Department of

Chemical Engineering

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Kinetics of Slurry Phase Fischer-Tropsch Synthesis

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OUTLINE

- **OBJECTIVES**
- **METHODOLOGY**
- **EXPERIMENTAL**
- **RESULTS**

  Effects of process conditions (T, P, feed ratio, and gas space velocity) on product distribution

- **SUMMARY/FUTURE WORK**

Objectives

- **Develop a comprehensive kinetic model for slurry phase Fischer-Tropsch synthesis on iron catalysts. The model will be able to predict formation rates of all major product species (1- and 2-linear olefins, n-paraffins, CO_2 and H_2O) and rates of disappearance of H_2 and CO.**

- **Determine kinetic parameters from experimental data obtained in a stirred tank slurry reactor (STSR) over a wide range of conditions.**

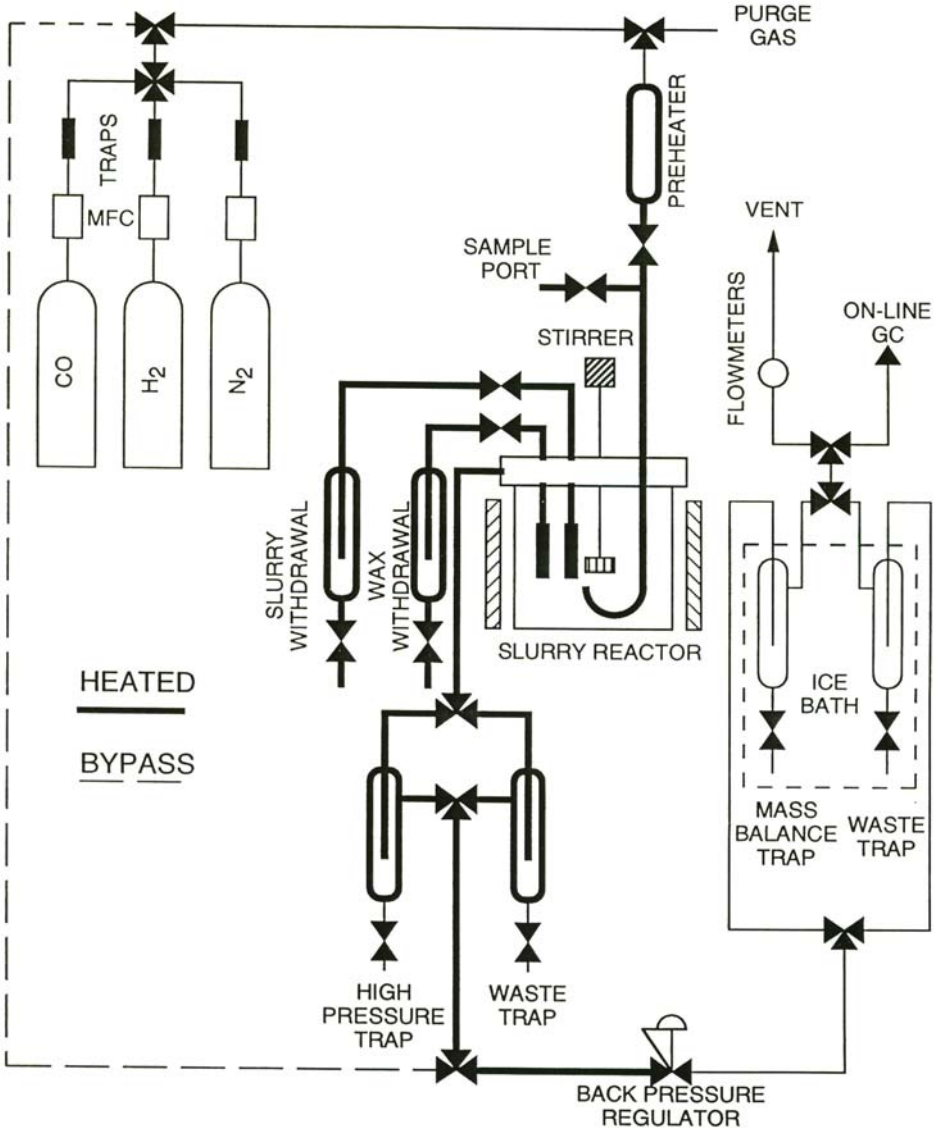
Methodology

- **Use high rotational speed in a STSR to eliminate gas-liquid mass transfer resistance and transport resistances in the bulk liquid and liquid film surrounding catalyst particles.**

- **Use small catalyst particles (45-100 μm) to minimize intraparticle diffusional effects.**

- **In the absence of intraparticle and interphase transport resistances, the reactor can be modeled as a perfectly mixed reactor.**

Slurry reactor apparatus



- Autoclave Engineers - 1 dm^3 reactor
- Stirring rate: 1200 RPM
- Six blade turbine impeller (3.2 cm in diameter)

Catalyst and Process Conditions

- **Ruhrchemie catalyst (precipitated Fe) with nominal composition 100 Fe/5 Cu/4.2 K/25 SiO_2 (mass basis) : 11.2 – 25 g; 140-325 mesh size.**
- **Pretreatment conditions:**

  CO at 280 °C and 8 bar for 12 h
- **Process conditions (Baseline):**

  T = 220, 240 and 260 °C; P = 8, 15 and 25 bar

  H_2/CO = 2/3 or 2/1; SV = 0.6-23.5 NL/g-Fe/h (4)
- **Three tests were conducted (337-694 h) and the catalyst was tested under 25 sets of different process conditions.**

