₂) with the aqueous solution of K₂CO₃. Prior to the preparation, the oxides were heat-treated at 850°C for 2 h. Their suspensions in the aqueous solution of carbonate salt were evaporated while being stirred at 90°C until achieving a paste, which was then dried at 120°C overnight and calcined at 850°C for 2 h. In this way, the obtained catalysts with different support were designated as K/MgO, K/CeO₂ and K/ZrO₂. According to our previous work, the weight loading amount of K is determined as 8 wt.%. The as-prepared samples are also called as the fresh catalysts. The catalysts named K/ZrO₂ were denoted as K/MgO–w, K/CeO₂–w and K/ZrO₂–w, respectively, which were obtained by stirring the suspension of the fresh catalysts in the deionized water, and then filtering, drying at 120°C overnight and calcinations at 850°C for 2 h.

Characterizations. Powder XRD patterns were recorded on a Rigaku D/max-rc diffractometer. Surface area and pore size distribution were determined by N₂ adsorption-desorption at 77 K with the BET method using a Micromeritics ASAP 2010 instrument after outgassing at 300°C for 5 h prior to analysis. XAFS measurements for the K K-edge were performed on the XAFS station of Beijing synchrotron radiation facility (BSRF, Beijing, China). The K K-edge (3608 eV) data were collected at the 4B7A beam line of the Spectra in fluorescence mode with a Si (Li) detector. IR experiments were carried out using FT–IR spectrometer (Bruker Tensor 27) over 400–4000 cm⁻¹ after 32 scans at a resolution of 4 cm⁻¹. The samples were diluted with KBr in the ratio of 1:100. XPS data were obtained on an AXIS–Ultra instrument from Kratos Analytical using monochromatic Al Kα radiation (225 W, 15 mA and 15 kV) and low-energy electron flooding for charge compensation. In order to confirm the existence of active oxygen species, UPS characterization was carried out using a He I emission lamp (21.22 eV) as an excitation source and an analyzer resolution of 0.025 eV.

In situ IR experiments. Soot combustion was further investigated using in situ IR spectroscopy. The IR spectra were recorded on the FT–IR spectrometer (Bruker Tensor 27) over 400–4000 cm⁻¹ after 32 scans at a resolution of 4 cm⁻¹. Additionally, in order to confirm the existence of active oxygen species, in situ IR experiments for NO adsorption were performed. The experimental details are provided in supporting information.

DFT calculations and Semi-empirical quantum chemistry calculations. The geometry of the complex of quinonoid ketene molecular and K⁺ was optimized at DFT levels using the well-known B3LYP hybrid exchange-correlation functional together with Ahlrichs split valence plus polarization (SVP) basis set for all atoms. A semi-empirical quantum chemistry program, MOPAC (Molecular Orbital Package) version 2012 was used to calculate the net charge of model soot based on NDDO (neglect of diatomic differential overlap) approximation. The program has been updated with a new and more accurate parameterization (PM7) for all the main group elements and transition metals. The details of calculation are provided in supporting information.

Figure 5 | (a) UP spectra of soot, K/ZrO₂ and soot + K/ZrO₂; (b) Graphene as the model structure of soot. Three locations of the K⁺ ions near to the structures are labeled. Label p indicates the top location perpendicular to the plane of the soot model, while Labels z and a represent the locations on the same plane as the soot model, near to the zigzag edge and armchair edge of the soot, respectively; (c) Contour plots of net charges calculated by semi-empirical methods for soot and soot in the presence of the K⁺ ion at the locations of p, z and a as referred to in (b).

In summary, for soot combustion on the K-supported catalysts, the following three conclusions have been made: (1) the catalytically active site has been identified as free K⁺ rather than K₂CO₃; (2) the ketene intermediate has been found to be common to these processes; (3) the oxygen spillover mechanism has been interpreted as an intrinsic electron transfer process on an atomic scale through the active K⁺ sites.
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Author contributions
Q. L. designed and performed experiments. X. W. prepared the samples used in this work. X. W. and Y. X. Z. helped synthesizing catalysts. Y. X. Z., L. R. Z. and L. Z. helped characterizing samples. Z. L. Z., C. H. and M. M. discussed the results. Q. L. and Z. L. Z. wrote the manuscript. Z. L. Z. supervised the project.

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