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In-situ QXAS investigation of the genesis of cobalt active phases in supported Fischer-Tropsch catalysts

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Cobalt Fischer-Tropsch catalysts are typically prepared by impregnation, followed by calcination in oxidizing atmosphere and activation in hydrogen. Decomposition of cobalt nitrate is a crucial step in the genesis of active phase and could involve several short-living intermediate species. In the present work, in-situ quick X-ray absorption spectros-copy (QXAS) in combination with other techniques has been used to investigate the genesis of active phases in silica-supported cobalt catalysts prepared using either activa-tion under 5%NO/He or sub-stoichiometric addition of sorbitol.
Cobalt nitrate decomposition in air or helium proceeds via dehydrated species at 140℃. These species convert into Co3O4 crystallites below 200℃. In diluted NO, in contrast to activation in air or He, an intermediate cobalt (II) hydroxynitrate phase is detected by both XANES and EXAFS above 110℃, before the formation of Co3O4. The quantitative QXAS results are consistent with FEFF, in-situ Raman and ex-situ XAS and XRD.
In the catalysts prepared with sorbitol addition, the in-situ XANES/EXAFS is indicative of higher temperature of cobalt nitrate decomposition in the presence of sorbitol. Organic acids produced during sorbitol oxidation stabilize cobalt precursor. The in-situ QXAS at Ru K-edge suggests incorporation of Ru ions into mixed CoRu oxides in the calcined catalysts, better catalyst reducibility and formation of CuRu bimetallic particles in the reduced catalysts.

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