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Low-Temperature Reactivity of Zn^+ Ions Confined in ZSM-5 Zeolite toward Carbon Monoxide Oxidation: Insight from in Situ DRIFT and ESR Spectroscopy

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Supporting Information

ABSTRACT: We report the low-temperature catalytic reactivity of Zn^+ ions confined in ZSM-5 zeolite toward CO oxidation. In situ DRIFT and ESR spectroscopy demonstrated that molecular O_2 is readily activated by Zn^+ ion to produce O_2^- species at room temperature (298 K) via facile electron transfer between Zn^+ ion and O_2 and that the formation of the active O_2^- species is responsible for the high activity of the ZnZSM-5 catalyst toward CO oxidation.

Coordinatively unsaturated metals such as Cr^{III}, Mn^{II}, and Ni^{I} are of great interest in catalysis because of their potential as active sites with distinct activity.[1] With a lower coordination number, the central metal trends to be in a lower oxidation state. The abundant electrons and incompletely filled orbitals endow the coordinatively unsaturated metals with unusual chemical properties, particularly exceptionally high activity, in comparison with their counterparts in a commonly higher oxidation state. Theoretical and experimental studies have indicated that electron transfer from coordinatively unsaturated metals to adsorbed reactants promotes molecule activation,[2] accounting for their high activity.

Heterogeneously catalyzed oxidation of CO at low temperature has attracted extensive attention because of its potential value in the industrial process.[3] Although precious-metal-based catalysts such as Au, Pt, Pd, Ru, and Ir supported materials[4] exhibit outstanding performance for CO oxidation, great interest in non-precious-metal catalysts (NPMCs) is promoted by their low price together with abundant reserves on earth. $CuMn_2O_4$[5] and Co_3O_4[6] are two classic examples of NPMCs for low-temperature oxidation of CO. Through strategies such as combinational chemistry,[7] morphological control,[8] and size effects,[9] some new advances in the development of efficient NPMCs for CO oxidation have been made. However, the rational design of NPMCs, especially their active sites, remains a great challenge.

In CO oxidation, the essential role of a coordinatively unsaturated metal site has been verified on metal oxide surfaces such as RuO_2,[4c] where the coordinatively unsaturated Ru atom acts as the active site for CO adsorption and oxidation. Recently, it was found that low-valent coordinatively unsaturated Fe^{2+} ions confined and stabilized at the interface between FeO_x and the Pt substrate offered distinct active sites for oxidation of CO at room temperature.[10] Zinc is a nonprecious metal that is widely used in catalysis. Although zinc oxide was previously utilized for CO oxidation,[11] the high reaction temperature required for CO oxidation (673 K) indicates the low reactivity of Zn active sites, normally Zn^{2+} ions. On the other hand, Zn^{2+} ions or ZnO particles supported on zeolite catalysts have also been used for activation and conversion of alkanes.[12−17] In addition to the typical Zn^{2+} ions, low-valent Zn^+ can be generated by loss of one 4s electron in irradiated calcite[18] or in a confined environment such as the channels (cavities) of microporous materials, including ZSM-5 zeolite.[15,19] However, in contrast to Zn^{2+} ions, the chemical reactivity of Zn^+ ions has rarely been explored. Here we report the low-temperature reactivity of coordinatively unsaturated Zn^+ ions in CO oxidation over a Zn-modified ZSM-5 zeolite catalyst (denoted as ZnZSM-5). To the best of our knowledge, this is the first example of Zn^+ ions as active centers with high reactivity at room temperature.

The ZnZSM-5 catalyst was prepared by reacting Zn vapor with H-ZSM-5 zeolite by a modified procedure based on our previous works[15,16] [see the Supporting Information (SI) and Figure S1]. X-ray diffraction and ^{27}Al magic-angle-spinning (MAS) NMR analyses revealed that the Zn modification of H-ZMS-5 did not lead to observable structural changes in the zeolite framework or the appearance of extraframework Al (Figures S2 and S3). The electron spin resonance (ESR) spectrum of the ZnZSM-5 catalyst showed a single signal with $g = 1.9966$, confirming the formation of stable isolated Zn^+ ions, which have an unpaired 4s electron[15,18] (see the following). As revealed by ^1H MAS NMR spectra (Figure S4), all of the Brønsted acidic protons (Si−OH−Al) were removed in the ZnZSM-5 catalyst, indicating that the Zn^+ ions are preferentially formed at the conjugate-base sites $[Si-(O^-)-Al]$, which compensate for their positive charge. Calibrated by the ESR spectrum, the concentration of Zn^+ ions was ca. 0.04 mmol/g (5.4% of the total Zn loading), corresponding to ca. 6.0% of the total acidic protons. This implies that Zn^{2+} ions residing on two neighboring conjugate-

