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**IMPROVED FISCHER-TROPSCH SYNTHESIS
CATALYSTS FOR INDIRECT COAL LIQUEFACTION**

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CATALYSTS FOR INDIRECT COAL LIQUEFACTION

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OBJECTIVE: Our goal (slide 1) is to develop Fischer-Tropsch synthesis (FTS) catalysts that produce less methane and less wax than the Anderson-Schultz-Flory product distribution.

TECHNICAL APPROACH: Two approaches to the synthesis of novel FTS catalysts have been pursued: (1) the organometallic synthesis and surface confinement of atomic ruthenium and multiatomic aluminum-ruthenium hydridocarbonyl clusters and (2) treatment of iron and alumina-supported cobalt and ruthenium catalysts with uniformly deposited, submonolayer levels of chemisorbed sulfur.

Catalysts developed by both approaches were screened for FTS activity and product distribution and selected catalysts were further evaluated in bench-scale slurry-phase and fixed-bed reactors at elevated pressures, as reported previously (slide 2). Admixtures of the sulfur treated iron and ruthenium FTS catalysts with sodium Y-zeolites were examined for the production of aromatics and oxygenates in 20-atm fixed-bed studies with low H_2/CO Ratio = 0.5 and temperatures from 573 to 700 K.

There are several technical advantages of direct synthesis of aromatic hydrocarbons with low H_2 syngas. The key difficulty of this approach is deactivation of the FTS component because of carbon deposits. Since we observed that sulfur-treated fused iron resisted deactivation, we extended the scope of our project (slide 2) to include studies of aromatics production with dual-function catalysts.

SIGNIFICANT ACCOMPLISHMENTS: Substantial changes in FTS selectivity of the fused iron and alumina-supported ruthenium catalysts were found following treatment with submonolayer quantities of chemisorbed sulfur. Following reduction and passivation by accumulation of a surface layer of carbon and chemisorbed CO, approximately 40% of a monolayer of sulfur was slowly adsorbed at 473 K on the fused iron catalysts. The passivating layer was removed and the sulfur locally dispersed by heating to 1000 K in hydrogen. The treated catalyst had a three-fold reduction in methane selectivity relative to the untreated reduced fused iron in 2:1 $H_2:CO$ syngas at 573 K and 100 kPa. The C_2 olefin selectivity approached 100% ($C_2H_4/C_2H_6 > 20$). The sulfur treatment decreased the C_{2+} production rate at 573 K to only about half the rate of the untreated catalyst per unit area and was comparable to the stationary-stable activity of the fused iron at 523 K. The medium-level sulfur treated catalysts had a two- to three-fold reduction in methane selectivity relative to the untreated fused iron catalyst (slide 3), with greatly increased olefin to paraffin ratio (slide 4). The medium-level sulfur-treated

(50% monolayer sulfur coverage) iron and cobalt catalysts were tested for FTS activity. The FTS performance of the medium-level sulfur-treated fused iron catalyst seems most promising, with a 50% reduction in methane yield, a narrower product distribution (chain growth probability factor (slide 5), α , was 20% less than that of the clean catalyst under the same reaction conditions), and a threefold increase in olefin selectivity. The sulfur-treated catalyst exhibited behavior at 2 MPa similar to that of the 100-kPa synthesis run; however, olefin selectivity decreased with increasing pressure or temperature. The sulfur treated catalysts were not observed to deactivate over a reaction period of 24 hours with H_2/CO as low as 0.5 and temperatures as high as 650 K. This phenomena may be related to poisoning of specific sites or an ensemble effect (slides 6&7).

Several sulfur-treated Fe and Ru/ Al_2O_3 and Na Y-zeolite (1:4 and 1:10) composite catalysts showed good activity, low methane selectivity (8 to 16 wt%), and high selectivity for oxygenates and aromatics under differential reactor conditions with low CO conversion. The medium-level sulfur-treated fused iron and sulfur-treated alumina-supported ruthenium were used as the FTS catalyst components and compared with results for the clean fused iron and clean ruthenium catalysts mixed with zeolite. The mixed catalysts containing sulfur-treated iron initially provided high yields of light oxygenates and aromatics with low yields of olefins (slides 8,9,&10), but deactivated rapidly, probably owing to carbon deposition (slide 11), especially with catalysts containing the more acidic low sodium zeolite components. The catalyst reactivity could be prolonged by using a higher zeolite/FTS catalyst ratio and by using zeolites with higher sodium weight loading. However, the acidic component deactivated after 2 hours at 650 K, restoring high olefin selectivity in the product distribution.

Additional studies with low acidity, shape-selective zeolites are recommended (slides 12,13,&14). We suggest that coking resistant FTS catalysts such as sulfur-treated iron, combined with high-silica, moderate-to-low pore size, shape-selective synthetic zeolites with variable acidity, could produce a catalyst system suitable for one-stage liquid hydrocarbon synthesis (slide 15). The acid strength of a zeolite, such as ZSM-5, correlates with catalytic activity for desirable wax cracking and octane enhancing reactions such as isomerization and dehydrocyclization. However, prior work suggests that those catalysts with good activity for cracking and formation of aromatics also deactivate more rapidly because carbon accumulates on their surfaces and within pores. At temperatures below 573 K, pentasil zeolites with very low aluminum content should give very low coking rates, but may not be active for wax cracking or isomerization. Zeolites with low Si/Al ratios have good activity, but rapidly coke. Satisfactory activity and coking resistance can probably be attained in a zeolite with an intermediate Si/Al ratio, particularly with the addition of coke-inhibiting promoters such as Ca, Sr, La, and framework Ga.

