Identification of Different Carbon Species in Alumina Supported Cobalt Fischer-Tropsch Catalyst after Catalytic Tests in an Autoclave Reactor

Diego A. Peña1, Anne Gribouval-Constant1, Melesio Quijada1, Vincent Lecocq2, Fabrice Diehl and Andrei Y. Khodakov1

1Unité de Catalyse et de Chimie du Solide (UCCS), UMR 8181 CNRS, Université Lille 1-USTL-ENSL-EC Lille, Bât C3, Cité scientifique, 59655 Villeneuve d’Ascq, (France)
2IFP Energies nouvelles, Rond-point de l’échangeur de Solaize, BP 3, 69360 Solaize, France
3Laboratoire GEOSYSTEMES UMR 8217 Université Lille 1- Bât SN5 59655Cité scientifique, 59655 Villeneuve d’Ascq, (France)

*andreikhodakov@univ-lille1.fr

Introduction

Fischer-Tropsch (FT) synthesis is a promising reaction to produce ultraclean fuels using syngas obtained from natural gas, coal or biomass. Alumina supported cobalt catalysts are generally preferred for FT synthesis due to their high activity, high selectivity towards linear paraffins and a lower water gas shift activity compared to iron based catalysts. As for many industrial processes, catalytic deactivation is a crucial problem for industrial application of this reaction. Cobalt sintering and deposition of carbonaceous species on the catalyst surface seem to be major reasons of catalyst deactivation [1-3]. The presence of different carbon containing species on the surface has been suggested in FT used catalysts [2, 4]. Recent DFT modeling report indicates possible presence of aromatic compounds and graphene in the used catalysts [5]. The present work focuses on the identification of the carbon species, which might form onto the surface of cobalt supported on a commercial alumina during the FT reaction in a continuously stirred tank reactor (CSTR) under different operating conditions and their possible role in the catalytic performance and catalyst deactivation.

Materials and Methods

A 15 wt% Co supported catalyst on a γ-alumina based commercial support was prepared by incipient wetness impregnation with cobalt nitrate in two steps. The catalyst was dried at 120°C, calcined at 420°C and reduced during 16h at 400°C under pure hydrogen. The catalytic performance was evaluated in a CSTR of 100 cm³ at 20 bar, at 220-230°C and stirring rate of 1000 rpm with H2/CO ratios adjusted between 1 and 3 and different gas-space velocities (GHSV). The remaining wax was removed from spent catalyst by Soxhlet extraction in hot toluene. Carbon species onto spent catalyst were extracted with a CH3Cl:CH3OH mixture in a proportion of 2:1 under ultrasound environment. The resulting solution was analyzed by GC-MS and relevant carbon structures were elucidated from the MS spectra.

Results and Discussion

Different carbon species have been uncovered in FT used catalysts. After wax extraction using Soxhlet method, a combination of characterization techniques (TPH-MS, XPS, TOF-SIMS) suggests the presence of (i) residual wax (surface), (ii) strongly adsorbed hydrocarbons and (iii) polymeric (not graphitic) carbon, also corroborated by the characterization of synthesized carbon reference compounds. The proportion of carbon species in used catalysts varied as a function of operating conditions in the reactor. When the catalyst showed higher CO conversion, the fraction of strongly adsorbed hydrocarbon increased. When the catalyst exhibited lower CO conversion at lower H2/CO ratio, the proportion of polymeric carbon was more important. Cobalt carbide species were not detected in the used catalysts by ex situ characterization technique. Paraffinic wax was extracted from the catalysts using Soxhlet method. After the Soxhlet extraction, more strongly adsorbed carbon species in the used catalysts were extracted using dichloromethane-methanol (2:1). GC-MS analysis showed that the species extracted by CH3Cl:CH3OH were principally constituted by linear α-olefins with higher relative abundance and both linear and branched alkanes. Most surprisingly, aromatic compounds such as cinnamic aldehydes were also uncovered. The cinnamic aldehydes groups could be possible precursors of polymeric carbon, which forms on the catalyst surface under hydrogen deficiency conditions (Fig.1). Interestingly these aromatic structures did not appear when the catalyst showed stable CO conversion and lower deactivation rate. Comparison of both characterization and catalytic results indicates that hydrocarbons strongly adsorbed on the catalyst are mainly constituted by α-olefins and n-paraffins, while polymeric carbon is probably formed from cinnamic aldehydes groups especially at lower H2/CO ratio. Both these species seem to be deleterious to the catalyst activity.

References