Results from STSR tests

Definitions of selectivities

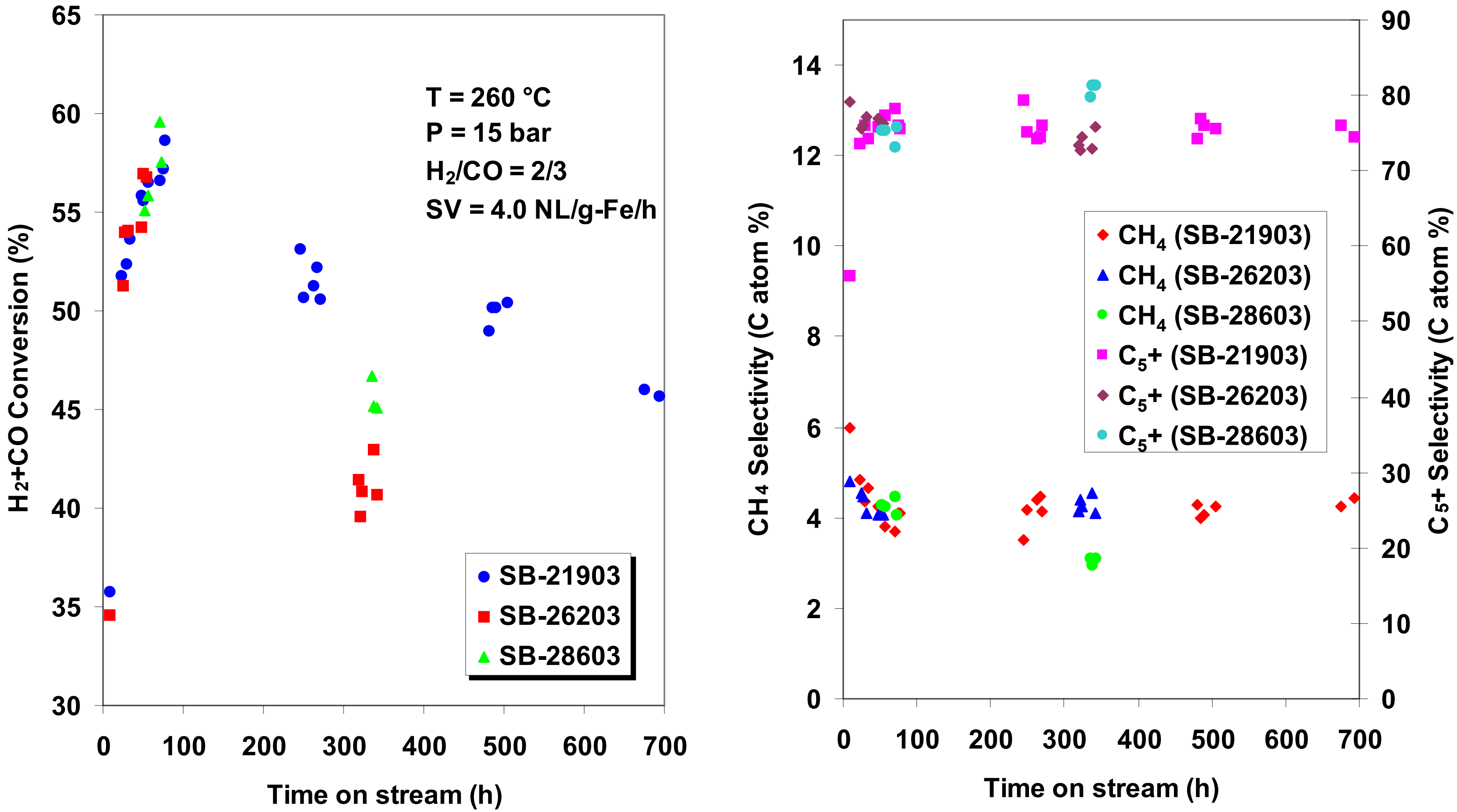
$$CO_2\ selectivity\,(\%) = 100\,x \left[\frac{(n_{CO_2})_{out}}{(n_{CO})_{in} - (n_{CO})_{out}} \right]$$

Hydrocarbon selectivity on carbon atom basis:

$$S_{ij}\,(\%) = \frac{100\,x\,(i\,n_{ij})}{(n_{CO})_{in} - (n_{CO})_{out} - (n_{CO_2})_{out}}$$

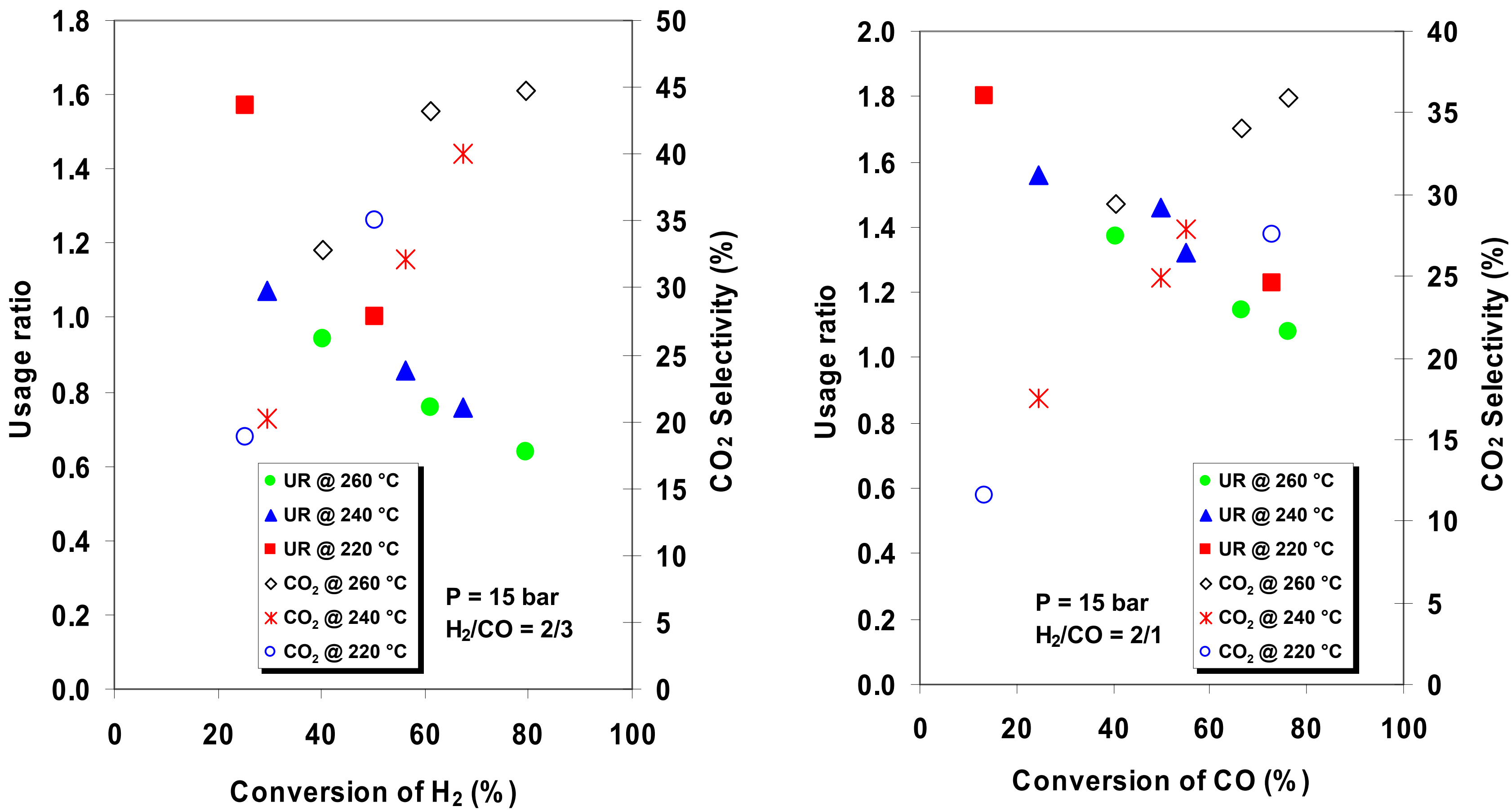
where: S_{ij} is selectivity of species j containing i carbon atoms, n_{ij} is molar flow of species j, n_{CO} is molar flow rate of CO, and n_{CO2} is molar flow rate of CO_2.

