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TABLE I

Mechanism Proposed by Masuda and Miyahara[19] for Water Gas Shift Reaction on Unsupported Platinum

$CO + M \rightleftharpoons M\text{-}CO$

$H_2O + 2\,M \rightleftharpoons M\text{-}H + M\text{-}OH$

$M\text{-}CO + M\text{-}OH \rightleftharpoons$ adsorbed intermediate

adsorbed intermediate $\rightleftharpoons M\text{-}CO_2 + M\text{-}H$

$M\text{-}CO_2 \rightleftharpoons M + CO_2$

$2\,M\text{-}H \rightleftharpoons 2\,M + H_2$

TABLE II

Mechanism Proposed by Grenoble, Estadt, and Ollis[20]

$H_2O + MO \rightleftharpoons HO\text{-}MO\text{-}H$

$H_2O + MO \rightleftharpoons H_2O\text{-}MO$

$H_2O + 2\ M \rightleftharpoons M\text{-}OH + M\text{-}H$

$CO + M \rightleftharpoons M\text{-}CO$

$M\text{-}CO + H_2O\text{-}MO \rightleftharpoons OM\text{-}O(H)C(H)O$

$OM\text{-}O(H)C(H)O + M \rightleftharpoons M\text{-}O(H)C(H)O$

$M\text{-}O(H)C(H)O \rightleftharpoons M + CO_2 + H_2$

TABLE III

Proposed Mechanism of Water Gas Shift on Metals

$H_2 + M \rightleftharpoons M\text{-}H_2(\text{physisorbed})$

$M\text{-}H_2(\text{physisorbed}) \rightleftharpoons H\text{-}M\text{-}H$

$CO + M \rightleftharpoons M\text{-}CO(\text{physisorbed})$

$M\text{-}CO(\text{physisorbed}) \rightleftharpoons M\text{-}CO$

$H_2O + M \rightleftharpoons M\text{-}H_2O(\text{physisorbed})$

$M\text{-}H_2O(\text{physisorbed}) \rightleftharpoons M\text{-}OH_2$

$CO_2 + M \rightleftharpoons M\text{-}CO_2(\text{physisorbed})$

$M\text{-}CO_2(\text{physisorbed}) \rightleftharpoons M\text{-}CO_2$

$M\text{-}CO \rightleftharpoons M\text{-}\overset{O}{\overset{\|}{C}}$

$M\text{-}\overset{O}{\overset{\|}{C}} \rightleftharpoons O\text{-}M\text{-}C$

$M\text{-}OH_2 \rightleftharpoons H\text{-}M\text{-}OH$

$M\text{-}OH \rightleftharpoons H\text{-}M\text{-}O$

$M\text{-}CO + M\text{-}O \rightleftharpoons M\text{-}CO_2$

$M\text{-} \quad + M\text{-}OH \rightleftharpoons M\text{-}C(O)OH$

$M\text{-}C(O)OH \rightleftharpoons H\text{-}M\text{-}CO_2$

TABLE IV

Proposed Mechanism for the Water Gas Shift Reaction on Metal Oxides

Reaction	Number
$H_2 + MO \rightleftharpoons MO\text{-}H_2$(physisorbed)	(4)
$MO\text{-}H_2$(physisorbed) $\rightleftharpoons$ H-MO-H	(5)
H-MO-H + 2 MO $\rightleftharpoons$ OM-H-MO-H-OM	(6)
$H_2O + MO \rightleftharpoons H_2O\text{-}MO$(physisorbed)	(7)
$H_2O\text{-}MO$(physisorbed) $\rightleftharpoons$ $H_2O\text{-}MO$	(8)
$H_2O\text{-}MO$(physisorbed) $\rightleftharpoons$ MO-HOH	(9)
$H_2O\text{-}MO \rightleftharpoons$ HO-MO-H	(10)
MO-HOH $\rightleftharpoons$ HO-MO-H	(11)
CO + MO $\rightleftharpoons$ OM-CO(physisorbed)	(12)
OM-CO(physisorbed) $\rightleftharpoons$ OM-CO	(13)
CO + MOMO $\rightleftharpoons$ M_2CO_3	(14)
$CO_2 + MO \rightleftharpoons MO\text{-}CO_2$(physisorbed)	(15)
$MO\text{-}CO_2$(physisorbed) $\rightleftharpoons$ $OM\text{-}CO_2$	(16)
$MO\text{-}CO_2$(physisorbed) $\rightleftharpoons$ $MO\text{-}CO_2$	(17)
$MO\text{-}CO_2$(physisorbed) $\rightleftharpoons$ OM-OCO	(18)
OM-OCO + OM-OH $\rightleftharpoons$ OM-OC(O)OH + MO	(19)
$MO\text{-}CO_2$ + OM-OH $\rightleftharpoons$ MO-C(O)OH + OM-O	(20)
$OM\text{-}CO_2$ + OM-OH $\rightleftharpoons$ OM-OC(O)OH + MO	(21)
OM-CO + OM-OH $\rightleftharpoons$ OM-C(O)OH + MO	(22)
OM-C(O)OH $\rightleftharpoons$ OM-OCOH	(24)