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base sites might be formed as well. In fact, as revealed by ^{13}C NMR of adsorbed acetone (Figure S5), two types of Zn^{2+} ions were present in the sample, which were well-characterized in our previous work.[15]

The reactivity of Zn^+ ions for CO oxidation was tested on ZnZSM-5 in the presence of O_2, and in situ diffuse-reflectance infrared Fourier transform (DRIFT) spectroscopy was employed to follow the reaction. At room temperature (298 K), the occurrence of CO oxidation was evidenced by appearance of the characteristic band of CO_2 at 2341 cm^{-1} after O_2 and CO were coadsorbed onto the catalyst (Figure 1a). Increasing the reaction time led to a gradual growth of the CO_2 signal. The simultaneous decrease in the CO stretching bands (2120−2170 cm^{-1}) indicated the consumption of the CO reactant. The reaction was further studied under flowing conditions in a fixed-bed reactor at standard pressure (Figures 1b and S6), in which CO_2 product was detected by GC−MS. The CO conversion was 65% at 298 K and reached ca. 98% above 310 K (Figure 1b). For comparison, at 298 K we found no CO conversion on a Zn^{2+}/ZSM-5 catalyst prepared by the ion-exchange method, in which only isolated Zn^{2+} ions were present,[15,20] (Figure S7). Recently, ZnO nanoparticles in complex oxides were also examined for CO oxidization, and it was found that although they were superior to the bulk forms,[21] high reactivity with CO conversion larger than 90% was achieved only at temperatures above 873 K. Thus, we suppose that the exceptionally high activity of ZnZSM-5 for CO oxidation at room temperature might originate from the Zn^+ ions, which act as the active sites. We also measured the apparent activation energy (E_a) for the reaction over the temperature range 296−308 K and obtained a value of ca. 5.0 kcal/mol (Figure S8), which is slightly higher than the value (near zero) for Au-based catalysts that also exhibit extraordinarily high reactivity over a similar temperature range for CO oxidation.[22]

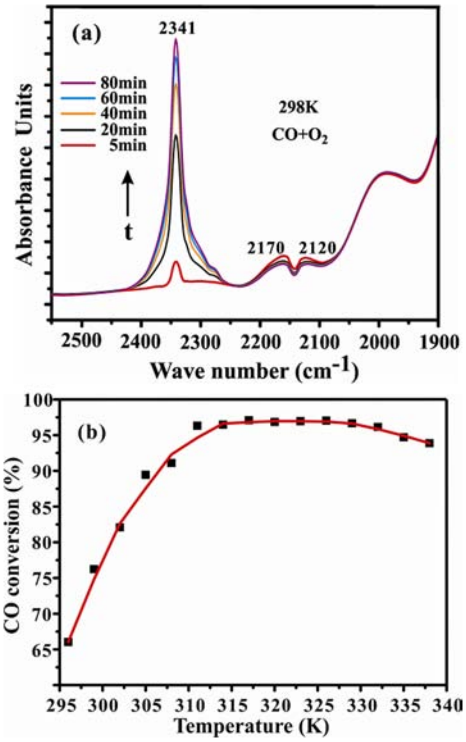

Figure 1. (a) In situ DRIFT spectra of CO oxidation on ZnZSM-5 at 298 K. (b) CO conversion at different temperatures (0.3 g of catalyst; gas hourly space velocity = 3000 h^{-1}; 1% CO/21% O_2/78% He).

