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The nature of the promotion effect of isolated potassium atoms anchored on surfaces of a Hollandite manganese oxide was investigated by studying their geometric and electronic structures. The results reveal that the surface isolated potassium atoms with hybridized d-sp orbitals specifically promote oxygen activation, so enhancing the low-temperature reactivity in catalytic oxidation.

The promotion effect of alkali metals in heterogeneous catalysis has been intensively studied in the past few decades, because alkali promoters such as potassium give rise to the positive effects on many important catalytic reactions. Two representative cases about potassium promoter are the synthesis of ammonia and the Fischer-Tropsch reaction over iron-based catalysts. In the ammonia synthesis, potassium promoter enhances the rate of N₂ dissociation on the metallic iron surfaces by 2-3 orders of magnitude. In the Fischer-Tropsch reactions, potassium increases the selectivity of iron-based catalysts. Similar promotion effects of alkali metals have also been reported for oxidation reactions on oxide catalysts. In general, the alkali promotion effect is attributed to the change of the electronic features of active components and adsorbed reactant molecules, so enhancing catalytic performance. However, few studies concern the geometric and electronic structures of the alkali promoters themselves due to their relatively “simple” electron orbital structures and easy mobility during catalytic reactions.

As a matter of fact, these structure features should be associated with the intrinsic nature of the promotion effect.

Owing to the structural diversity and surface complexity of alkali metals (salts or oxides), experimental investigations of these characteristics of the promoters remain challenging. As a consequence, the promotion effect including the determination of the geometric and electronic structures of alkali metals is generally investigated by theoretical studies. In water-gas shift reactions, a PtK₀ octahedron with the Pt core was theoretically predicted to be the most promising active structure by the charge transfer from K to Pt, which is favourable for activation of oxygen species. The electron donor effect is commonly regarded to be intimately associated with the outermost orbitals (4s and 4p) of potassium. Note that the contribution of the K 3p orbitals to the electron-donor effect was theoretically predicted by the outer d-sp orbital hybridization, but the related experimental evidence is lacking.

Herein we investigate the nature of the promotion effect in catalytic oxidation, focusing on the immediate geometric and electronic structures of potassium stably anchored on surfaces of a Hollandite manganese oxide (HMO), and experimentally evidence the d-sp orbital hybridization of potassium. First, we use scanning transmission electron microscopy (STEM) to image the isolated potassium atoms on the HMO surfaces, and conduct the extended X-ray absorption fine structure (EXAFS) spectra to determine the local geometric structures. Next, the electronic structures of the isolated potassium atoms are studied by using the X-ray absorption near edge structure (XANES) spectroscopy and X-ray photoelectron spectroscopy. Finally, we investigate the promotion effect of potassium in catalytic oxidation together with reaction kinetic studies.

The isolated potassium atoms anchored on the surfaces of the HMO (K/HMO) are clearly observed by the TEM from the HMO [001] zone axis, as shown in Fig. 1a. The closest K distance on the HMO (001) plane is determined to be ~7.1 Å (Fig. 1b), much longer than the K-K bonds (~4.6 Å) in the bulk potassium. The synchrotron X-ray diffraction (SXRD) pattern and Rietveld refinement analysis of K/HMO evidence that the K-K distance along HMO [001] direction is ~5.7 Å, twice of the lattice parameter along the HMO [001] direction according to K atoms and hollow sites with an alternate stacking in the HMO pores (Fig. S1, Tables S1, S2, ESI†). The results are further confirmed by the high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) with line-scanned energy dispersive X-ray (EDX) spectra (ESI†).
Fig. 1 Identification of the isolated potassium atoms anchored on the HMO surfaces. (a) HRTEM image of K₀/HMO viewed from the HMO [001] zone axis. (b) Stimulated HRTEM image in the dot square in (a) with a structural model. The grey, red, and blue balls represent K, O, and Mn atoms, respectively. Blue octahedra are MnO₆. (c) HAADF-STEM image of the K₀/HMO rod with horizontal and vertical line-scanned EDX spectra along the grey line (d) and the yellow line (e), respectively. Scale bar: 1 nm, 0.5 nm and 5 nm in (a), (b) and (c), respectively. (f) NO-TPD profiles of K₀/HMO (red circles) and HMO (black circles) after saturation adsorption of NO at 250 °C, and a red shade represents the desorbed amount of NO₂ from K₀/HMO. 

1c-e). Hence, the results demonstrate the presence of the isolated individual potassium atoms. 