Reproducibility of catalyst performance and deactivation



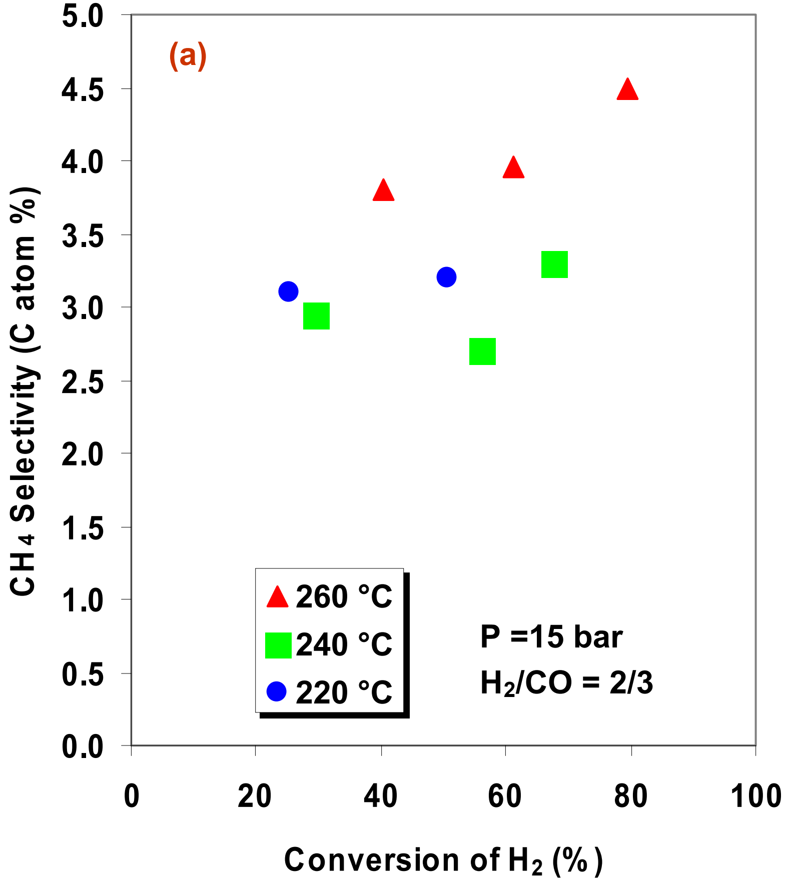
Initial catalyst performance was the same in all tests. Small effect of deactivation on selectivity in SB-21903 & 26203.

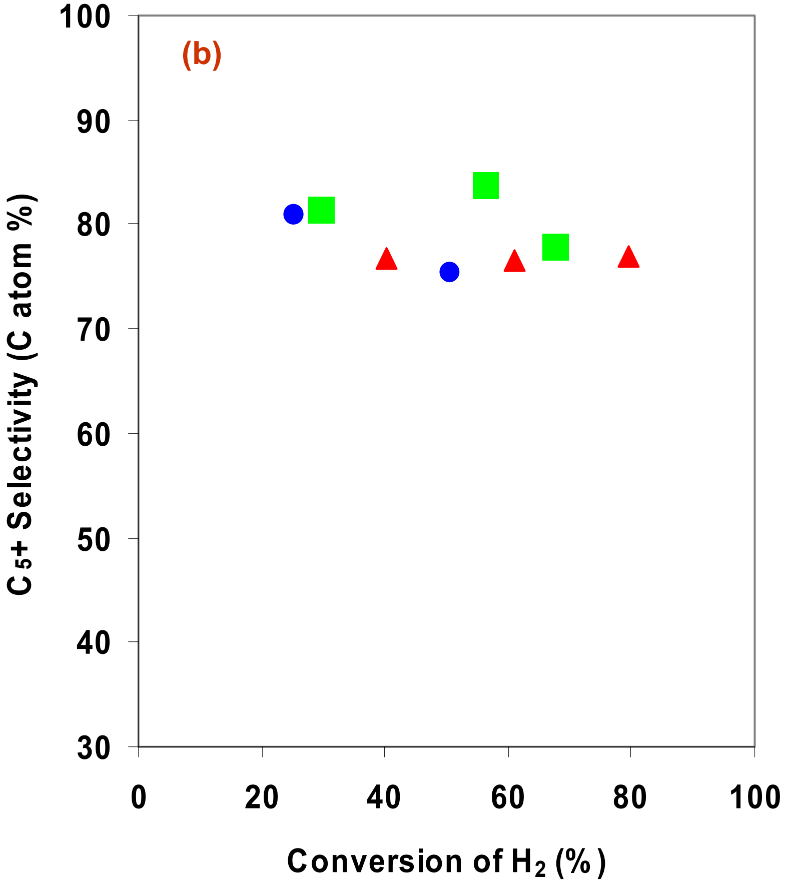
Effect of temperature and conversion (SV)



UR decreases whereas CO_2 increases with increase in conversion or with increase in reaction temperature.

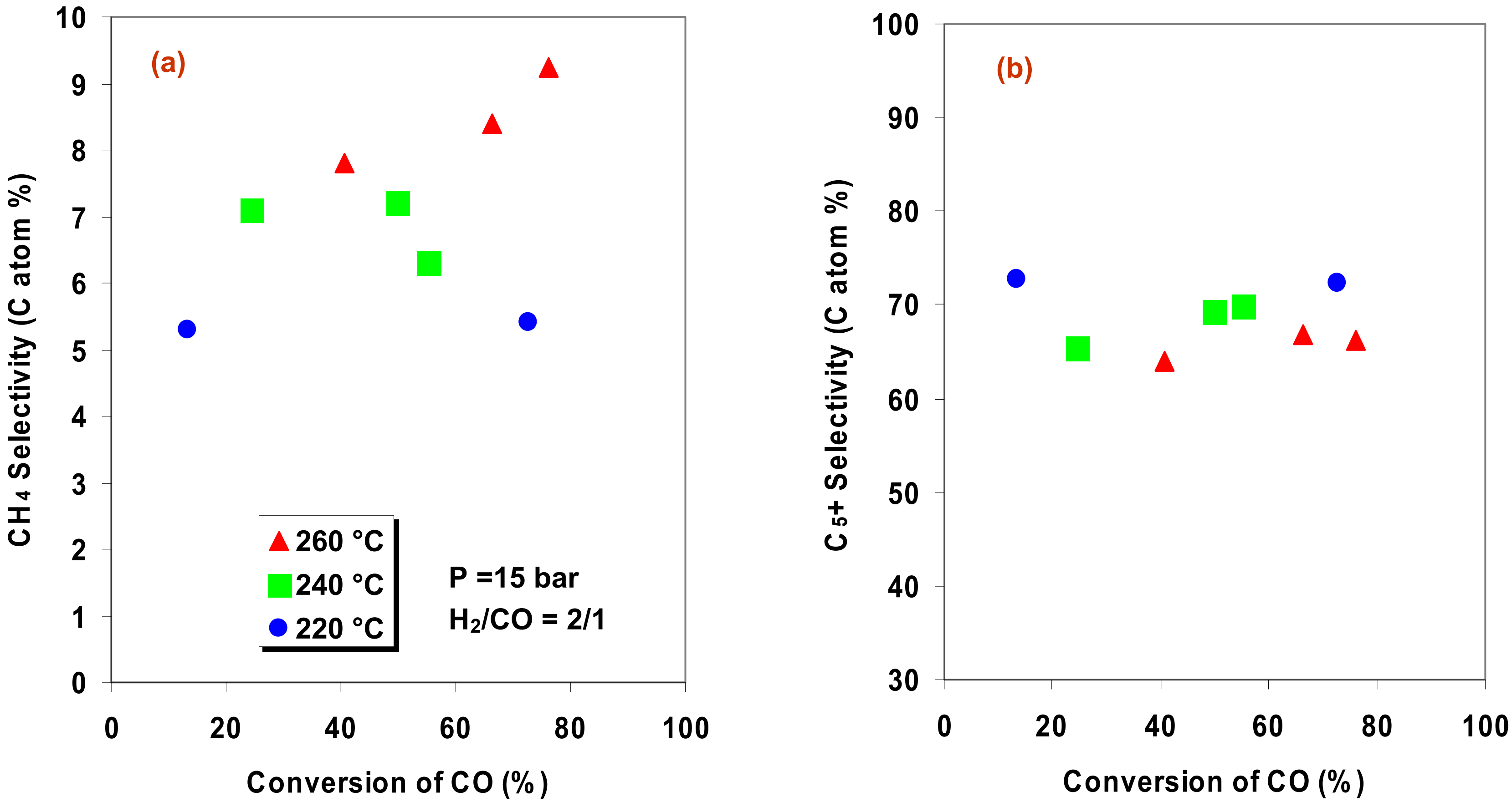
Effect of temperature and conversion (SV)