SELECTIVE SULFUR POISONED CATALYSTS FOR FISCHER TROPSCH SYNTHESIS

Advantages:

- Selective poisoning of hydrogenation sites
- Ensemble effect inhibits carbon deposition and hydrogenolysis
- FTS activity remains high

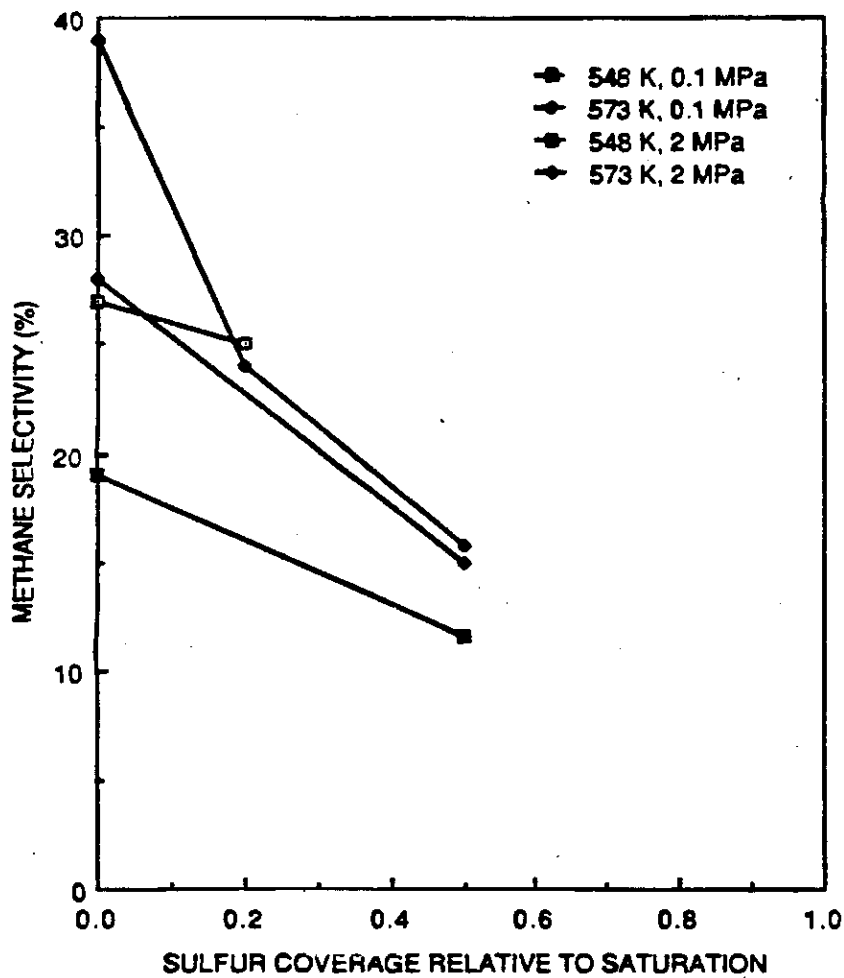
Problem Areas:

- Chain growth factor lowered
- Light alkane selectivity more sensitive to H₂ pressure
- Sulfur treatment difficult

Objective:

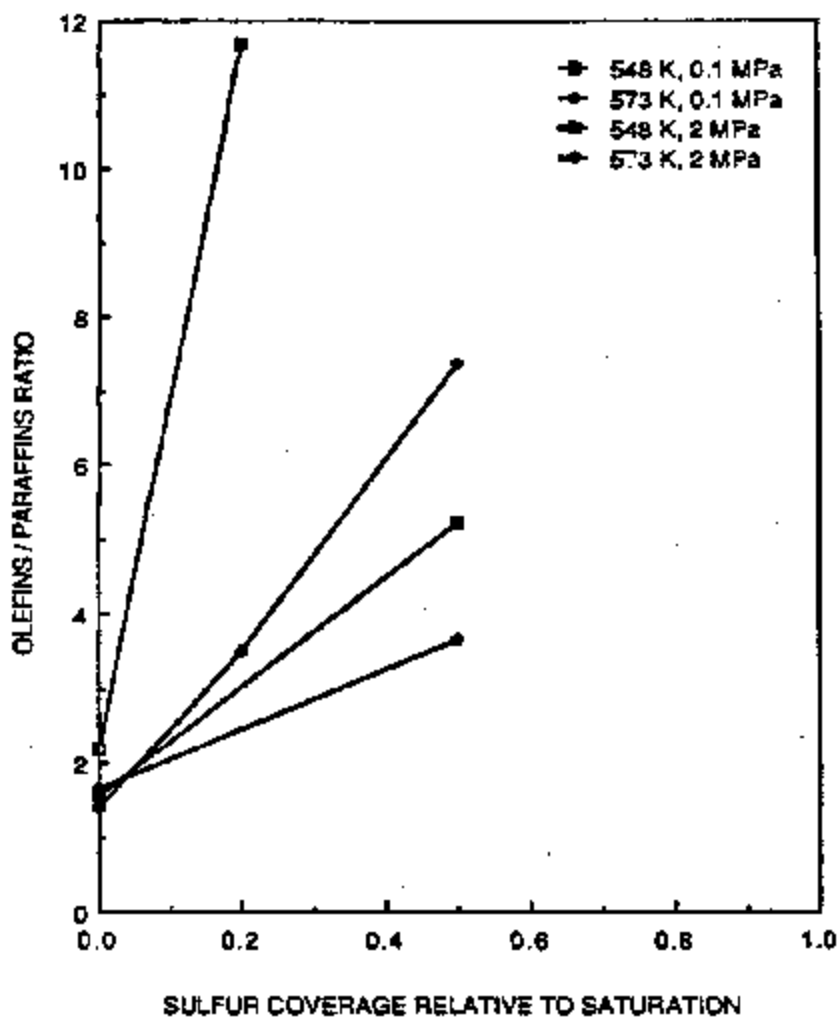
- Produce aromatics by addition of Y zeolite components
- Monitor deactivation with low H₂ syngas

