In situ AP-XPS, EXAFS/XANES, synchrotron powder diffraction studies of three-dimensionally ordered macroporous Cu-Fe catalyst for higher alcohol synthesis from syngas
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Introduction
Higher alcohol synthesis (HAS) [1] from syngas is an important process for the production of oxygenates fuels, fuels additives and other intermediates for value-added chemical feedstock such as medicine, cosmetic, lubricants, detergents, and polyester. Cu-Fe based catalyst [2], is considered as one of the most promising catalysts for HAS from syngas. Generally, the active state of a catalyst on the surface is instantly generated in reaction conditions and can be changed after removing from the reactor [3]. The in situ characterization study is prospective and essential to understand the catalytic reaction mechanism, which can help us to correlate catalytic intrinsic activity with the molecular structure of active sites in approximate catalytic conditions.

Materials and Methods
3DOM Cu-Fe catalyst was prepared by poly(methyl methacrylate) colloidal crystal template method, using ethylene glycol (EG)-methanol solution of metal nitrates Cu(NO3)2·6H2O and Fe(NO3)3·9H2O as precursors [1]. The catalysts were characterized by in situ ambient-pressure x-ray photoelectron spectroscopy (AP-XPS), in situ extended x-ray absorption fine structure/x-ray absorption near edge structure (EXAFS/XANES) and in situ synchrotron powder diffraction to identify the active site for HAS from syngas.

Results and Discussion

Figure 1 (a) SEM image and inset (b) TEM image of fresh 3DOM CuFe1 catalyst. (c) The corresponding selected area electron diffraction pattern. (d) HRTEM image of CuO, inset is a Fast Fourier Transform (FFT) image and (e) HRTEM image of Fe3O4, inset is a FFT image. [1]

Figure 2. In situ AP-XPS study of Cu 2p, Cu (LMM), Fe 2p and C1s spectra of 3DOM CuFe1 catalyst using syngas (0.5 mbar H2 and 0.5 mbar CO) at various temperatures.

Figure 3. Temperature-resolved synchrotron powder diffraction patterns during the in situ reduction of 3DOM CuFe1 catalyst under 3.5% H2/He from room temperature to 500 °C (a) contour image and (b) the selected diffraction patterns.

Significance
3DOM Cu-Fe catalysts were prepared for higher alcohol synthesis (HAS) from syngas, with high selectivity of higher alcohols. In situ characterizations revealed that the high intrinsic activity was ascribed to three factors. First, the unique ordered structure has a large pore size and interconnected macroporous tunnels of the catalyst with a large accessible surface area improves the catalytic activity. Second, a high density of uniformly distributed defective Cu6 and γ-FeC3 nanoparticles derived from the glyoxylate route helps to provide abundant, active, stable dual sites. Third, atomic steps on the Cu surface, induced by planar defects and lattice strain, serve as high-activity oxygenation sites; and active γ-FeC3 chain-growth sites surround the defective and strained form of Cu surface intimately, which results in a synergistic effect between the active and stable Cu-FeC3 dual site for HAS.

References