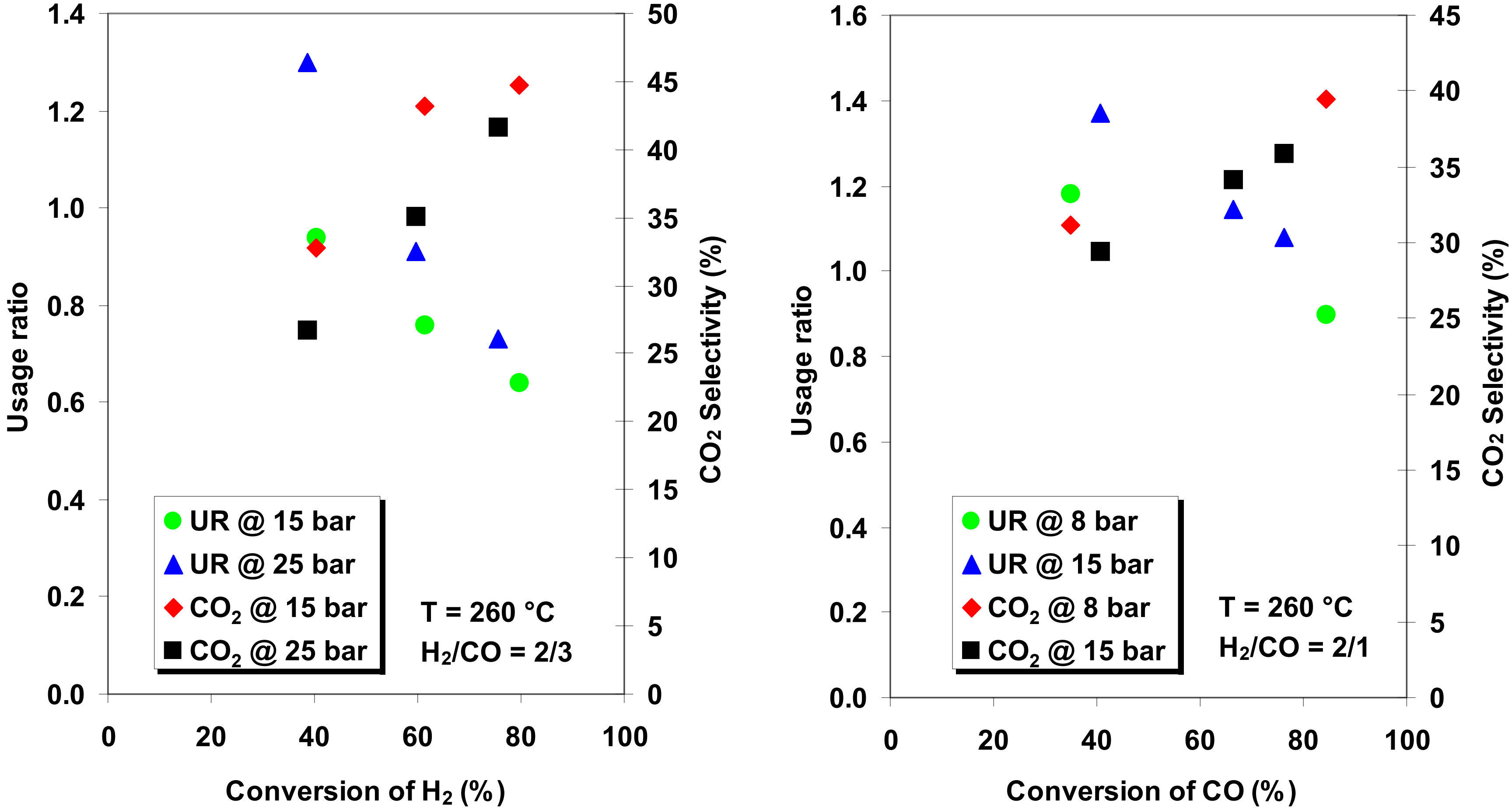
Methane increases whereas C_5^+ decreases with increase in conversion or increase in temperature (except 220 vs. 240°C).

Effect of temperature and conversion (SV)



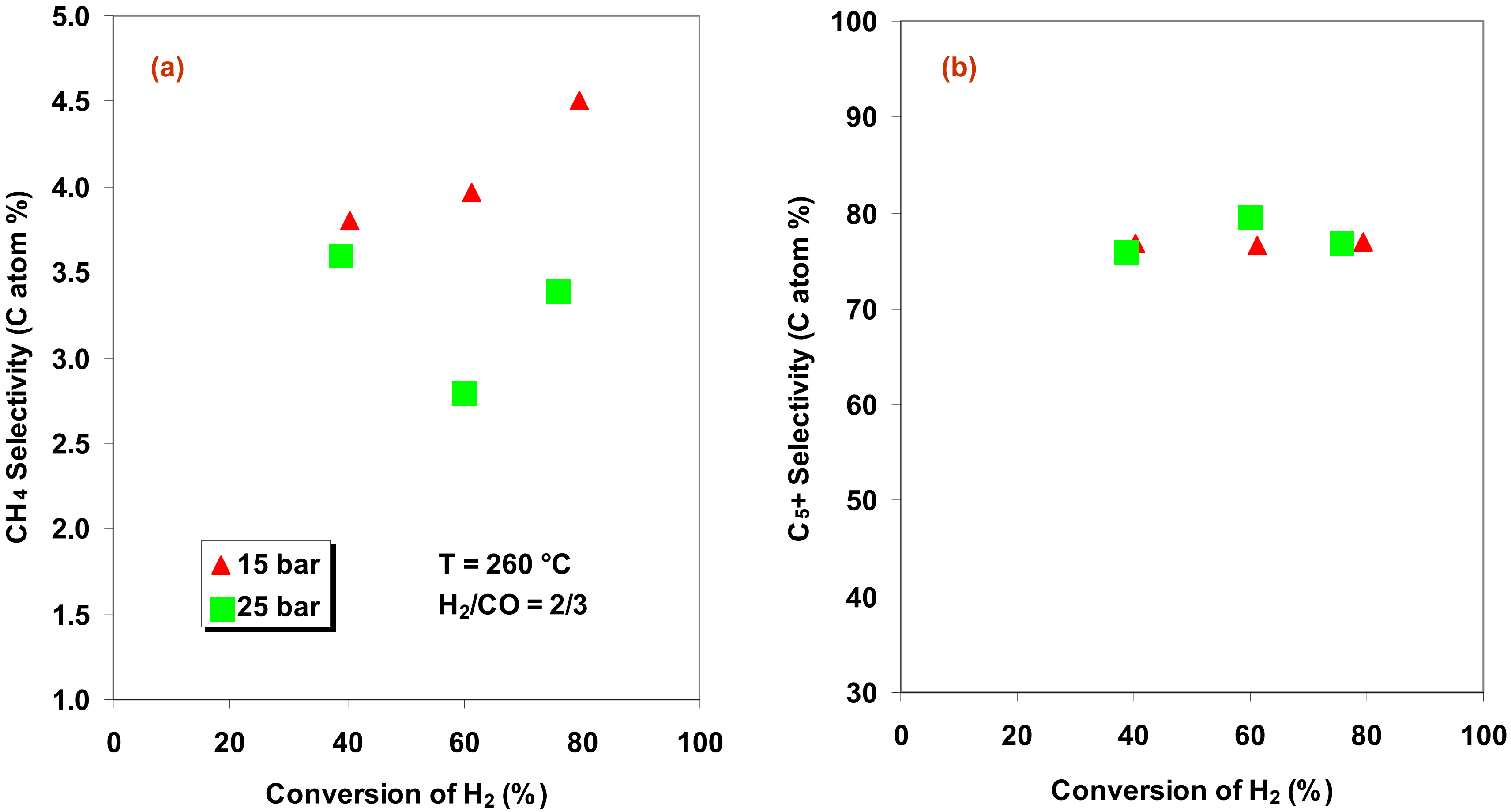
Methane increases whereas C_5^+ decreases with increase in temperature. Effect of conversion - varies with T.