To substantiate the presence of surface potassium atoms, we use nitric oxide (NO) as a sensitive probing molecule by a temperature-programmed desorption (TPD) procedure (NO-TPD) for K₀/HMO and HMO after saturation adsorption of NO in the presence of O₂ at 250 °C. According to the NO-TPD profiles in Fig. 1f, it is convincing that the NO₂ molecules desorbed from K₀/HMO originate from nitrate/nitrite oxides adsorbed on the surface potassium atoms,²⁻⁴ because the desorption amount of NO₂ on the potassium-free HMO can be ignored under the identical conditions. These results combined with the electron micrographs above strongly evidence the presence of the isolated potassium atoms on the HMO surfaces. 

The local geometric structures of the isolated potassium atoms are investigated by using the EXAFS spectroscopy and the SRXD measurement. Fig. 2 displays the Fourier transform (FT) amplitudes of the EXAFS spectra at the K K-edge of K₀/HMO with different k^n weights (n = 1, 2 or 3) and KCl with k^2 weight. The structural parameters obtained by fitting the spectra with theoretical models are listed in Table S3 (ESI†) and the curve-fitting of R-space, and inverse FT spectra are given in Fig. S2 (ESI†). The local environments of the isolated potassium atoms of K₀/HMO are significantly different from those of KCl judging from their FT spectra (Fig. 2). As expected, the first shell in the FT spectra of KCl represents the K-Cl bond, with an average bond length of ~3.1 Å and a coordination number (CN) of six, consistent with a KCl₆ octahedron with an O₆ symmetry (Fig. 2, inset). The interatomic distance in the first shell for K₀/HMO can be attributed to the K-O bonds with the bond length of ~2.9 Å and a CN of eight (Table S3, ESI†), and the second shell should be assigned to both the second K-O distance and the near neighbor K-Mn distance according to the different amplitudes with different k weights and the Rietveld SRXD refinement (Table S4, ESI†). The absence of an intensive EXAFS amplitude of the K-K distance indicates the potassium atoms are at the atomically dispersed states. These results are consistent with the Rietveld refinement analysis of the SRXD pattern of K₀/HMO, which gives a coordination configuration of a KO₆ polyhedron with a D₄h symmetry (Fig. 2, inset).

The electronic structures of the isolated potassium atoms are studied by using the XANES spectroscopy and the X-ray photoelectron spectroscopy (Fig. 3). The XANES spectra at the K K-edge of K₀/HMO is distinguished from that of KCl by the presence of a low intensity pre-edge (Fig. 3a, Fig. S3, ESI†). In particular, the 1s → 3d pre-edge features are sensitive to the coordination geometry of excited atoms.²⁹ As the octahedral potassium centers in KCl are centro-symmetric without d-p mixing, only rather low intensity pre-edge appears due to the quadrupole transition. The relatively intense pre-edge of the K centers with a pseudo-tetragonal prism structure in K₀/HMO indicates the presence of 1s → 3d dipole allowed contribution due to 3d-4p mixing, that is, d-sp hybridization. Therefore, the XANES spectrum evidently indicates that the presence of the hybridized d-sp orbitals of potassium atoms are apparently analogue to the outermost orbital hybridization of metal K.¹³
achieved over K/HMO, while the potassium-free HMO only gives less than 50% conversion of HCHO at this temperature. The catalytic activities toward HCHO or acetate oxidation also increase with the amount of potassium, as shown in Fig. S5 (ESI†). Therefore, the surface isolated potassium atoms have the great promotion effect in catalytic oxidation at low temperatures.

The steady-state reaction rates in terms of a turnover frequency (TOF, number of converted HCHO molecules per surface K atoms per second) are shown in an Arrhenius plot (Fig. S5, ESI†) in order to clearly understand the promotion effect of potassium. The pre-exponential factor (Fp) for K/HMO is $1.0 \times 10^6$ s⁻¹, ten times more than the corresponding Fp ($9.9 \times 10^4$ s⁻¹) for the potassium-free HMO. This suggests that the promotion effect originated from direct bonding between potassium atoms and adsorbed reaction molecules (HCHO and/or O₂), leading to the higher reaction rates of K/HMO than those of the potassium-free HMO in HCHO oxidation.

To shed light on the promotion effect of the isolated potassium atoms on HCHO and/or O₂ in the HCHO oxidation, we conduct surface reaction kinetics of the HCHO oxidation at low temperature over K/HMO and the potassium-free HMO at the conversions less than 20%,. As shown in Fig. 4, the reaction order of O₂ is 0.9 for K/HMO, much higher than that (only 0.2) of the potassium-free HMO (Fig. 4a), and the reaction orders of HCHO over both K/HMO and the

Fig. 3 Electronic structures of the isolated potassium atoms. (a) XANES spectra of K/HMO and KCl at the K K-edge together with the corresponding pre-edge XANES spectra (inset, and spectral fitting edges are red dotted curves). (b) K 2p₃/₂ XPS of K/HMO (red curve with the red shade) and KCl (black curve).