To gain insight into the role of Zn^+ ions, in situ ESR experiments were performed to monitor the CO oxidation reaction over the ZnZSM-5 catalyst. Figure 2 shows the corresponding ESR spectra recorded under different conditions. For the bare ZnZSM-5 catalyst, only a signal with $g = 1.9966$ due to Zn^+ ions was observed (Figure 2a). When O_2 was adsorbed onto the catalyst at 298 K and then the sample was evacuated to remove weakly adsorbed or free O_2 molecules, the Zn^+ signal completely disappeared. More interestingly, a series of new lines with $g = 2.0014$−2.0512 appeared (Figure 2b), indicating the formation of new radicals due to the interaction between O_2 and Zn^+ ions. According to previous reports,[23,24] the signals at $g_1 = 2.0512$, $g_2 = 2.0173$, and $g_3 = 2.0046$ can be ascribed to adsorbed O_2^- ions, which might be generated by single electron transfer from Zn^+ ion to adsorbed O_2 (Scheme 1). Such an electron transfer process was previously observed after adsorption of O_2 on low-valent Cr^{2+}, Cu^+, and Ni^+ ion-exchanged zeolites,[25] generating O_2^- ions and high-valent metal ions. Moreover, we tentatively assign the signals at $g_1 = 2.0365$, $g_2 = 2.0091$, and $g_3 = 2.0014$ to another type of O_2^- ion. Generally, a smaller g_1 value corresponds to a larger orbital energy difference in the crystal field, indicating a more pronounced influence of zinc ions on the charged oxygen species and thus a stronger adsorption state.[26] Therefore, we propose that two types of charged oxygen species,

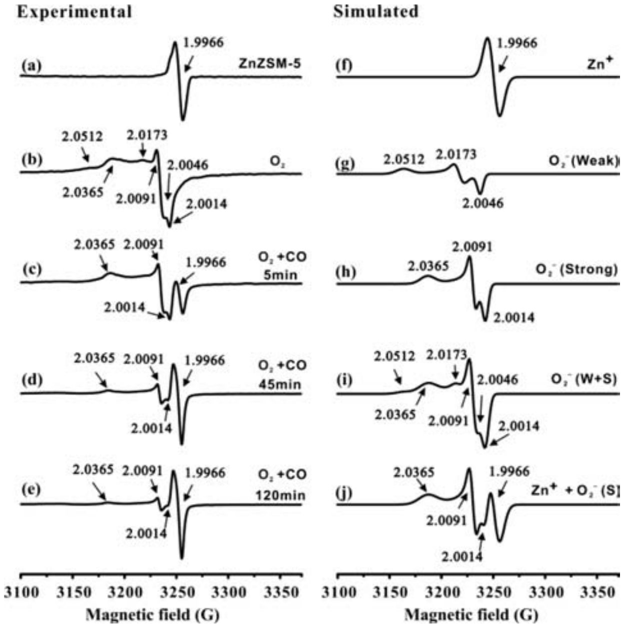

Figure 2. In situ ESR spectra of ZnZSM-5 recorded at 298 K: (a) bare ZnZSM-5; (b) after adsorption of 2 kPa O_2 on (a) followed by evacuation; (c−e) after adsorption of 2 kPa CO on (b) and reaction for 5, 45, and 120 min, respectively. (f−j) Simulated spectra: (f) $g = 1.9966$; (g) $g_1 = 2.0512$, $g_2 = 2.0173$, $g_3 = 2.0046$; (h) $g_1 = 2.0365$, $g_2 = 2.0091$, $g_3 = 2.0014$; (i) sum of (g) and (h); (j) sum of (f) and (h).

Scheme 1. Proposed Pathway for O_2 Activation and CO Oxidation on ZnZSM-5

$$Zn^+ + O_2 \longrightarrow Zn^{2+}O_2^- \qquad (1)$$

$$Zn^{2+}O_2^- + 2CO \longrightarrow 2CO_2 + Zn^+ \qquad (2)$$

weakly (g_1 = 2.0512) and strongly (g_1 = 2.0365) adsorbed O_2^- ions, are simultaneously generated on the catalyst. The initially formed Zn^+ ions are probably located in different chemical environments as a result of the heterogeneous distribution of acid sites in the zeolite channels, which may be responsible for the different adsorption states of O_2^- species. To obtain a more detailed analysis, spectral simulations were also performed for Zn^+ ions and these O_2^- ions (Figure 2f−j). As shown in Figure 2i, the sum of the simulated spectra for the weakly (Figure 2g) and strongly (Figure 2h) adsorbed O_2^- ions reproduced well the experimental spectrum of O_2 adsorbed on ZnZSM-5 (Figure 2b). This unambiguously demonstrates the generation and existence of two types of charged oxygen ions in the catalyst. Our ESR experimental results indicate that all of the observed Zn^+ ions are involved as electron donors in the electron transfer to O_2, accounting for the disappearance of the Zn^+ signal due to the formation of diamagnetic Zn^{2+} ions. In constrast to the O_2^- ions usually observed on the surface of delicately treated oxides as a result of adsorption of O_2 on oxygen defects,[27] here direct electron transfer from Zn^+ to adsorbed O_2 might lead to the formation of $Zn^{2+}-O_2^-$ complexes (Scheme 1), which reside on the Si−(O^-)−Al conjugate base sites as well. It is well-known that O_2^- ions or metal−superoxide complexes such as $Co-O_2^-$ are reactive species for oxidation of hydrocarbons.[28] However, the role of reactive O_2^- species in CO oxidation on low-valent coordinatively unsaturated metal-exchanged zeolites has rarely been explored.[25]