Effect of pressure and conversion (SV)



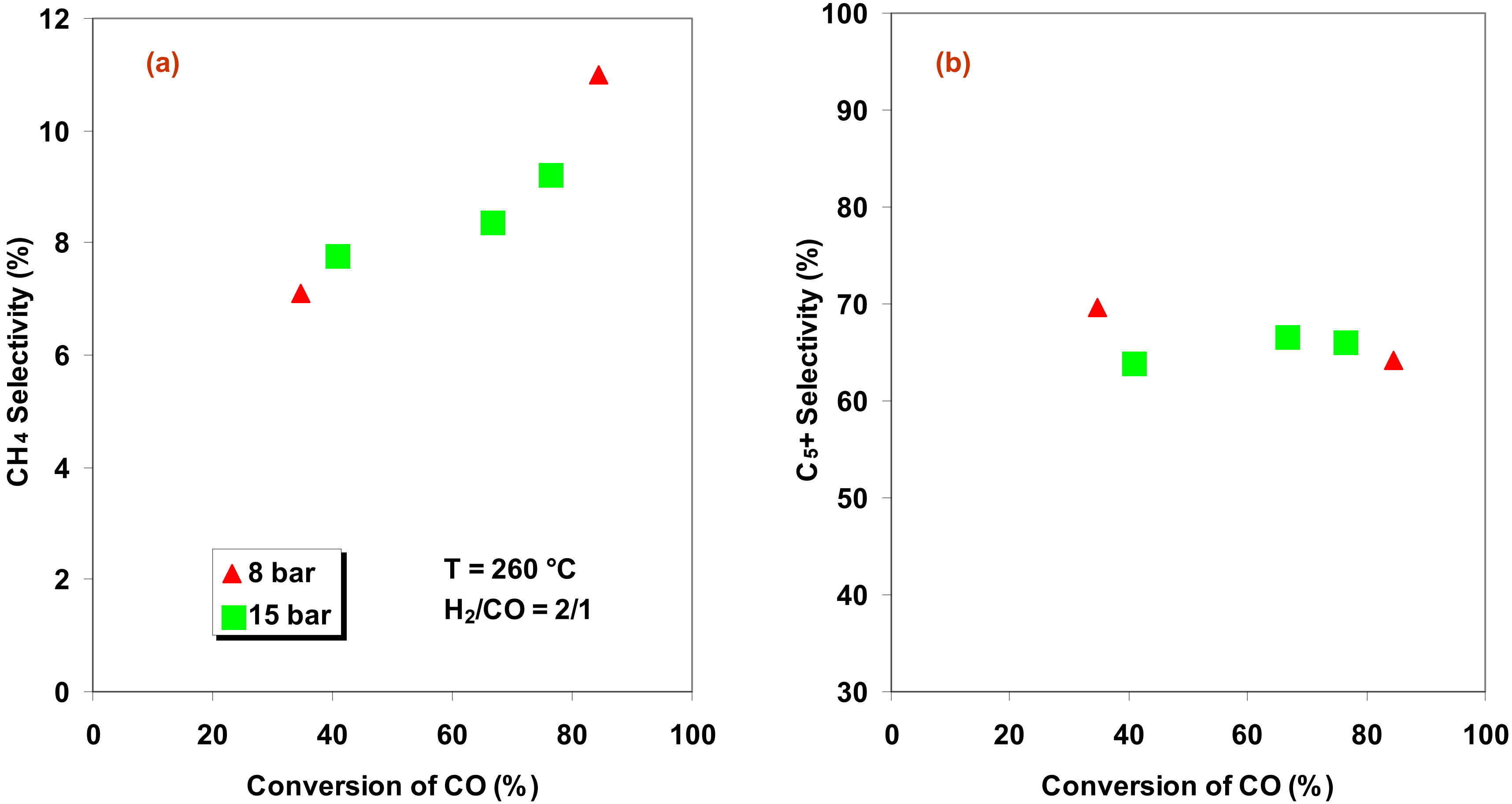
UR decreases whereas CO_2 increases with increase in conversion.
UR increases whereas CO_2 decreases with increase in pressure.

Effect of pressure and conversion (SV)



