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THE WATER-GAS SHIFT REACTION: DEACTIVATION STUDIES

John Ramsdon Mellor

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ABSTRACT

The water-gas shift reaction is extensively used in the industrial production of hydrogen, or to adjust the CO/H_2 ratio of synthesis gas for the subsequent manufacture of chemicals. The current procedure for the production of high purity hydrogen involves a two stage catalytic process utilising a high temperature iron-chromium catalyst to decrease the CO concentration from an initial value of ca 10 - 60 mole% to ca 3 mole% followed by a low temperature copper-zinc oxide-alumina/chromia catalyst to further reduce the CO content to ca 0.3 mole%. Novel Raney copper catalysts were shown to be highly active for low temperature operation, and form the basis of the investigations reported in this thesis.

Raney copper catalysts were prepared by the caustic leaching of extractable metals, aluminium and/or zinc from composite alloys, to produce high specific surface areas with porous reaction product zones active for the WGSR. In contrast, alloys leached in nitric and perchloric acids resulted in catalysts with low surface areas and low WGS activities. Characterisation studies showed that the chemical nature of the reactant surface could be determined by controlling the caustic leaching process. Initial high WGS activity decreased as a result of copper crystallite sintering which was attributed to a deficiency in zinc oxide support. Stability was improved by increasing the Raney copper rim zinc content by leaching the alloys in caustic solutions containing zincate, or by direct incorporation using ion implantation. Leaching precursor alloys rich in zinc was an effective method for increasing the content of zinc in the rim without compromising the formation of high copper surface areas, important because a correlation was shown to exist between WGS activity and copper surface area. Specific copper surface area was determined using a nitrous oxide pulse chemisorption technique.

Statistically designed experiments were employed to optimise the Raney copper catalyst system for maximum long term activity and stability. A 2_{III}^{11-7} fractional factorial design was effective in screening the large number of process and catalyst preparation variables. $CO:H_2O$ ratio, alloy particle size, zincate leach concentration and caustic/soluble metal ratio were found to significantly influence both the long term final activity and overall change in activity. The preparation variables were optimised using a central composite design in conjunction with response surface methodology, and the optimised Raney catalyst performance was evaluated as a function of time-on-stream, reactor temperature and GHSV. The WGS activity of Raney copper catalysts was observed to be further enhanced by the addition of small amounts of cesium.

Model reagent studies revealed that the WGSR proceeds via the formation of a surface formate-type intermediate over the optimised Raney copper catalyst.

Due to both the sensitivity of copper-based low temperature shift catalysts in trace amounts of sulphur and the decreased performance of the iron-chromium high temperature shift catalyst in higher sulphur concentrations, scope still exists to design a catalyst to operate in coal-based process gas containing variable concentrations of sulphur. This thesis presents results to show that a co-precipitated cobalt chromium high temperature shift catalyst demonstrates high WGS activity in both the oxide and sulphided forms, and in the presence or absence of trace or concentrated sulphur.

DECLARATION

I declare that the work presented in this thesis was conducted on my own, under the supervision of Prof. N.J. Coville. It is being submitted for the degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.



John Ramsdon Mellor

15th day of March, 1993.

In Loving Memory of my Father, John Wyndham Mellor

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LIST OF ABBREVIATIONS

AAS	-	Atomic Absorption Spectroscopy
BET	-	Brunauer, Emmett, Teller (surface area)
DSC	-	Differential Scanning Calorimetry
EDAX	-	Energy Dispersive Analysis by X-ray
FID	-	Flame Ionisation Detector
FPD	-	Flame Photometric Detector
FTIR	-	Fourier Transform Infra-Red Spectroscopy
GC	-	Gas Chromatograph
GHSV	-	Gas Hourly Space Velocity
HDS	-	Hydrodesulphurisation
ICP-MS	-	Inductively Coupled Plasma-Mass Spectroscopy
ID	-	Internal Diameter
MP	-	Melting Point
SEM	-	Scanning Electron Microscopy
TCD	-	Thermal Conductivity Detector
TGA	-	Thermogravimetric Analysis
UHV	-	Ultra High Vacuum
WGSR	-	Water-Gas Shift Reaction
XPS	-	X-ray Photoelectron Spectroscopy
XRD	-	X-ray Powder Diffraction

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