To investigate the reactivity of the observed O_2^- ions on the ZnZSM-5 catalyst, the interaction between the O_2^- ions and CO was monitored by in situ ESR spectroscopy. When CO was introduced onto the catalyst after the adsorption of molecular O_2 and allowed to react for 5 min, the ESR signals of weakly adsorbed O_2^- ions readily disappeared and that due to Zn^+ ions (g = 1.9966) partially recovered (Figure 2c). This is supported by the fact that the sum of simulated spectra for the Zn^+ ions and the strongly adsorbed O_2^- ions (Figure 2j) is similar to the experimental spectrum (Figure 2c), in which the weakly adsorbed O_2^- is supposed to be consumed. As the reaction time increased from 5 to 120 min, the signals of strongly adsorbed O_2^- gradually decreased while the Zn^+ signal grew (Figure 2c−e). Since CO_2 was simultaneously produced (see Figure 1a), the results demonstrate that the two types of O_2^- ions are definitely responsible for CO oxidation, though the weakly adsorbed O_2^- species exhibit a relatively higher reactivity. Most importantly, the restoration of Zn^+ ion indicates the occurrence of a reverse electron transfer from the reactive O_2^- species to Zn^{2+} ion. The reversible transformation of the Zn^+ ion ($Zn^+ \rightleftarrows Zn^{2+}$) accompanied by the formation of CO_2 points to a complete catalytic cycle for CO oxidation in which the Zn^+ ions function as catalytic centers (Scheme 1). The reactive O_2^- species formed on ZnZSM-5 show CO oxidation reactivity similar to that of the reactive species generated on Au supported catalysts[29] after adsorption of O_2.

To gain further insight into the relationship between the Zn^+ ion and the activity of the ZnZSM-5 catalyst, we quantitatively measured the concentrations of both Zn^+ and O_2^- ions as functions of reaction time during CO oxidation. The concentration variation of Zn^+ ion is well-correlated with that of O_2^- ion in one catalytic cycle (Figure 3a). That is, the increment of Zn^+ ion is nearly equal to the decrement of O_2^- ion and vice versa. This unambiguously demonstrates that the activation of O_2 solely occurs on Zn^+ ion to generate O_2^- ion, and thus, the contribution of the other two types of Zn^{2+} ions to the catalytic reaction can be excluded. Figure 1b shows that the activity of ZnZSM-5 toward CO oxidation slightly declines above 330 K, indicating a gradual deactivation of the catalyst at higher temperatures. This is likely due to oxidation of Zn^+ ion to generate unreactive Zn^{2+}, which likely exists in the form of zinc oxide. The irreversible redox reaction would lead to the loss of the active site, as evidenced by the notable decrease in the ESR signal of Zn^+ ion after deactivation of the catalyst (conversion below 10%; Figure S9). This process was also confirmed by X-ray absorption spectroscopy experiments. As shown in the corresponding X-ray absorption near-edge structure (XANES) spectra (Figure 3b), the absorption edge of fresh ZnZSM-5 falls between those of Zn foil (Zn^0) and ZnO/ZSM-5 (Zn^{2+}) reference materials, implying that the Zn^+ ion (whose presence was also proved by ESR spectroscopy) coexists with the dominant Zn^{2+} ion in the sample. The deactivation led to a shift in the absorption edge to higher energy, near that of ZnO/ZSM-5 prepared by impregnation, in which ZnO nanoparticles were present.[15]. This may indicate a transformation of the valence state of Zn from +1 to +2. Gaseous H_2S is usually employed as a poisoning reagent. We also found that the Zn^+ active sites could be readily poisoned by H_2S molecules. Adsorption of H_2S led to a remarkable decrease in the Zn^+ concentration, which eventually deactivated the catalyst toward CO oxidation (Figures S9 and S10). Therefore, all of the experimental results indicate that the Zn^+ ion is the sole active site on the ZnZSM-5 catalyst for CO oxidation and that the deactivation is due to the oxidation of Zn^+ to form unreactive Zn^{2+}. Probably because of its low concentration, the detailed structure of the unreactive Zn^{2+} could not be clearly identified by the various techniques applied.