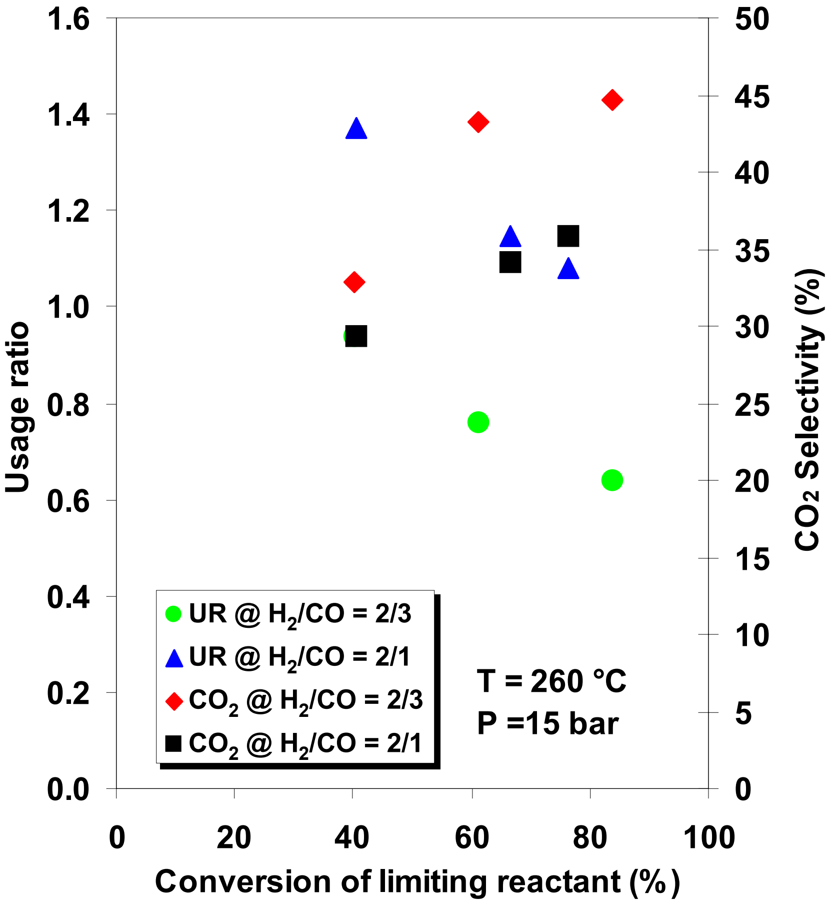
C_5^+ selectivity is not affected much by pressure or X. CH_4 decreases with increase in P (X effect varies with P).

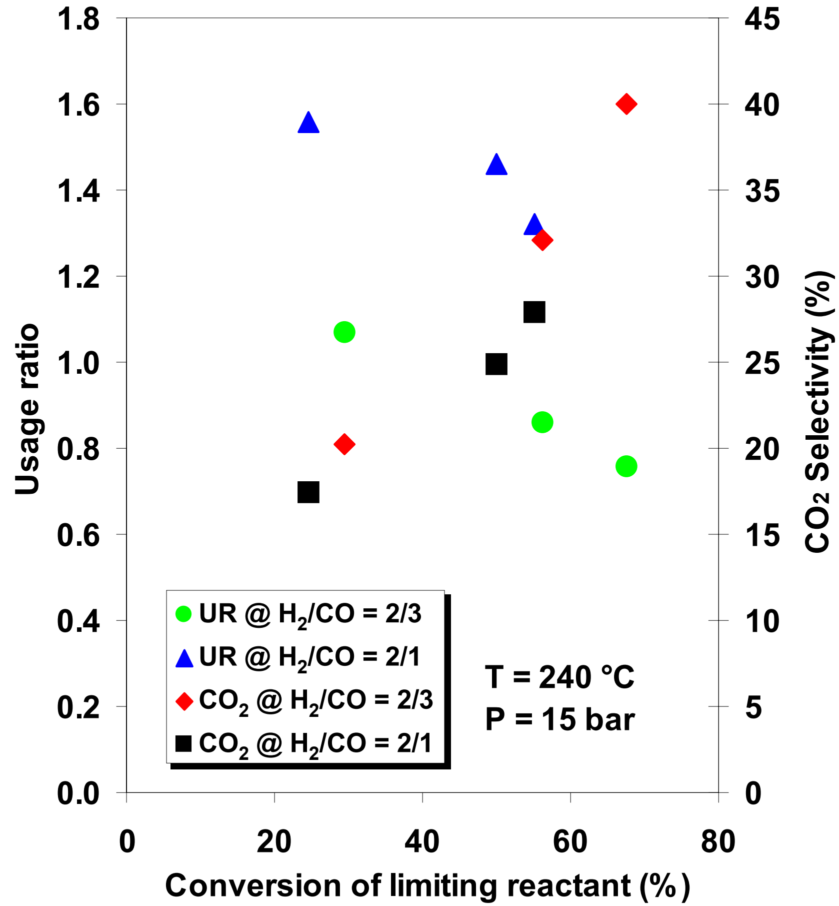
Effect of pressure and conversion (SV)



C_5^+ selectivity is not affected significantly by pressure or X.
Methane increases with increase in X (P effect – small).

