Short communication

In situ FT-IR investigation of CO oxidation on CuO/TiO$_2$ catalysts

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ABSTRACT

The present work tentatively investigated anatase- or rutile-supported copper oxide catalysts. 5% copper oxide can be well dispersed on anatase or rutile surfaces. The copper oxide dispersed on rutile surface exists in Cu^{2+} and Cu$^+$ ions, which is more readily reduced, and show higher catalytic activity of CO oxidation. The mechanism of CO oxidation over rutile support is different from anatase support.

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1. Introduction

As known to all, TiO$_2$ has three kinds of crystal form: brookite (orthorhombic), anatase (tetragonal), and rutile (tetragonal). The brookite and anatase crystalline phases are stable at the low temperature, and transform into rutile at the higher temperatures. Among them, anatase and rutile are widely investigated as catalyst supports in the literatures [1–4]. Although anatase and rutile have the same chemical composition as TiO$_2$, they have different crystalline structures, the (001) and (110) planes are the preferentially exposed planes for anatase and rutile, respectively [5]. The structures of the preferentially exposed plane for anatase and rutile play an important role in determining the properties of supported catalysts.

Copper supported on TiO$_2$ presents interesting properties in the field of heterogeneous catalysis and has been widely used for CO oxidation [6–8]. Notably, most of these researchers focused on catalysts with anatase used as support. However, limited information could be found about rutile-supported catalysts as well as the difference between anatase and rutile-supported catalysts [9,10], especially for the mechanism of CO oxidation. Recently, in situ FT-IR studies are applied to gain insight into the mechanism of NO + CO and NO + NH$_3$ + O$_2$ over metal oxides catalysts [11,12]. However, it is few to investigate the mechanism of CO + O$_2$ by the in situ FT-IR method.

In this work, copper oxide is supported on different structure TiO$_2$, to study the support effects of rutile and anatase on the physicochemical

properties and catalytic properties for the CO oxidation. The focus is on the reductively properties of copper oxide, the sates of copper species, CO and/or O$_2$ interaction with catalyst, and the mechanism of CO oxidation over rutile and anatase.

2. Experimental sections

2.1. Catalysts preparation

Anatase TiO$_2$ support was prepared via hydrolysis of titanium isopropoxide, the product was washed, dried and then calcined in flowing air at 500 °C for 5 h. The BET surface area is 56 m$^2 \cdot$g^{-1}. Rutile TiO$_2$ support was prepared by direct calcination of commercial TiO$_2$ (P25, Degussa) at 750 °C for 5 h. The BET surface area is 25 m$^2 \cdot$g^{-1}. TiO$_2$ (Anatase + Rutile) support is P25. The BET surface area is 51 m$^2 \cdot$g^{-1}. CuO/TiO$_2$ samples were prepared by impregnation of TiO$_2$ [13]. For simplicity, these synthesized samples were signed as 5CuTiO$_2$(A), 5CuTiO$_2$(A + R), and 5CuTiO$_2$(R) which represented support Anatase, Anatase + Rutile, and Rutile, and CuO loading was 5 wt.%, respectively.

2.2. Catalyst characterization

XRD patterns were collected with a Philips X'pert Pro diffractometer with high temperature chamber using Ni-filtered CuKα radiation (0.15418 nm). BET surface areas were measured by nitrogen adsorption at 77 K on a Micromeritics ASAP-2020 adsorption apparatus. H$_2$-TPR was carried out in a quartz U-tube reactor, and H$_2$ consumption was analyzed by using thermal conduct detector. XPS experiments were

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performed on a PHI 5000 Versa Probe high performance electron spectrometer, using monochromatic Al Kα radiation (1486.6 eV) operating at an accelerating power of 15 kW. The binding energies were referenced to the C 1s line at 284.6 eV. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker A300 spectrometer using a 100-kHz modulation and a 4-G standard modulation width. The spectra were recorded at the room temperature. In situ FT-IR was carried out according to literature [13].

2.3. Activity measurement for CO oxidation

The activities of the 5CuTxSy catalysts in CO + O_2 reaction were measured in a flow micro-reactor with a gas composition of 1.6% CO, 20.8% O_2 and 77.6% N_2 by volume at a space velocity of 30,000 mL·g^{-1} h^{-1}.

3. Results and discussion

3.1. XRD and H_2-TPR results

Fig. S1 shows the XRD patterns of the samples. The characteristic peaks for anatase TiO_2 and rutile TiO_2 are detected. The characteristic XRD peak for CuO is not found in the three samples. This suggests that the highly dispersed CuO are successfully formed on the TiO_2 supports. The characteristic reducibility of the samples is determined by TPR measurements. Fig. S2 displays the reduction profiles for the three samples, TiO_2(A + R) support, and pure CuO. CuO supported on rutile TiO_2 surface is easier to be reduced than that of anatase TiO_2. For further understanding, the detailed information of these reduction peaks is summarized in Table S1. As a result, it can follow that the states of Cu species are different between the two TiO_2 crystalline phase surface [10], i.e. copper oxide species is in the 6-coordination environment for 5CuTiO_2(R) sample and in the 5-coordination environment for 5CuTiO_2(A) sample.