METHANE SELECTIVITY FOR FIXED-BED FTS BY CLEAN AND SULFUR-TREATED FUSED IRON CATALYSTS WITH H_2/CO RATIO = 1.0



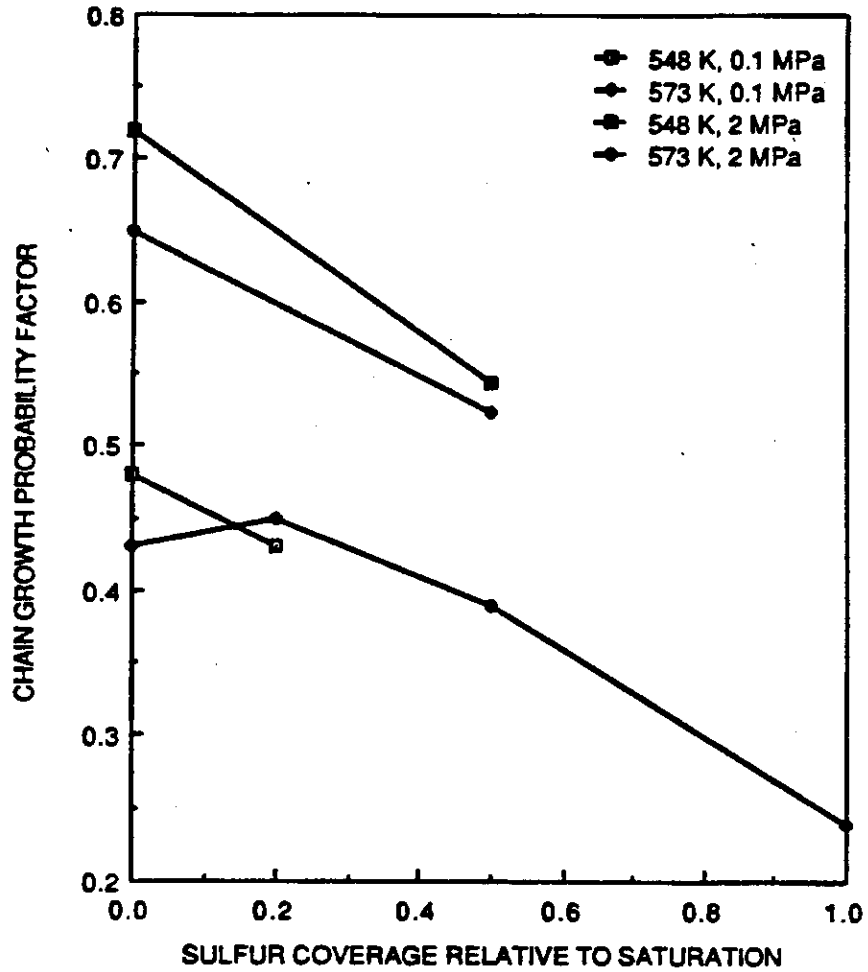
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**LIGHT OLEFIN SELECTIVITY FOR FIXED-BED FTS
BY CLEAN AND SULFUR-TREATED FUSED IRON
CATALYSTS WITH H₂/CO RATIO = 1.0**

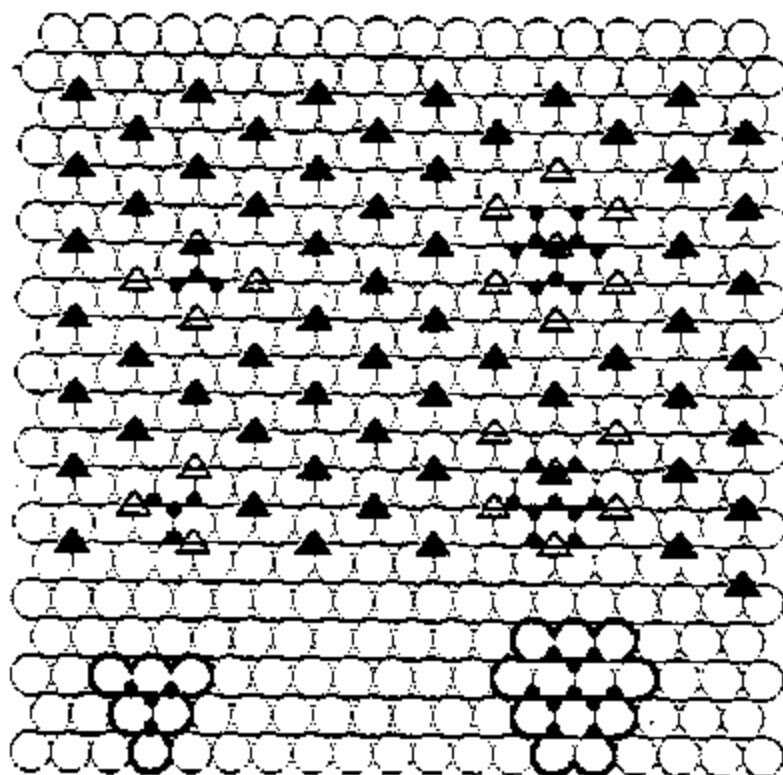


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CHAIN GROWTH PROBABILITY FACTOR FOR CLEAN AND SULFUR-TREATED FUSED IRON CATALYSTS WITH H₂/CO RATIO = 1

