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CO HYDROGENATION OVER COBALT FISCHER-TROPSCH CATALYSTS

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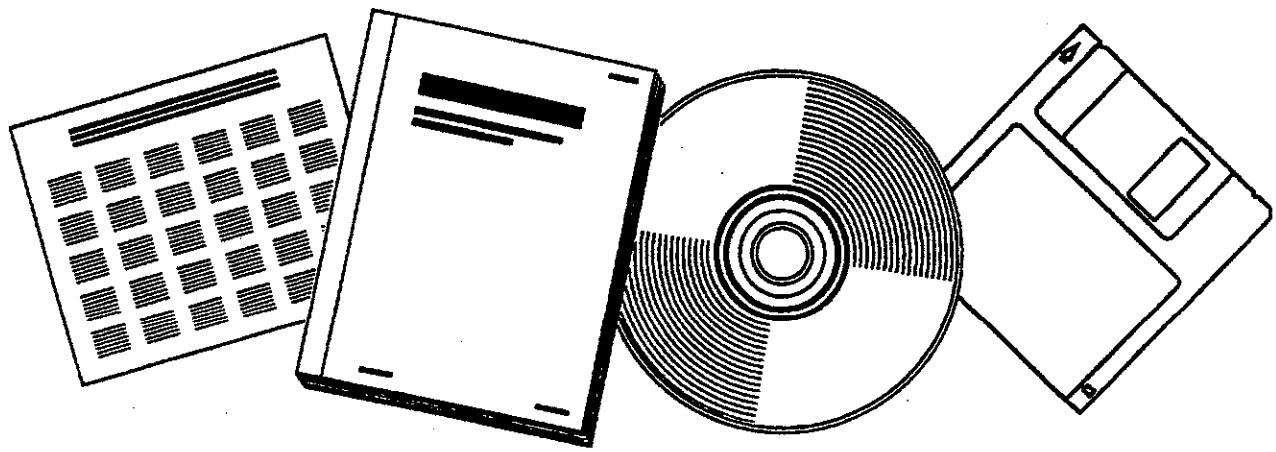

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ABSTRACT

The main aim of the present work has been to study in what way the addition of a second metal influences the CO hydrogenation rate over alumina supported cobalt catalysts.

Temperature programmed reduction studies (298 - 1173 K) show that calcined 9%Co/Al_2O_3 contains two main cobalt phases: Crystalline Co_3O_4 particles and a cobalt oxide layer containing cobalt ions interacting with the alumina support surface. Some amounts of heavily reducible $CoAl_2O_4$ are also present in the catalyst. Addition of 0.1 and 1.0 wt% Pt from a chloride containing precursor lowers the temperature for Co_3O_4 reduction with about 80 K, while the reduction temperature of the oxidic cobalt surface layer is lowered with 100 - 200 K compared to the monometallic cobalt catalyst. The temperature shift increases with increasing platinum amount. 1 wt% Pt from a chloride free platinum precursor increases the shift for the reduction of Co_3O_4 to 140 K, while reduction of the cobalt surface phase is shifted 100 K compared to the monometallic catalyst.

Other second metals (Pd, Ru, Ir or Re) also lowers the cobalt reduction temperature. The size of the shift dependens on the type of metal. It is suggested that the second metal must be reduced itself before it promotes the reduction of cobalt.

It is found that the bimetallic CoPt and CoRe catalysts are reduced to a larger extent compared to the monometallic cobalt catalyst during an isothermal reduction for 16 hours at 623 K. In the bimetallic catalysts the oxidic cobalt surface layer are reduced, while this is not the case for the monometallic catalyst.

Both the extent of decomposition of cobalt nitrate during the calcination and the reductive decomposition temperature are unaffected by addition of a second metal.

Temperature programmed reduction also shows that increasing the calcination temperature from 573 to 698 K increases the extent of oxydative decomposition of cobalt nitrate, and lowers the amount of oxidic cobalt surface layer. The amount of cobalt as Co_3O_4 particles remains constant with increasing calcination temperature in this range. It is assumed that Co^{2+}

diffusion from the surface layer into the alumina lattice increases with increasing calcination temperature, giving more heavily reducible $CoAl_2O_4$.

Volumetric chemisorption measurements at 298 K show that both Pt and Re addition to $9\%Co/Al_2O_3$ results in a large increase in CO adsorption. The H_2 adsorption increases also with addition of Pt and Re, but the increase is smaller for Re addition compared to Pt addition. The difference between the two promoted catalysts is assumed to be due to hydrogen adsorption on Pt. Both CO and H_2 adsorption increases with increasing amount of Pt addition.

The CO:H adsorption ratio increases in the order

$$Co1.0Re > Co1.0Pt > Co0.5Pt > Co.$$

Chemisorption of H_2 on chloride containing, platinum promoted catalysts shows that these catalysts adsorb somewhat less hydrogen compared with the monometallic cobalt catalyst. Increased calcination temperature of the $9\%Co/Al_2O_3$ catalyst also slightly decreases the H_2 uptake on the catalyst.

