Quasi free K cations confined in hollandite-type tunnels for catalytic solid (catalyst)-solid (reactant) oxidation reactions

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ARTICLE INFO

ABSTRACT

Identification of catalytically active species and reaction pathway in catalytic solid (catalyst)-solid (reactant) reactions is a nontrivial task as exemplified in diesel soot oxidation (combustion), the technology for control of diesel particulate emissions. A physical contact between catalytically active species and solid soot is usually deemed necessary. Herein, thermally-stable hollandite-type α-MnO_2 ($K_xMn_8O_{16}$) nanorod catalysts have been synthesized with one-dimensional tunnel structures partially filled with relatively mobile K cations. These tunnel-confined quasi free K cations are revealed to be responsible for the catalytic soot oxidation activity, proving that physical contact between soot and K cations is unnecessary for solid-solid reaction. A novel catalyst, $K_yTi_8O_{16}$ has been successfully designed to boost the catalytic activity in TiO_2 toward soot oxidation by engineering a K-contained hollandite-type isostructure.

1. Introduction

The characterization and identification of catalytically active species are essential but nontrivial for understanding catalytic mechanism and designing advanced heterogeneous catalysts [1], which are particularly challenging when dealing with solid (catalyst) and solid (reactant) reaction systems due to their usually poor contact between each other [2–6]. For example, during catalytic diesel soot oxidation in gaseous O_2 (the technology for control of diesel particulate emissions), alkali metals such as potassium (K)-containing oxides are typical robust catalysts which are suggested to improve the physical contact bewteen soot and catalyst through free KO_x species and thus the catalytic activity [7,8]. On the other hand, a few work has proposed that K species confined in hollandite-type tunnel structures such as cryptomelane (2 × 2 edge-shared MnO_6 octahedral chains are corner connected to form a one-dimensional tunnel, which is partially filled with K cations) may help enhance the surface oxygen defects to improve soot oxidation activity [9,10]. It is unclear how these KO_x species exactly distribute and function although it is predicted that the K cations are partially filled and loosely bounded inside the tunnels [11–13] to create non-

contact scenarios between soot and K cations. Such an intriguing possibility was raised in a striking enhancement of the catalytic activity observed in Rh particles encapsulated inside carbon nanotubes for the conversion of CO and H_2 to ethanol [14].

Mn-based oxides possess many applications in gaseous heterogeneous catalytic reactions for environmental applications [15], such as catalytic CO oxidation [16] and volatile organic compounds (VOCs) combustion [17]. Recently, Wasalathanthri et al investigated the potential of mesoporous Mn oxides in catalytic oxidation of diesel soot [18]. Transition metal (Co, Cu and Ni)-doped α-MnO_2 nanowires were also reported [19]. Specifically, Bueno-López and his colleagues have found that the cryptomelane is more active for soot combustion than all the commercially available pure manganese oxides, namely MnO, MnO_2, Mn_2O_3, Mn_3O_4, and natural MnO_2 [20–22]. Unfortunately, effects of the K concentration on the catalytic activity are still far from clear [23]. Even though the cryptomelane has been reported for catalytic combustion of VOCs, the effect of the amount of alkali doping to activity is controversial [11,13]. In this paper, the intrinsic activity for soot combustion on cryptomelanes with quasi free K cations confined in the tunnel ($K_xMn_8O_{16}$) shows a clear positive correlation with the K

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contents. This is the first direct experimental evidence for K cations being active species for soot oxidation. As a proof of concept, we demonstrated that TiO_2, a poor oxidation catalyst, can be greatly improved by using a hollandite-type iso-structure ($K_yTi_8O_{16}$). The K cations in tunnels serve as catalytically active species.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by a solid phase method. The manganese carbonates ($MnCO_3$) and potassium methoxide (CH_3OK) were first ground in an agate mortar for 30 mins. The molar ratios of $MnCO_3$ and CH_3OK were 4:1, 4:1.1 and 4:1.2. The mixture was calcined in tube furnace at 620 °C for 12 h in air flow, and then the precursor powder was washed by deionized water to remove the surface K species completely [10,24–26], and then calcined again in tube furnace at 620 °C for 2 h in air flow. The catalysts obtained were named KMnO-10, KMnO-11 and KMnO-12, respectively. The Mn_2O_3 was obtained by calcining the $MnCO_3$ in tube furnace at 620 °C for 12 h in air.