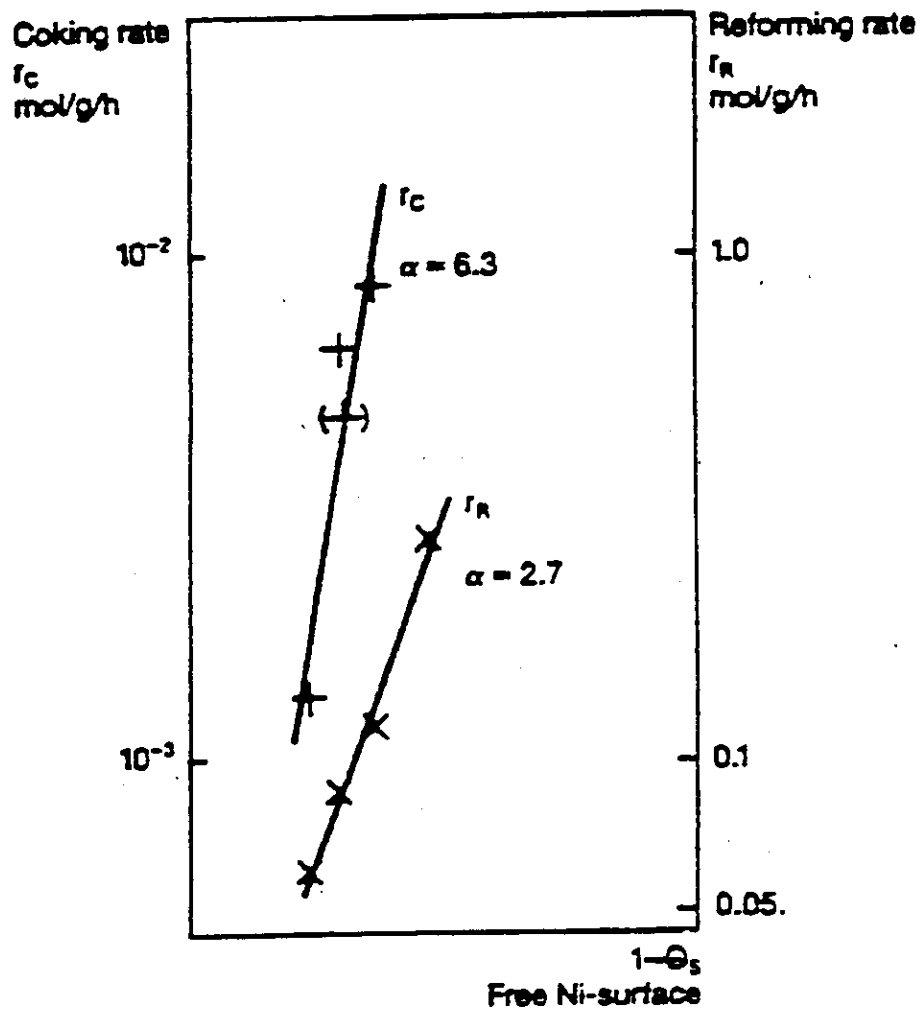


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ENSEMBLE EFFECT FOR SELECTIVE POISONING ON Ni(111).

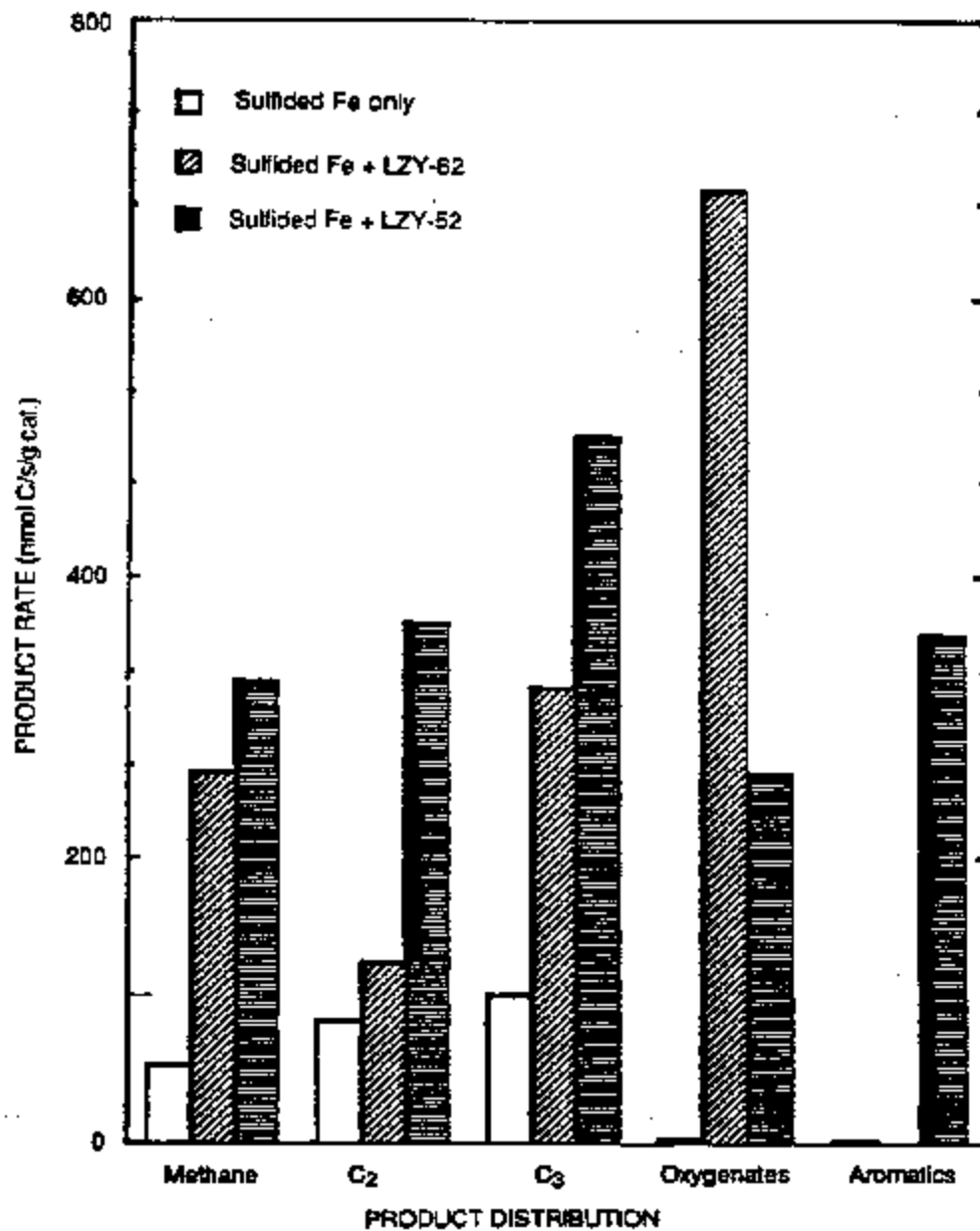
From J. Rostrup-Nielsen and I. Alstrup, Catalysis 1987.