Activity measurements done with differential conditions at 473 K and 1 bara show that promotion of the cobalt catalyst with Pt or Re increases the rate of CO conversion to hydrocarbons. Re addition gives the largest increase. The increase in CO conversion over the rhenium promoted catalyst is larger than the increase in H_2 uptake. The increase in CO conversion rate over the platinum promoted catalyst is in agreement with the observed increase in degree of reduction and the increase in H_2 uptake. However, some of the hydrogen uptake was considered to be on platinum. Promotion with rhenium as well as platinum then gives increased turnover frequency on the cobalt sites. The results therefore indicate that the increase in rate for both the Pt and the Re promoted catalysts is due to increased number of active sites, and also probably to increased intrinsic activity.

Activity measurements done with differential conditions at 513 K and 7 bara did not show any differences between the unpromoted and the promoted catalysts. It is suggested that the reaction rates in this case are limited by the reactant diffusion through liquid products present in the catalyst pores.

Selectivity measurements did not show significant differences in hydrocarbon chain length between the unpromoted and platinum promoted cobalt catalysts, but a decreased α-olefin/n-paraffin ratio could be observed with increasing platinum addition.

CONTENTS

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LIST OF SYMBOLS AND ABBREVIATIONS

A	Preexponential factor related to numbers of surface collisions
ASF	Anderson-Schulz-Flory kinetic
AES	Auger Electron Spectroscopy
B	XRD experimental line width
BET	Adsorption isotherm named after Brunauer, Emmet and Teller
DRS	Diffuse Reflectance Spectroscopy
D	Dispersion
D_r	Dispersion, taking into account reduction extent
d	Particle size, diameter
E_{CO}, Ea_{CO}	Activation energy for CO conversion [kJ/mol]
E_{CH4}, Ea_{CH4}	Activation energy for CH_4 formation [kJ/mol]
EPR	Electron Paramagnetic Resonance
ESR	Electron Spin Resonance
EXAFS	Extended X-ray Absorption Fine Structure
eV	Electron Volt (1 eV = $1.602 \cdot 10^{-19}$ J)
FT	Fischer-Tropsch
f	Fraction of cobalt reduced to metal, determined from O_2 titration
fcc	Face centered cubic
HDS	Hydrodesulfurization
hcp	Hexagonal close packed
ISS	Ion Scattering Spectroscopy
K	Scherrer constant = 0.9
K_X	Total rate constant for a elementary reaction step, where x is the main product of the reaction step
k_X	Rate constant for a elementary reaction step in the direction against product x
N_{CO}	Turnover frequency for CO conversion [mol/mol·s]
N_{CH4}	Turnover frequency for CH_4 formation [mol/mol·s]
N_s	Number of surface atoms, measured by H2 chemisorption
N_{tot}	Total number of metal atoms
n	Number of carbon atoms in the hydrocarbon product
Pt*	Pt from a chloride containing precursor
p_{CO}	Partial pressure of CO
p_{H2}	Partial pressure of H_2
r_{CO}	Rate for CO consumption
r_{HC}	Rate for hydrocarbon formation
r_p	Chain propagation rate
r_t	Chain termination rate
SIMS	Secondary Ion Mass Spectroscopy

s	Site density [atoms/Nm^2]
TEM	Transmission Electron Microscopy
TOF	Turnover Frequency [mol/mol·s]
TPR	Temperature Programmed Reduction
W_n	Weight fraction of hydrocarbon product containing n carbon atoms
XAS	X-ray Absorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
α	Chain growth probability
β	Broadening of the X-ray diffraction line, B - 0.20
λ	XRD wavelength, 1.5418 Å
Θ	Bragg angle, 18.433
*	Surface site active for adsorption of gas molecules
[*]	Concentration of empty surface site
[x*]	Concentration of surface sites with gas x adsorbed
$[*]_{tot}$	Concentration of total numbers of surface sites

LIST OF FIGURES AND TABLES

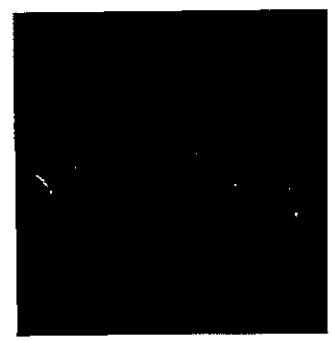

Table 4-14. Activity at 473 K and 1 bara after 300 and 1400 minutes reaction time, H_2:CO = 2, GHSV = 5000 h^{-1}, CO conversion = 4-10 %.

Table 4-15. Turnover frequency (TOF) of cobalt catalysts after 5 h reaction time. T = 473 K, P = 1 bara, H_2:CO = 2, GHSV = 5000 h^{-1}, conversion = 4 - 10 %.