3.2. XPS and EPR results

Fig. S3 shows the XPS spectra of Ti 2p for three samples. Two peaks corresponding to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ are observed. The binding energies of Ti 2p$_{3/2}$ shift to lower values from 5CuTiO_2(A) to 5CuTiO_2(R), suggesting the existence of oxygen vacancy. Fig. 1 shows the XPS spectra of Cu 2p, and O 1s for three samples. The Cu 2p spectra mostly show Cu^{2+} and small amount Cu^+, located at 933.2 and 930.8 eV respectively [14]. The reason for the generation of Cu^+ may result from oxygen vacancy, indicating that there are more Cu^+ ions existing on 5CuTiO_2(R) sample surface. Additionally, the relative intensity of the satellite with respect to the main line is estimated to be in the range of 0.40 ~ 0.45 (Table S2), which is between the value of 0.55 for pure Cu^{2+} and zero for pure Cu^+ [14]. The low intensity of the satellite structure suggests the presence of reduced copper species in the 5CuTiO_2(R) catalyst.

The high-resolution spectrum for the O 1 s ionization features presents the primary O 1s ionization feature and chemically shifted O 1s features from chemisorbed surface species. The strong band O′ (529.9 eV) is attributed to characteristic O^{2-} of metal oxides surface [13], while the shoulder O″ (O_2^- species) with higher binding energy (532.1 eV) is the result of chemisorbed oxygen [13]. This result further confirms the existence of oxygen vacancy on the rutile surface. Furthermore, Table S2 shows the detail information of atom concentrations. In order to further prove the existence of O_2^- species, the EPR characterization is performed, as shown in Fig. S4. For all samples, a strong axially symmetric signal associated with Cu^{2+} ions is observed [15]. Simultaneously, a weak signal appears at g = 2.016, many works assign this signal to the O_2^- [16], i.e., O_2 is adsorbed on the surface oxygen vacancies, moreover, the intensities of the signal increase gradually in the order
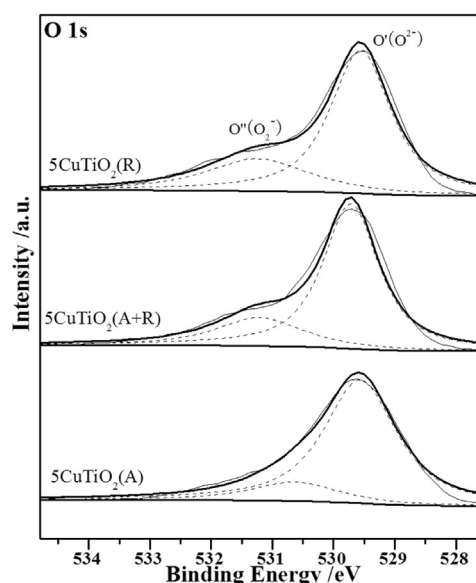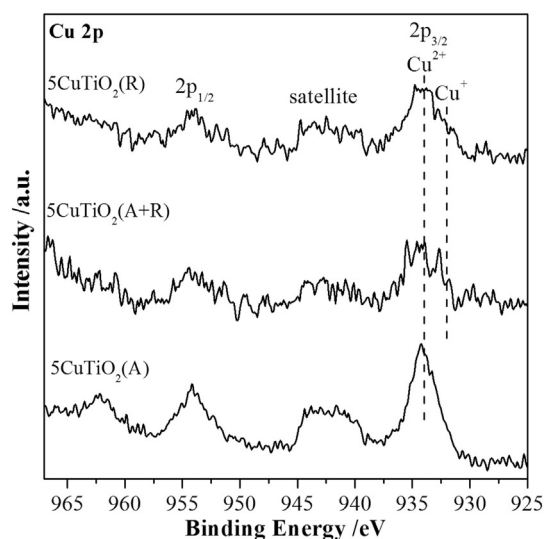

Fig. 1. XPS spectra (Cu 2p, and O1s) of samples.

of 5CuTiO_2(A) < 5CuTiO_2(A + R) < 5CuTiO_2(R). The result indicates that more oxygen vacancies exist on the rutile surface.

3.3. Activities of catalysts

Fig. 2 shows the catalytic activities of these catalysts for CO oxidation. Activities of catalysts are intimately related to the titanium oxide structure, increasing in the order of 5CuTiO_2(A) < 5CuTiO_2(A + R) < 5CuTiO_2(R). 5CuTiO_2(R) catalyst shows the best reactivity for the catalytic oxidation of CO, providing a total CO oxidation at 200 °C. From H_2-TPR, XPS and EPR results, we know that 5CuTiO_2(R) catalyst contains more the low valence Cu species (Cu^+) and surface oxygen vacancy. 5CuTiO_2(R) sample shows the best catalytic performances of all these catalysts, which may be related to reduction behavior, Cu^+ species, and surface oxygen vacancy concentration of the sample.

3.4. In situ FT-IR results

The CO adsorption behavior in situ FT-IR spectra are recorded, as shown in Fig. 3. The peaks of CO adsorption on the Cu^+ are evident at