COKING AND STEAM REFORMING RATES FOR SULFUR POISONED CATALYSTS.

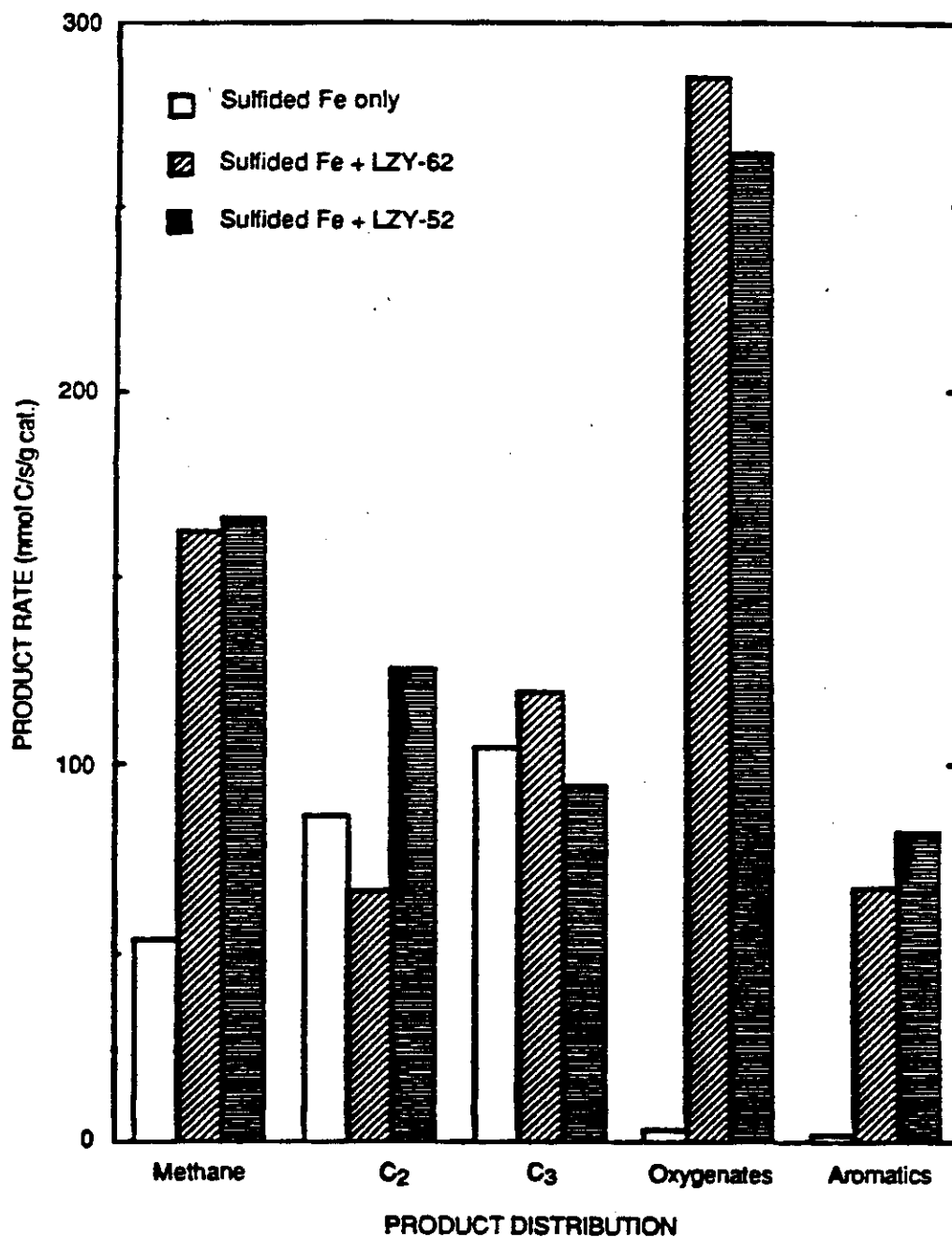
From J. Rostrup-Nielsen and I. Alstrup, Catalysis 1987.