The isostructural hollandite-type $K_yTi_8O_{16}$ were prepared by a solid phase method [27,28]. Typically, the mixture of K_2CO_3 and TiO_2 (anatase) was grinded in an agate mortar for 1 h, and then calcined at 1000 °C for 8 h under an 5% H_2/N_2 atmosphere. Therein, the molar ratios of K_2CO_3 and TiO_2 were 1:9 and 1:10. In order to remove the surface K species, the resultant specimens were treated by copious amount of deionized water under stirring for 24 h [10]. The final products were filtered and dried at 120 °C overnight. The catalysts obtained were named KTiO-1 and KTiO-2, respectively. For reference, the pure anatase TiO_2 was also calcined at 1000 °C for 8 h under an 5% H_2/N_2 atmosphere, which is denoted as reduced TiO_2.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max-rc diffractometer. Transmission electron microscopy (TEM) equipped with selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS) was conducted on a JEOL JEM-2010 microscope at an accelerating voltage of 200 kV. Surface area and pore size distribution were determined by N_2 adsorption/desorption at 77 K using Brunauer-Emmett-Teller (BET) method with a Micromeritics ASAP 2020 instrument after off gassing at 300 °C for 5 h prior to analysis. Inductively coupled plasma-atomic emission spectrometer (ICP–AES) experiments were carried out on an IRIS Intrepid IIXSP instrument from Thermo Elemental. X-ray absorption fine-structure (XAFS) measurements were performed on Beijing synchrotron radiation facility (BSRF, Beijing, China). IR experiments were carried out using a FTIR spectrometer (Bruker Tensor 27) over the range 400–4000 cm^{-1} with 32 scans at a resolution of 4 cm^{-1}. The samples were diluted with KBr in a ratio of 1:100. The temperature programmed reduction with H_2 (H_2–TPR) experiments were performed in a quartz reactor with a thermal conductivity detector (TCD) to monitor H_2 consumption. A 50 mg sample was pretreated in situ at 500 °C for 30 mins in a flow of O_2 (30 ml/min) and cooled to room temperature in the presence of O_2. After purging by N_2, TPR was conducted at 10 °C/min up to 600 °C in a 30 mL/min flow of 5 vol.% H_2 in N_2. To quantify the total amount of H_2 consumption, the CuO was used as a calibration reference. X-ray photoelectron spectroscopy (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. To compensate for surface charge effects, the binding energies were calibrated using the C 1 s hydrocarbon peak at 284.60 eV.
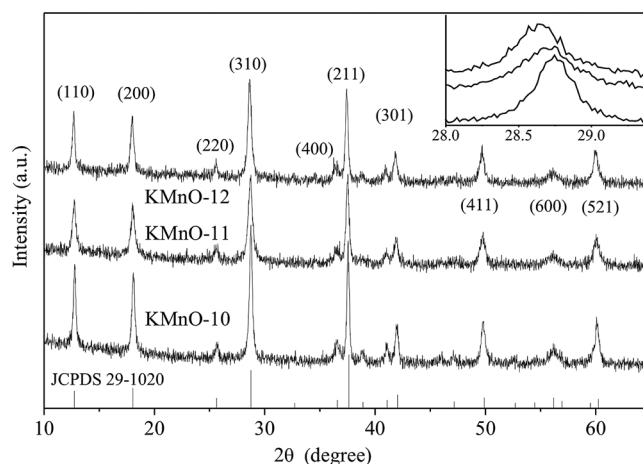

Fig. 1. XRD patterns of $K_xMn_8O_{16}$.

2.3. Activity measurement

Temperature-programmed oxidation (TPO) reactions were conducted in the fixed bed micro-reactor. Printex-U from Degussa is used as the model soot. The soot was mixed with the catalyst in a weight ratio of 1:9 in an agate mortar for 30 min, which results in a tight contact between soot and catalyst. While in loose contact conditions, the soot is mixed with the catalyst via shaking in a sample bottle for 24 h. A 50 mg sample of the soot/catalyst mixture was pretreated in a flow of He (100 mL/min) at 200 °C for 30 min to remove surface-adsorbed species. After cooling down to room temperature, a gas flow with 5 vol.% oxygen in He was introduced and then TPO was started at a heating rate of 5 °C/min until 620 °C. CO and CO_2 concentrations in the effluent gas were online monitored using a gas chromatograph (GC) (SP-6890, Shandong Lunan Ruihong Chemical Instrument Corporation, China) fitted with a methanator. The temperature of the maximum rate for soot oxidation is named T_m. The selectivity to CO_2 formation is defined as the percentage CO_2 outlet concentration divided by the sum of the CO_2 and CO outlet concentrations.

The CO oxidation experiments were performed in the fixed bed micro-reactor. A 50 mg sample of the catalyst was pretreated in a flow of He (100 mL/min) at 200 °C for 30 mins to remove surface-adsorbed species. After cooling down to room temperature, a gas flow with 5 vol. % O_2 and 500 ppm CO in He (100 ml/min) was introduced and then TPO was started at a heating rate of 5 °C/min until 620 °C. CO and CO_2 concentrations in the effluent gas were online monitored using a gas chromatograph (GC) (SP-6890, Shandong Lunan Ruihong Chemical Instrument Corporation, China) fitted with a methanator. The conversion of CO was defined as the percentage CO_2 outlet concentration divided by the CO enterance concentrations.

The isothermal reactions were performed at 270 and 290 °C for $K_xMn_8O_{16}$ and $K_yTi_8O_{16}$ respectively, at which, a stable and low soot conversion (< 15%) was achieved in a kinetic regime [29]. The reaction rate for soot combustion is obtained from the slope of the conversion lines with time. Specific rates normalized by BET surface areas were used to characterize the intrinsic activity for soot combustion.

Isotopic isothermal reaction was performed by switching the flowing gas from 1% $^{16}O_2$ to 1% $^{18}O_2$ diluted in Ar at 340 °C. 50 mg of a mixture of the soot and catalyst in tight contact mode was employed. The effluent gas from the reactor was continuously monitored by a MS for all of the isotopic molecules of CO_2 (at m/z = 44, 46 and 48) [30].

3. Results and discussion

$K_xMn_8O_{16}$ nanorods were prepared by solid-phase reactions between $MnCO_3$ and CH_3OK at 620 °C. To ensure the absence of the surface K species, the as-prepared $K_xMn_8O_{16}$ nanorods were further