(a)

(b)

The K 2p X-ray photoelectron spectra (XPS) of K/HMO and KCl are conducted and shown in Fig. 3b (Fig. S4, ESI†). The binding energy (BE) of the K 2p peak shifts down to lower BE by ~0.6 eV for the isolated potassium atoms with respect to that of KCl, from 292.5 eV for KCl to 291.9 eV for K/HMO. The BE of K 2p₃/₂ for K/HMO is much lower than that (~293 eV) of K⁺ in K₂O. This indicates that the isolated potassium atoms have higher electron density than K⁺, coincident with the d-sp orbital hybridization of potassium evidenced by the above XANES spectra. Hence, the isolated potassium atoms with the high electron density should have a much greater promotion effect than K⁺ in potassium compounds, so high catalytic activity in oxidation reactions.

The promotion effect of the isolated potassium atoms is investigated in complete oxidation of formaldehyde (HCHO) and acetate, which are typical air pollutants, and contributes greatly to atmospheric particulate emissions, leading to the increase of severe haze events. The conversion of HCHO over K/HMO and the potassium-free HMO as a function of reaction temperature is shown in Fig. S5 (ESI†), and the temperature-dependent conversion is observed. K/HMO has the high catalytic activity for complete oxidation of HCHO at low temperatures lower than 100 °C, whereas the potassium-free HMO shows low catalytic activity under the same reaction conditions. The conversion over K/HMO is 5% at 80 °C, which increases up to 50% at 100 °C. At 120 °C, almost complete oxidation of HCHO into CO₂ and H₂O can be

Fig. 4 Reaction kinetics of the catalytic oxidation of HCHO. Reaction orders for O₂ (a) and HCHO (b) over K/HMO and the potassium-free HMO at the reaction temperature of 90 °C. The slope k represents the reaction order.
potassium-free HMO are -0.3 (Fig. 4b), indicative of the high concentration of the adsorbed HCHO species covering the surfaces of both catalysts. The adsorbed HCHO inhibits O$_2$ activation unless consumed by surface lattice oxygen, generating oxygen defects. The increase of the O$_2$ concentration decreases the HCHO coverage on the K$_2$/HMO surface by promoting CO$_2$ and H$_2$O formation, leading to an almost first-order dependence on O$_2$ concentration, while very weak dependency on O$_2$ concentration over the potassium-free HMO is due largely to the low reaction rates of HCHO oxidation. Reaction kinetics indicates that the surface isolated potassium atoms play an important role in the oxygen activation in catalytic oxidation. In fact, the HCHO oxidation in the low-reactivity steady state regime often follows a Mars-van Krevelen mechanism, and oxygen activation includes both molecular O$_2$ and surface lattice oxygen. Hence, the promotion effect of the isolated potassium atoms should cover the activation of molecular O$_2$ and surface lattice oxygen.

The dissociation step of O$_2$ is often considered as one of the important rate-limiting steps in catalytic oxidation. The activation of O$_2$ is intimately associated with the electronic states of potassium. A previous theoretical calculation reported that electron-abundant potassium atoms are energetically favorable for dissociation of O$_2$ by charge transfer from potassium to antibonding π* and σ* orbitals of O$_2$. As a consequence, the isolated potassium atoms with the high electron density are favorable for promoting O$_2$ activation. From the kinetic point of view, during such an activation process of O$_2$, the d-sp hybridization of the isolated potassium atoms plays an important role, and local transfer of sp electrons to empty d shell weakens the Pauli repulsion and allows O$_2$ molecule to approach and continue into the chemisorption region, and finally leads to O$_2$ dissociation. Therefore, the isolated potassium atoms have the strong promotion effect on oxygen activation in catalytic oxidation.

In conclusion, we investigated the promotion effect of potassium anchored on the HMO surfaces in catalytic oxidation. The HRTEM image, the HAADF-STEM image, and the EXAFS spectra showed that the isolated potassium atoms were anchored on the HMO surfaces to give the geometric configuration of the K$_2$ polyhedron with a D$_{4h}$ symmetry. The combination of the XANES spectra and XPS with catalytic reaction kinetics demonstrated that the isolated potassium atoms had the hybridized d-sp orbitals and the high electron density, specifically promoted oxygen activation, and enhanced the low-temperature catalytic reactivity in the complete oxidation of HCHO and acetylate. This finding gives direct evidence for explaining the alkali promotion effect by investigating the geometric and electronic characteristics of alkali metal promoters themselves, and provides a reasonable strategy to develop improved catalysts promoted by alkali metals.

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**Notes and references**