AROMATIC SYNTHESIS AT 2 MPa, 573 K, H₂/CO RATIO = 0.5,
ON MIXED MEDIUM-LEVEL SULFUR-TREATED FUSED IRON
AND Na-Y ZEOLITE CATALYSTS (1:4 weight ratio)



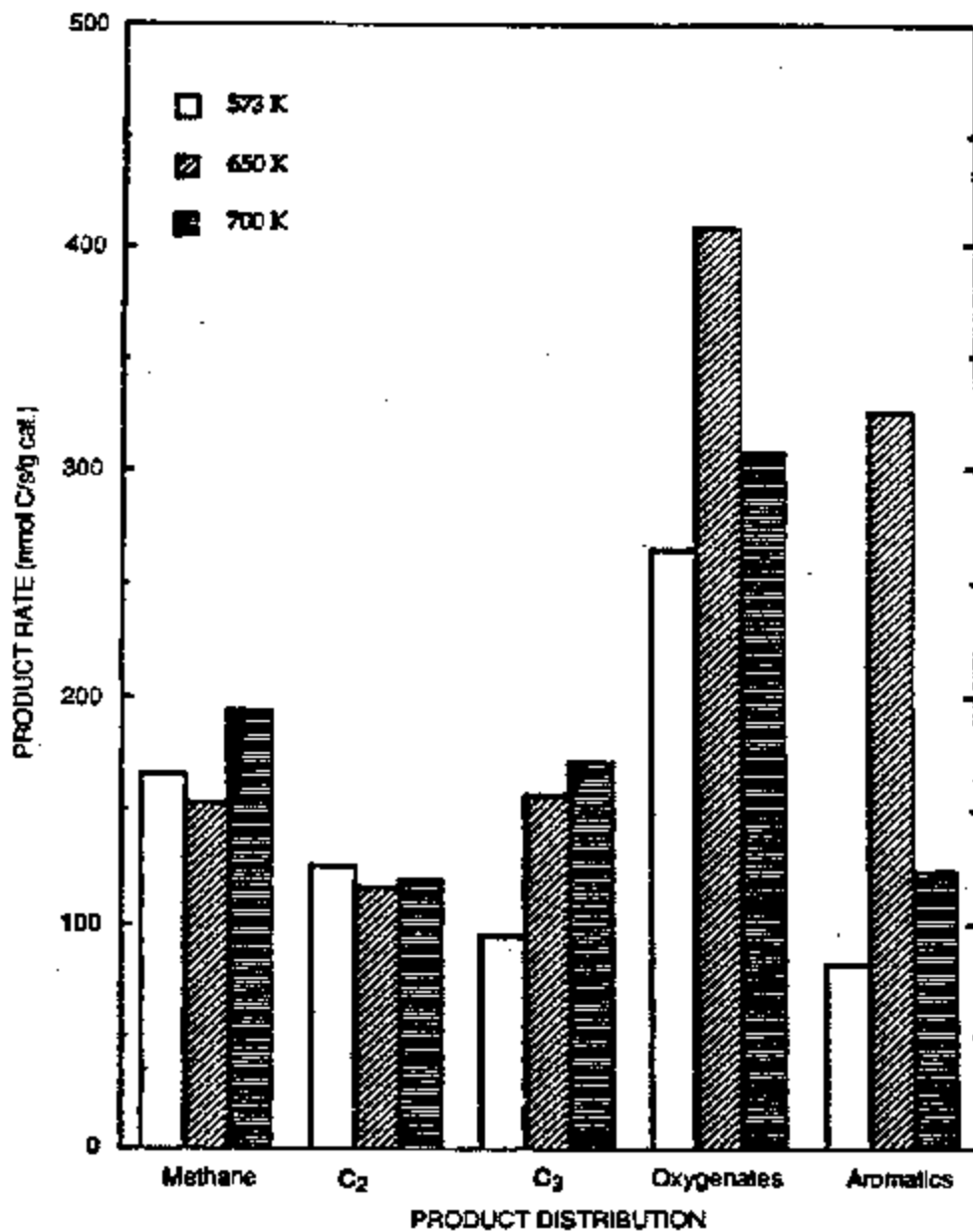
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AROMATIC SYNTHESIS AT 2 MPa, 573 K, H₂/CO RATIO = 0.5, ON MEDIUM-LEVEL SULFUR-TREATED FUSED IRON CATALYST AND Na-Y ZEOLITES



