

Characterization CoMn catalyst by in situ X-ray absorption spectroscopy for Fischer–Tropsch to Olefins Reaction

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1.introduction: To explore the atomic structure and active site of CoMn catalysts in FT synthesis, we synthesized CoMn catalysts by co-precipitation method. The formation of the Co_2C was found at operando conditions by in situ XAFS method. Additionally, CoMn catalysts exhibited a high selectivity for the production of lower olefins and a low methane selectivity. Wavelet transform was been used to elucidate the Co_2C phase which is indiscernible in EXAFS.

2.experimental methods

2.1 Preparation of catalyst: CoMn catalyst was synthesized by a co-precipitation method.

2.2 Catalytic test: Reaction conditions: 250°C , 0.1 MPa, $3,000\text{mlh}^{-1}\text{ g}_{\text{cat}}^{-1}$.

2.3 TEM characterization: The spent catalysts were prepared for HRTEM characterization by drop-casting ethanol suspension of ground catalysts onto lacey carbon Cu grids as described previously.

2.4 TPR measurement: The reduction behavior of the CoMn catalyst was tested by temperature-programmed reduction (H_2 -TPR, Micromeritics AutoChem P 2920).

2.5 XAFS measurement: Transmission mode Co K-edge X-ray absorption spectra (XAS) were acquired on the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility.

3. Results and discussion

3.1 Catalytic test: The CoMn catalyst displays a high selectivity for the production of lower olefin and a low methane selectivity under reaction conditions. Moreover, a high olefin/paraffin ratio for C_2 - C_4 suggests promising potential industrial application.

3.2 XRD and TEM characterization: The XRD patterns result corresponds well with the HRTEM images, suggesting that the formation of cobalt carbide phase under reaction.

3.3 TPR analysis: The difference of TPR profiles between the reference Co_3O_4 and CoMn catalyst indicates the interaction of Co species with promoter Mn.

3.4 XAFS analysis

3.4.1 in situ XAFS: With creasing reaction, the stage was characterized by an almost complete depletion of $\text{Co}_x\text{Mn}_{1-x}\text{O}$ and the presence of Co_2C phase after 180 min under 250°C , 1 bar environment with syngas. Moreover, in the Fourier transform curves depicted, the two main peaks at 1.53 and 2.45 Å without phase-corrected correspond to the nearest Co-O and the next-nearest Co-Co coordination in the CoMn coordination before 60 min under reaction. After 60 min, the Co-Co coordination shell decreased fast, accompanying a new coordination shell at 2.0 Å which was correspond to Co-Co in Co_2C .

3.4.2 Wavelet transform: It is obvious that the metallic character of catalyst sample was getting greater under reaction after 180 min, which is related to Co-Co for metallic Co. For compare with Co_2C sample, the new maximum intensity indicated the Co_2C has been formed.

4. Conclusion: CoMn catalyst exhibited a great catalytic activity of FTO. Detailed and exhaustive structural characterization of the CoMn catalyst under reaction conditions by in situ XAFS method. Wavelet transform results of calcined, reduced and reacted catalysts indicate that a fraction of the Co reduced to a form of Co_2C that was active under FTO synthesis conditions. It is demonstrated that active site was cobalt carbide which was transformed by CoMn catalyst.