TABLE IV (continued)

Reaction	Number
$OM\text{-}OCOH \rightleftharpoons OM\text{-}OC(H)O$	(25)
$M\text{-}OCO + M\text{-}H \rightleftharpoons M\text{-}OC(H)O + M$	(26)
$OM\text{-}CO + OM\text{-}O \rightleftharpoons OM\text{-}CO_2 + MO$	(27)
$OM\text{-}CO_2 + OM\text{-}O \rightleftharpoons OM\text{-}OCO_2 + MO$	(28)

TABLE V

Previously Proposed Elementary Reactions

for Homogeneous Water Gas Shift Reaction

Reaction	Reference
$M\text{-}CO + OH^- \rightleftharpoons M\text{-}C(O)OH^-$	126,128,130,131
$M\text{-}CO + OH^- \rightleftharpoons M\text{-}H + CO_2$	137
$M\text{-}CO + OH^- \rightleftharpoons M\text{-}H^- + CO_2$	133
$[M\text{-}CO]OH \rightleftharpoons M\text{-}C(O)OH$	138
$M\text{-}CO + H_2O \rightleftharpoons H\text{-}M\text{-}C(O)OH$	128,131
$M\text{-}CO + Me_3N \rightleftharpoons M\text{-}C(O)NMe_3$	132
$M\text{-}C(O)NMe_3 + H_2O \rightleftharpoons M\text{-}H^- + CO_2 + Me_3NH^+$	132
$M\text{-}CO^+ + H_2O \rightleftharpoons H\text{-}M\text{-}C(O)OH^+$	129
$M\text{-}C(O)OH \rightleftharpoons M\text{-}H + CO_2$	128,131,138
$H\text{-}M\text{-}C(O)OH \rightleftharpoons M + HC(O)OH$	138
$M\text{-}C(O)OH^- + H_2O \rightleftharpoons H\text{-}M\text{-}C(O)OH + OH^-$	128,131
$M\text{-}C(O)OH^- \rightleftharpoons M\text{-}H^- + CO_2$	126
$M\text{-}C(O)OH^- + B \rightleftharpoons M\text{-}C(O)O^{2-} + BH^+$	130
$M\text{-}C(O)O^{2-} + H_2O \rightleftharpoons M\text{-}H^- + HCO_3^-$	130
$M\text{-}(Cl)C(O)OH^+ \rightleftharpoons M^+ + CO_2 + H^+ + Cl^-$	129
$M\text{-}OC(H)O \rightleftharpoons M\text{-}H + CO_2$	138
$M\text{-}OC(H)O^- \rightleftharpoons M\text{-}H^- + CO_2$	124,126,132
$H\text{-}M\text{-}H \rightleftharpoons M + H_2$	124,126,128,131, 132,136,137,138
$H\text{-}M\text{-}H + CO \rightleftharpoons M\text{-}CO + H_2$	128,131,136

TABLE V (continued)

Reaction	Reference
$M\text{-}H^- + CO \rightleftharpoons M\text{-}CO + H^-$	126,133
$M\text{-}H^- + H_2O \rightleftharpoons M + H_2 + OH^-$	133
$M + CO \rightleftharpoons M\text{-}CO$	125,126,128,131, 132,136,137
$M^+ + CO \rightleftharpoons M\text{-}CO^+$	129
$M^- + CO \rightleftharpoons M\text{-}CO^-$	133
$M + H_2O \rightleftharpoons H\text{-}M\text{-}OH$	136,138
$M^- + H_2O \rightleftharpoons M\text{-}H + OH^-$	125,126,132,137
$M + HC(O)OH \rightleftharpoons H\text{-}M\text{-}OC(H)O$	138
$M + HCOO^- \rightleftharpoons M\text{-}OC(O)H^-$	125,126,132
$H\text{-}M\text{-}OH + S \rightleftharpoons [H\text{-}M\text{-}S]OH$	136,138
$[H\text{-}M\text{-}S]OH + CO \rightleftharpoons [H\text{-}M\text{-}CO]OH + S$	136,138
$CO + OH^- \rightleftharpoons HCO_2^-$	126,128,131,132
$CO_2 + OH^- \rightleftharpoons HCO_3^-$	128,131
$HCO_2^- + H_2O \rightleftharpoons H_2 + CO_2 + OH^-$	128,131
$H^- + H_2O \rightleftharpoons H_2 + OH^-$	126,133