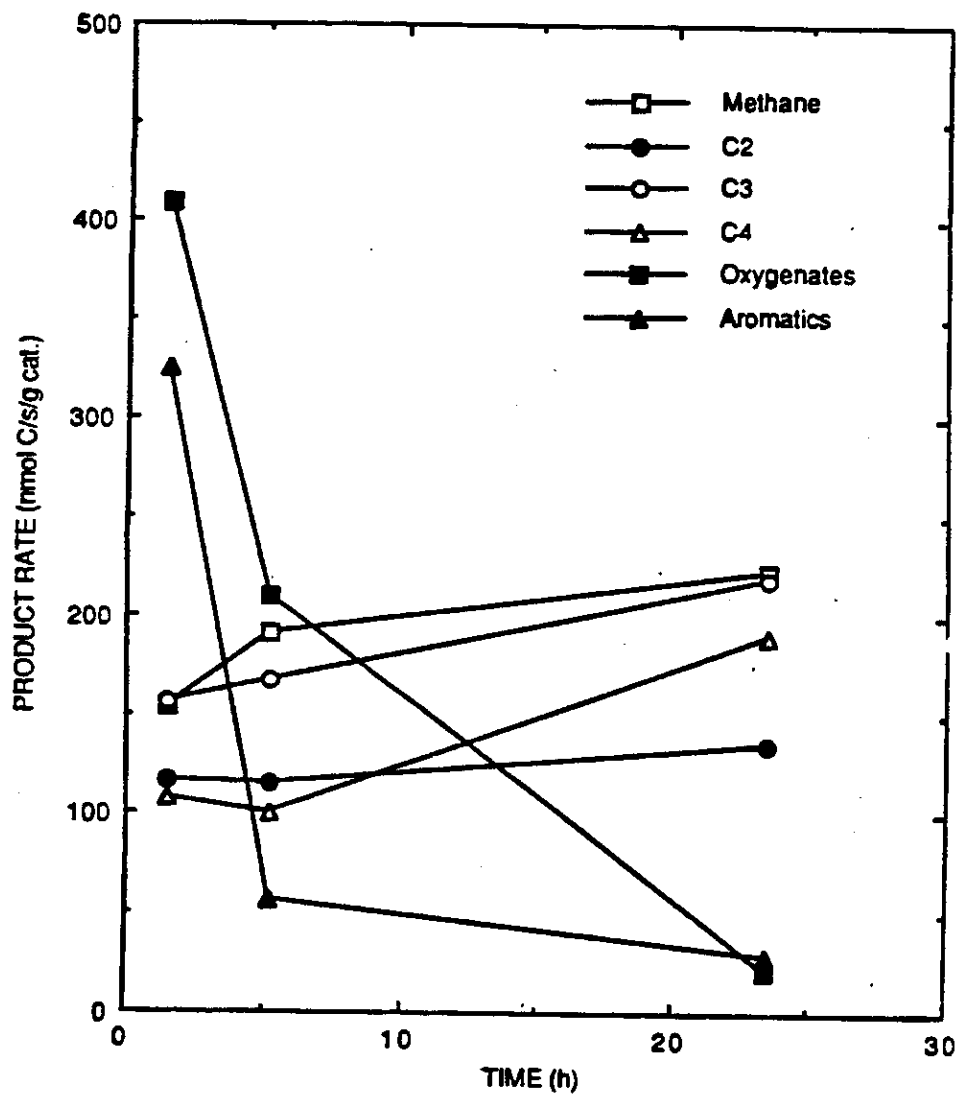
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**AROMATIC SYNTHESIS AT 2 MPa, H₂/CO RATIO = 0.5
ON MEDIUM-LEVEL SULFUR-TREATED FUSED IRON
CATALYST AND LZV-52 ZEOLITE**



RA1245-28

AROMATIC SYNTHESIS AT 2 MPa, 650 K, H₂/CO RATIO = 1.0,
ON MEDIUM-LEVEL SULFUR-TREATED FUSED IRON
CATALYST AND LZY-52 ZEOLITE



RA-1245-25

SHAPE SELECTIVE ZEOLITES

Catalyst	Ring Size	Largest Channel (nm)	Constraint Index ^a	Distribution of Aromatics ^c	
				C ₆ -C ₁₀	C ₁₁ -C ₁₂
Linde 5A	8-8-8	0.41	—	--	--
Erionite	8-8	0.36 x 0.52	38	--	--
ZSM-5	10-10	0.54 x 0.56	8.3	99	1
ZSM-11	10-10	0.51 x 0.55	8.7	100	--
ZSM-23	10	0.45 x 0.56	--	--	--
ZSM-12	12	0.57 x 0.61	2	75	25
Mordenite	12-8	0.67 x 0.70	0.4	25	75
Offretite	12-8-8	0.64	3.7	--	--
Faujasite	12-12-12	0.74	0.4 ^b	--	--

Reference: W. O. Haag and N.Y. Chen. "Catalyst Design with Zeolites" in Catalyst Design, L. L. Hegadus, ed., Wiley-Interscience, 1987.

^a Defined as ratio of cracking rates of n-hexane and 3-methylpentane

^b Rare earth exchanged zeolite Y

^c For products of methanol conversion at 644 K and 1 atm.

