METAL-SUPPORT INTERACTIONS: THEIR EFFECTS UPON ADSORPTION, ELECTRONIC, AND ACTIVITY/SELECTIVITY PROPERTIES OF COBALT IN CO HYDROGENATION

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Research Scope and Objectives

This investigation focuses on cobalt and to a lesser extent iron metal-support interactions and their effects upon adsorption, electronic and activity/selectivity properties of these metals. The objectives of this research are to (i) determine the effects of cobalt-support interactions on dispersion, oxidation state and adsorption properties of cobalt over a range of cobalt loading; (ii) determine the effects of support, dispersion and oxidation state on the activity/selectivity properties of cobalt for hydrocarbon synthesis and (iii) measure directly the extent of interaction of various supports with iron and cobalt using Moessbauer Spectroscopy and correlate the strengths of interaction with previously determined adsorption and activity/selectivity properties. The research approach features a quantitative experimental investigation of unsupported cobalt and cobalt supported on Al_2O_3, SiO_2, TiO_2, MgO, and carbon to determine physical and chemical, bulk and surface properties of each catalyst using BET, H_2 and CO chemisorption, XRD, TEM, and TPD measurements.

Description of Research Effort

During the past two years, measurements of dispersion, extent of reduction, H_2 and CO adsorption stoichiometries, H_2 adsorption/desorption kinetics and CO hydrogenation activity/selectivity properties were conducted on a series of 18 cobalt catalysts.

From TPD and static adsorption measurements it was determined that hydrogen adsorption on cobalt is reversible and highly activated; the degree of activation, the kinds of adsorption states and heats of adsorption vary with support and metal loading. Hydrogen adsorption occurs with a stoichiometry of one hydrogen atom per surface cobalt atom on unsupported Co, Co/Al_2O_3, Co/SiO_2, and Co/Carbon. CO adsorption stoichiometries, on the other hand, vary considerably with support, dispersion and preparation.

The specific activity and selectivity of cobalt in CO hydrogenation vary significantly with support, dispersion and preparation. The order of decreasing specific activity for CO conversion of catalysts containing 3 wt.% cobalt is Co/TiO_2, Co/SiO_2, Co/Al_2O_3, Co/Carbon, and Co/MgO. Specific activity and selectivity for heavier hydrocarbons both decrease with increasing dispersion and decreasing extent of reduction. These observations are among the most significant to date since they provide a basis for understanding how catalyst properties affect product selectivity in hydrocarbon synthesis.

Well-dispersed, Fe^{57}-enriched Fe/TiO_2 ad Fe/C catalysts have been prepared for Moessbauer studies to determine how the electronic properties of the metal are affected by the support. The investigation by TPD of CO adsorption states and energetics of unsupported cobalt, Co/SiO_2 and Co/TiO_2 is in progress. Experiments to determine separately the effects of dispersion and percent reduction on the activity/selectivity properties of Co/Al_2O_3 are also in progress.

Future Research

Future TPD and IR studies will focus on the effects of support and dispersion on the binding states and binding energies of CO on cobalt. Catalysts containing radioactive Co^{57} will be prepared for the direct investigation of cobalt-support interactions using Moessbauer spectroscopy, to determine how the electronic structure of the metal is affected by the support. The adsorption and CO hydrogenation activity/selectivity properties of well-dispersed supported cobalt catalysts prepared from decomposition of metal carbonyls on alumina, silica and titania supports will also be examined.