TABLE VI

Proposed Mechanism for the Homogeneous Water Gas Shift Reaction

Reaction	Number
$M\text{-}CO + OH \rightleftharpoons M\text{-}C(O)OH$	(29)
$M\text{-}CO + H_2O \rightleftharpoons H\text{-}M\text{-}C(O)OH$	(30)
$M\text{-}C(O)OH \rightleftharpoons M\text{-}H + CO_2$	(31)
$CO_2 + M\text{-}H \rightleftharpoons M\text{-}OC(H)O$	(32)
$CO + OH^- \rightleftharpoons HCO_2^-$	(33)
$M + HCO_2^- \rightleftharpoons M\text{-}OC(H)O^-$	(34)
$H_2O + M \rightleftharpoons H\text{-}M\text{-}OH$	(35)
$H\text{-}M\text{-}H \rightleftharpoons M + H_2$	(36)
$CO + M \rightleftharpoons M\text{-}CO$	(37)
$H\text{-}M\text{-}H + CO \rightleftharpoons M\text{-}CO + H_2$	(38)
$M\text{-}H + CO \rightleftharpoons M\text{-}CO + H$	(39)

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Call No.: DOE\PC\70020-T1
Title: Methane suppression in the Fischer-[illegible] synthesis : Final report
Author: Pittsburgh Univ., PA (USA). Dept. of Chemical and Petroleum Engineering
Published: 31 January 1988
Description: 50 p.
Tech. Rept. No.: DOE\PC\70020-T1 ; DE88006658
Report type: Progress report
Funding Info.: AC22-84PC70020
Abstract: The objective of the project was to investigate the possiblity of modifying methane formation during the F-T synthesis independent from other hyfrocarbons by systematically changing catalyst characteristics. It would seem that the best way to decrease methane selectivity is still via the use of catalyst modifiers. Inorder to "tailor-make" catalyst surfaces which minimize "extraneous" methane synthesis without disrupting F-T synthesis, it is necessary for us to fully understand the mechanism(s) by which such modifiers operate. An investigation of Fischer-[illegible] synthesis on K- and Cl-modified Ru Catalysts was carried out. The steady-steady reaction results illustrate how chlorine enhances the selectivity of methane formation while potassium decreases it. In order to better understand methane slectivity changes, a detailed study of Cl-modification of Ru catalysts was made. Amonnia synthesis and methanation reaction results on the same series of catalysts (obtained by using the steady-state isotopic transient technique) in addition to the deactivation results for F-T suggest that structural rearrangements induced by the presence of chlorine, rather than selective site blocking or electronic interactions, may be the primary mechanism of chlorine modification of supported ruthenium catalysts. The results of this study indicate that catalyst modifiers may act to change the catalytic properties by inducing certain metal surface structures. This is a mechanism of modification which has, yet, not been addressed in detail. 49 refs., 16 figs., 7 tabs.

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Call No.: DOE\PC\70023-T2
Title: The development of a selective ruthenium Fischer- catalyst Final report, October 1, 1984--February 28, 1989
Author: UOP, Inc., Des Plaines, IL (United States). Technical Center
Published: [1989]
Description: 577 p.
Tech. Rept. No.: DOE\PC\70023-T2 ; DE92002723
Report type: Progress report
Funding Info.: USDOE, Washington, DC (United States) AC22-84PC70023
Abstract: A new stable Fischer- catalyst with very high selectivity to distillate fuels and with low light ends production was developed. This catalyst, which was made by a reverse micelle technique, contains 2.8% (by weight) ruthenium in the form of 4--6 nm particles on alumina and a proprietary modifier. The new modified ruthenium catalyst did not noticeably deactivate during 814 hours at about 80% CO conversion, 2H[sub 2]:1 CO feed ratio, 208[degree]C at inlet, 62 atm and 150 gas hourly space velocity. In order to determine the catalyst's tolerance, the operational severity was increased between 814 hours and 1700 hours by increasing the temperature and space velocity to 225[degree]C at inlet and to 205 hr[sup [minus]1], respectively. A deactivation rate of about 0.016%/hour was measured under these more severe conditions at about 70% conversion level. These results with the new modified ruthenium catalyst compare favorably with those reported for the two commercial Sasol processes. The Arge process makes approximately 38% distillate fuel with 14--18% light ends, while the Synthol process makes about 48% distillate with 38% light ends. 82 refs., 360 figs., 66 tabs.

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