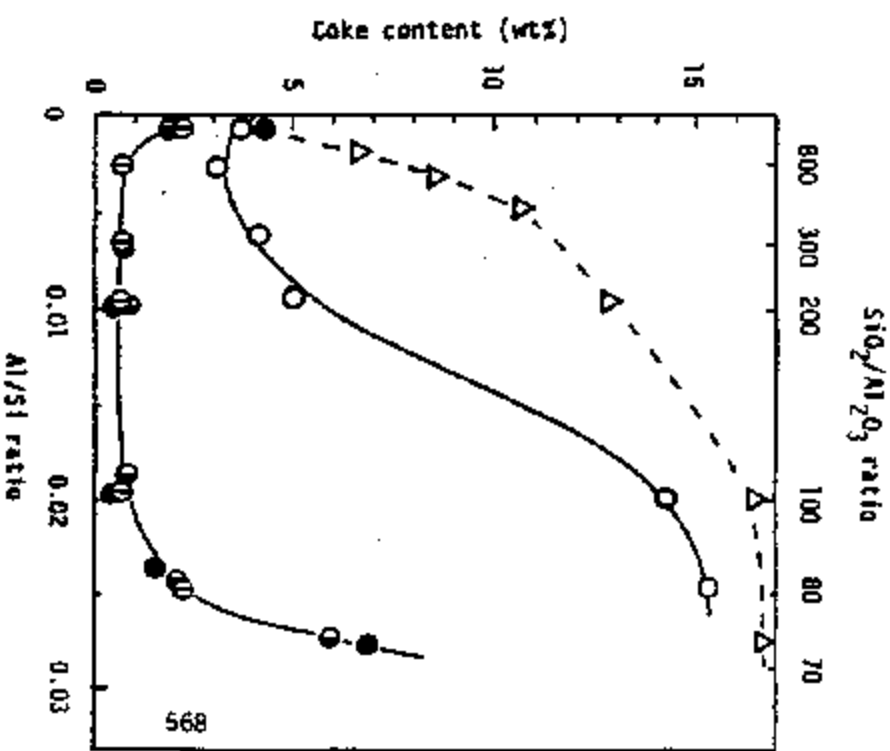
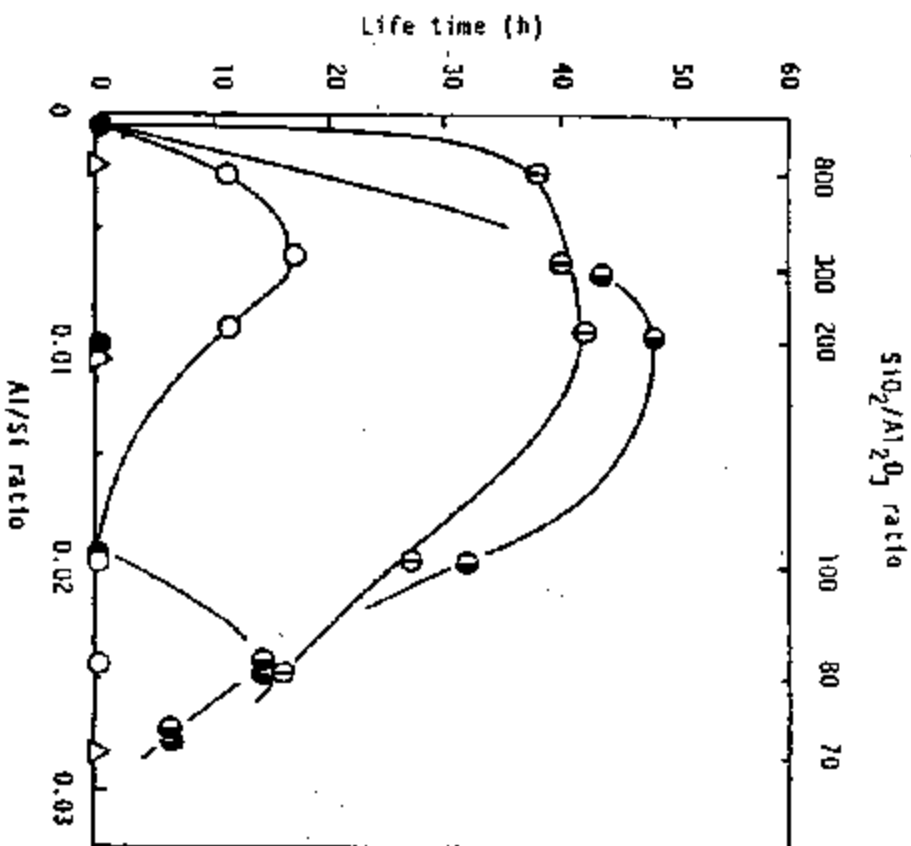
RELATIVE RATES OF ALKANE CRACKING OVER ZSM-5

Alkane	Relative Rate ^a at 340°C	Relative Rate ^b at 450°C
n-pentane	.23	--
2-methyl butane	.01	--
n-hexane	.71	--
2-methyl pentane	.38	--
3-methyl pentane	.22	--
2,3-dimethyl butane	.09	--
2,2-dimethyl butane	.09	--
n-neptane	1.00	1.0
2-methyl hexane	.52	--
3-methyl hexane	.38	--
2,3-dimethyl pentane	.09	--
2,2-dimethyl pentane	.17	--
2,4-dimethyl pentane	.05	--
3,3-dimethyl pentane	.06	--
3-ethyl pentane	.08	--
n-nonane	--	3.2
n-dodecane	--	23.0

Reference: W. O. Haag and N.Y. Chen. Catalyst Design, (1987)

^a 1.4 LHSV, 35-atm

^b 1.0 LHSV, 1-atm



RELATIONSHIPS BETWEEN Al/Si RATIO AND CATALYST LIFETIME (FOR DME APPEARANCE) AND COKE CONTENT FOR METHANOL CONVERSION OVER VARIOUS ALKALINE EARTH ZSM-5 ZEOLITES.

Reaction conditions: 0.5 atm methanol in Ar, 600 °C, 2.3 h⁻¹ LHSV.
 From Okado, et. al., Applied Catalysis 41, 121 (1989).

IMPROVED FTS CATALYSTS CONCLUSIONS AND RECOMMENDATIONS

Sulfur Treated FTS Catalysts

- Uniform submonolayer sulfur on fused iron selectively poisoned methane production and enhanced olefin yields
- Chain growth factor reduced by sulfur treatment
- Coking resistance was noted with $H_2/CO=1$ at 300 °C, 20 atm
- Operation in slurry reactor with low H_2 syngas recommended

Cluster Catalysts

- Novel synthesis of multiatomic ruthenium clusters and surface bonding to a various supports demonstrated
- Activity, stability, and product distribution of Ru_4 and Ru_6 cluster catalysts comparable to commercial Ru/Al_2O_3
- FTS performance of Ru_1 catalysts varied greatly with support material unlike multiatomic clusters
- Long-term slurry reactor studies necessary to evaluate selectivity of cluster catalysts

Dual Function Catalysts for Production of Aromatics

- Olefins converted to oxygenates and aromatics
- Acidic component deactivates with $H_2/CO = 0.5$, 300 °C
- Need shape selective, low Al zeolite for improved coking resistance