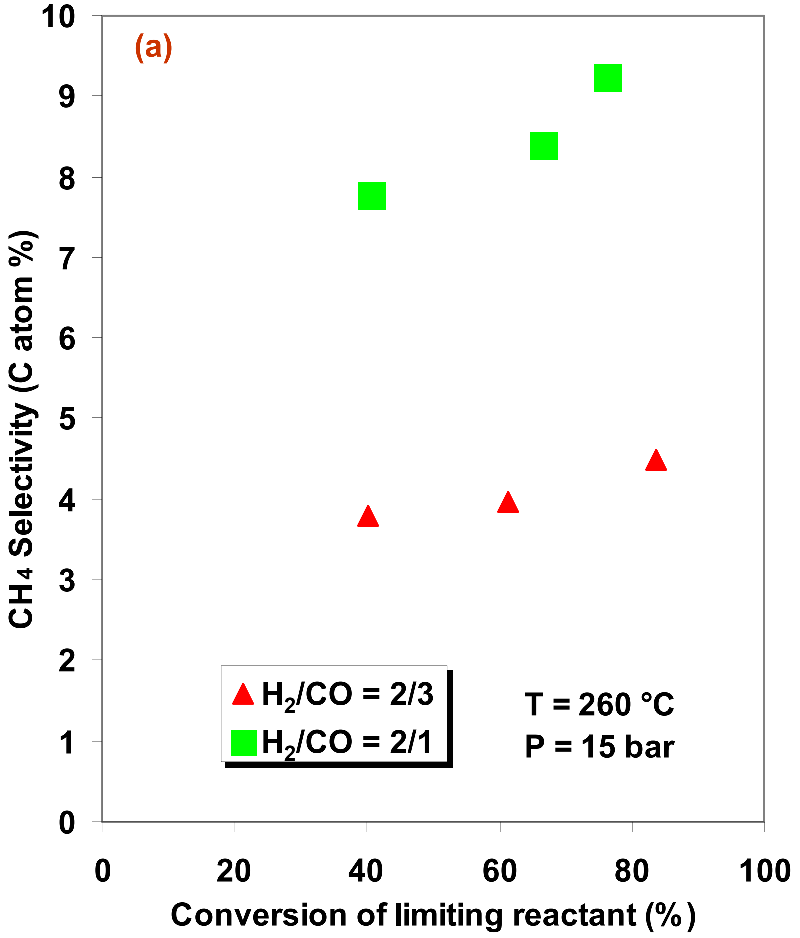
Effect of feed composition

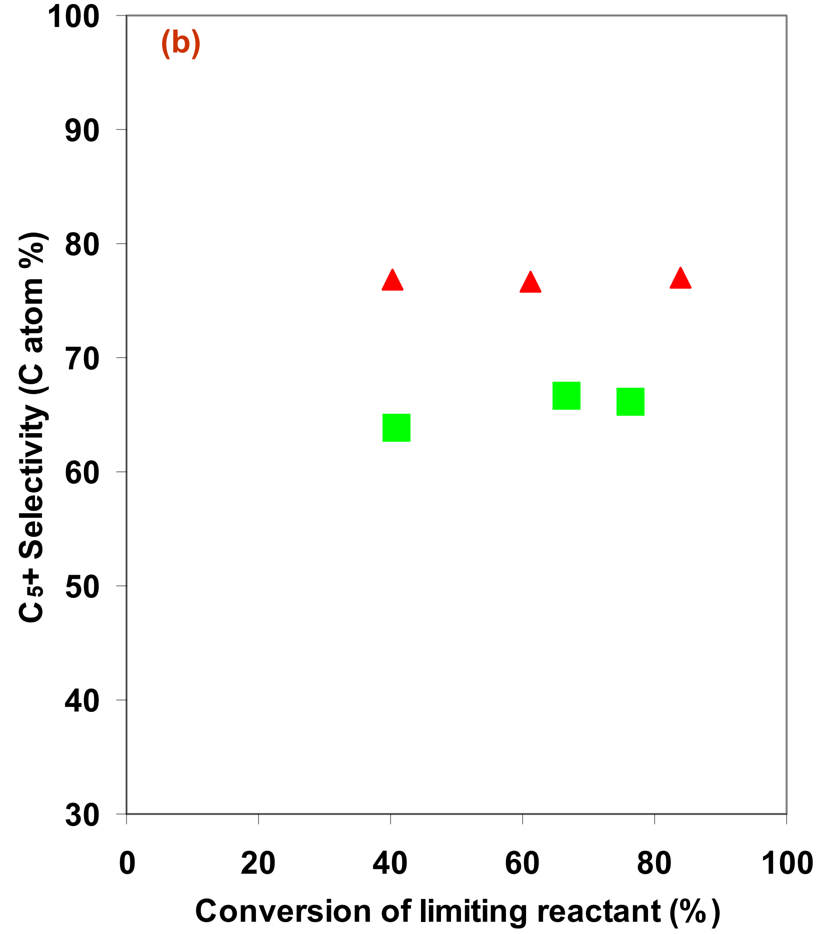




UR decreases whereas CO_2 increases with increase in conversion or with decrease in H_2/CO feed ratio.

Effect of feed composition





Methane selectivity increases and C_5^+ decreases with increase in H_2/CO feed ratio.

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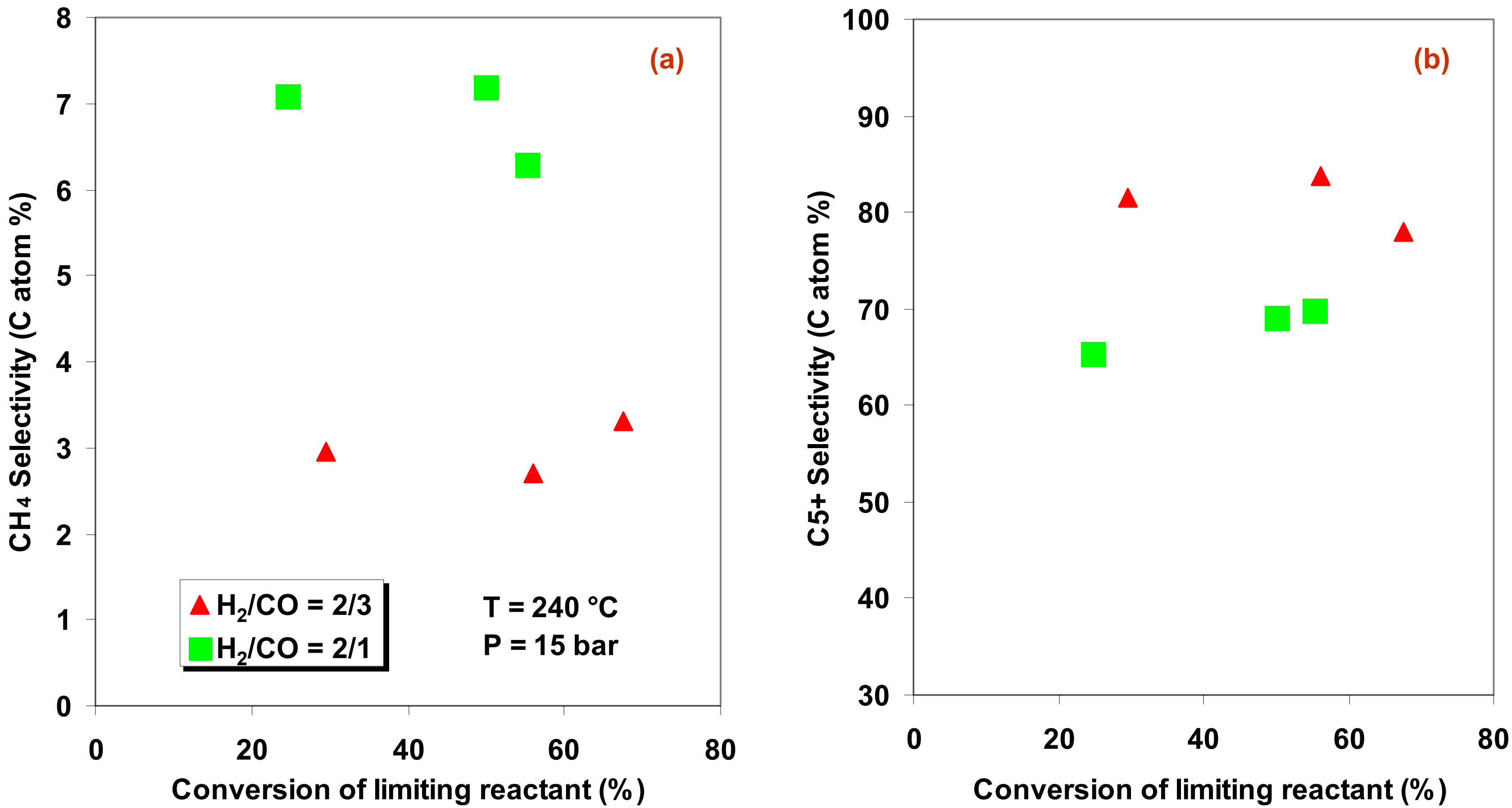


Methane selectivity increases and C_5^+ decreases with increase in H_2/CO feed ratio.