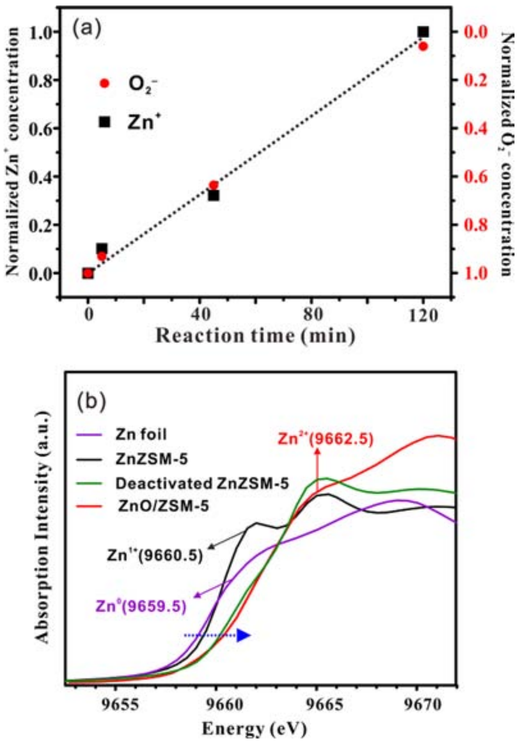

Figure 3. (a) Normalized concentrations of Zn^+ and O_2^- ions on ZnZSM-5 versus reaction time in one catalytic cycle (see the SI for details). (b) Zn K-edge XANES spectra of fresh ZnZSM-5, deactivated ZnZSM-5, and Zn foil and ZnO/ZSM-5 reference materials. Values of E_0 (in eV) determined from the first derivatives are given in parentheses.

Since no strongly bound CO molecule was observed under the reaction conditions (Figure 1a), we also studied the CO adsorption at room temperature under a controlled atmosphere using FTIR spectroscopy. Only gaseous CO stretching bands at 2120−2170 cm^{-1} were observable over a pressure range of 0.25−40 kPa (Figure S11) for CO adsorption on ZnZSM-5, and these bands could readily be removed by evacuation. This indicates the absence of strong interactions of CO molecules with either the zeolite support or the Zn sites. Thus, CO oxidation on the ZnZSM-5 catalyst may follow a Eley−Rideal mechanism,[30] in which gas-phase CO directly interacts with adsorbed reactive oxygen to form CO_2. In particular, the O_2^- species reacts with CO to form CO_2 and an adsorbed O atom, with the latter being involved in a subsequent reaction to form another CO_2. The unfavorable adsorption of CO may facilitate O_2 adsorption and reduce poisoning of the active site by CO. For comparison, apart from the Eley−Rideal mechanism, the Mars−van Krevelen redox mechanism (involving transfer of lattice oxygen from oxides to CO)[4c,31] and the Langmuir−Hinshelwood mechanism[32] (involving reaction between chemisorbed CO and reactive oxygen) have also been proposed for CO oxidation on precious-metal-based catalysts.

In summary, the present work has demonstrated for the first time the low-temperature catalytic reactivity of Zn^+ ions confined in ZSM-5 zeolite toward CO oxidation. Molecular O_2 is readily activated by Zn^+ ions at room temperature, leading to the formation of Zn^{2+} ions and two types of reactive O_2^- species. The active O_2^- species oxidize CO into CO_2, and the Zn^+ ions are simultaneously recovered from the Zn^{2+} ions. The reversible electron transfer between molecular O_2 and Zn^+ indicates a complete catalytic cycle for CO oxidation. Although the catalytic performance of the ZnZSM-5 catalyst is still inferior to that of well-established precious-metal (e.g., Au or Pt)-based catalysts, especially in terms of oxidation/deactivation, the present findings may not only provide valuable insights into the mechanism of CO oxidation at low temperature but also be helpful for the rational design of new non-precious-metal-based zeolite catalysts for O_2 activation and related oxidation reactions via modification of their electronic properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and additional results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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