Olefin selectivities

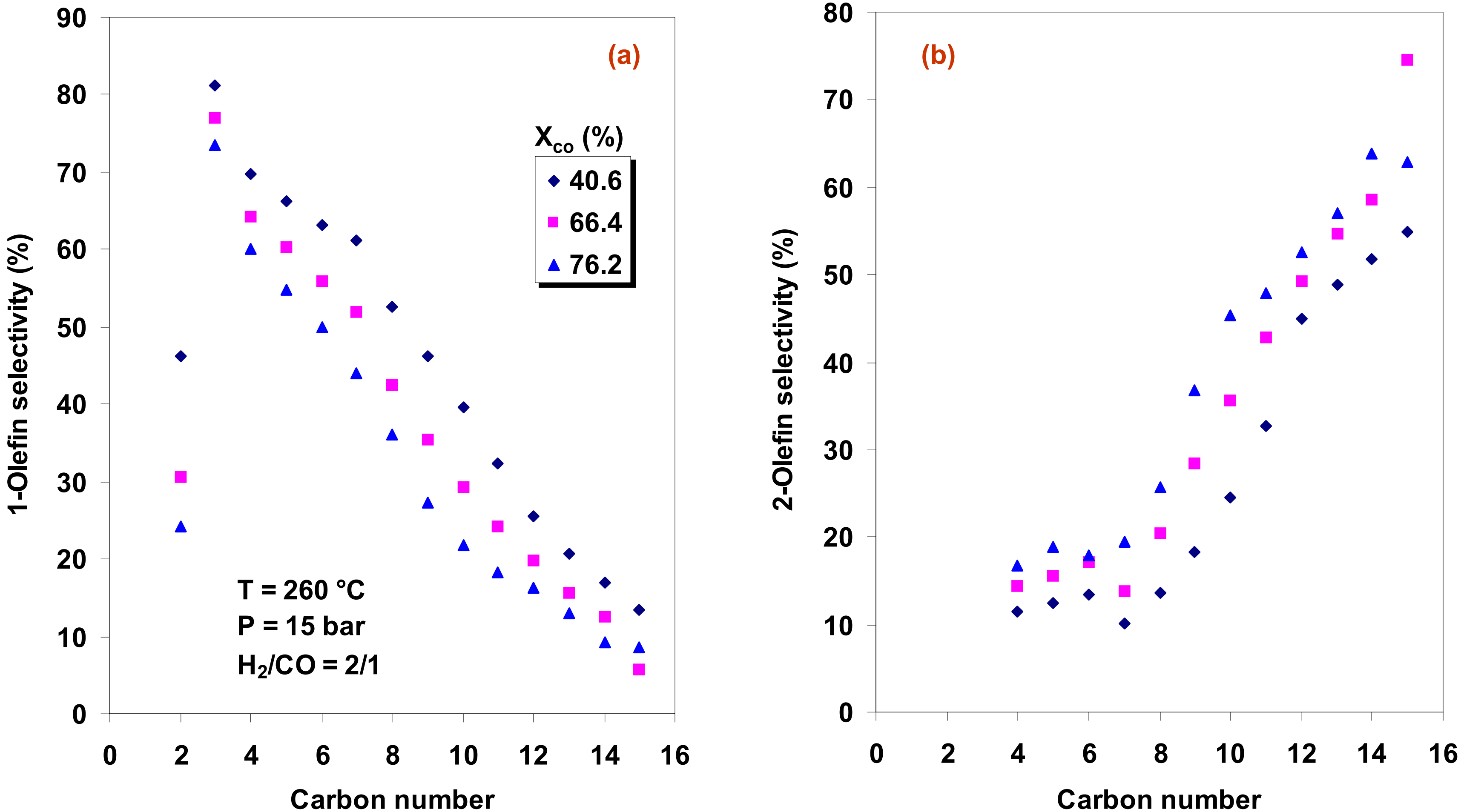
Olefin selectivities (contents) for C_nH_{2n}

$$1-olefin(\%) = \frac{100\,x\,(1-olefin)}{(n-paraffin + linear\ olefins)}$$

= fraction of 1-olefin among linear hydrocarbons

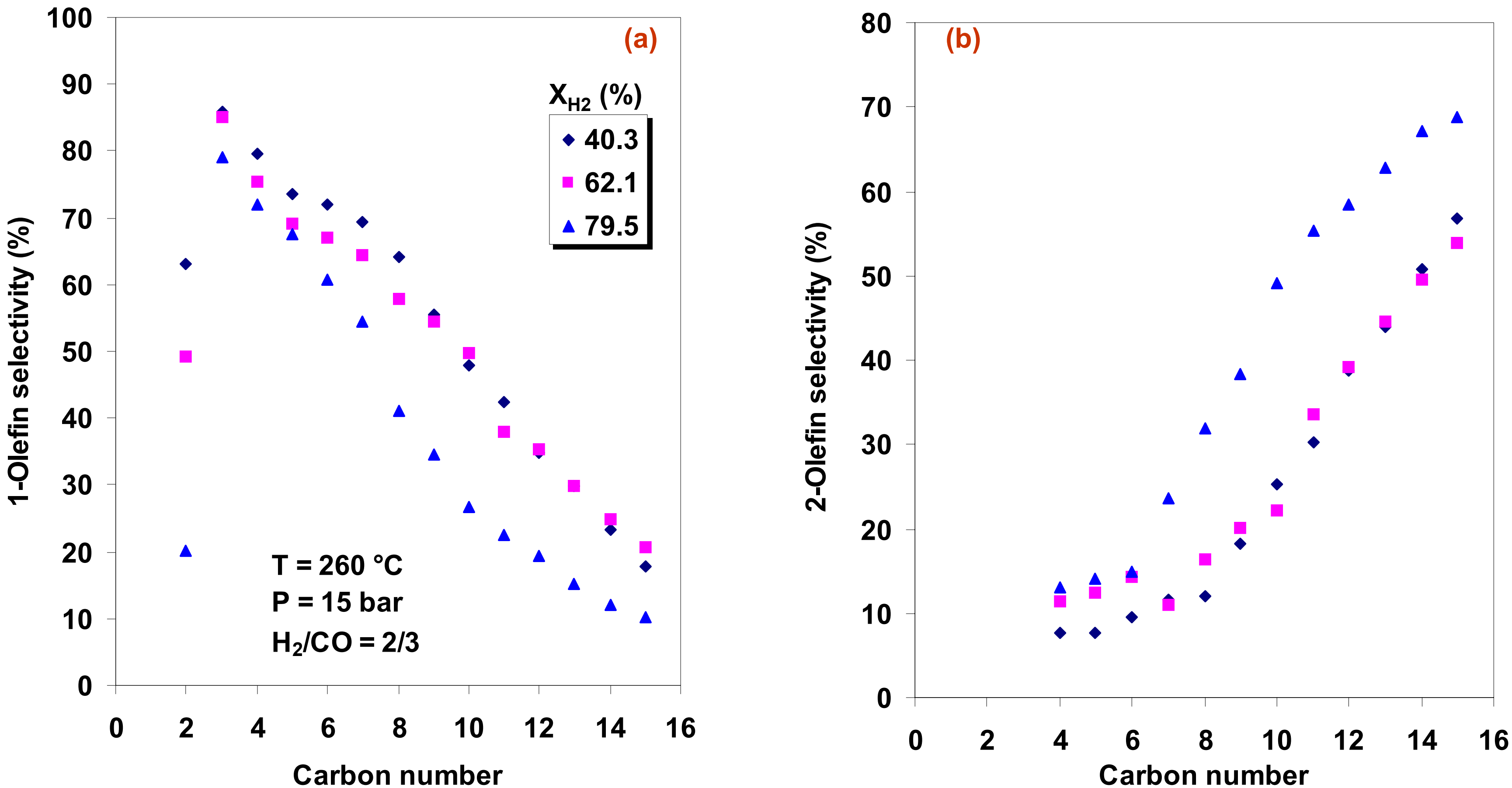
2-olefin (%) = 100 x (2-olefin)/(1-olefin + 2-olefin)
= fraction of 2-olefin among linear olefins

Effect of conversion (gas space velocity)



1-olefin content decreases whereas 2-olefin content increases with increase in conversion and MW weight (carbon number).

Effect of conversion (gas space velocity)



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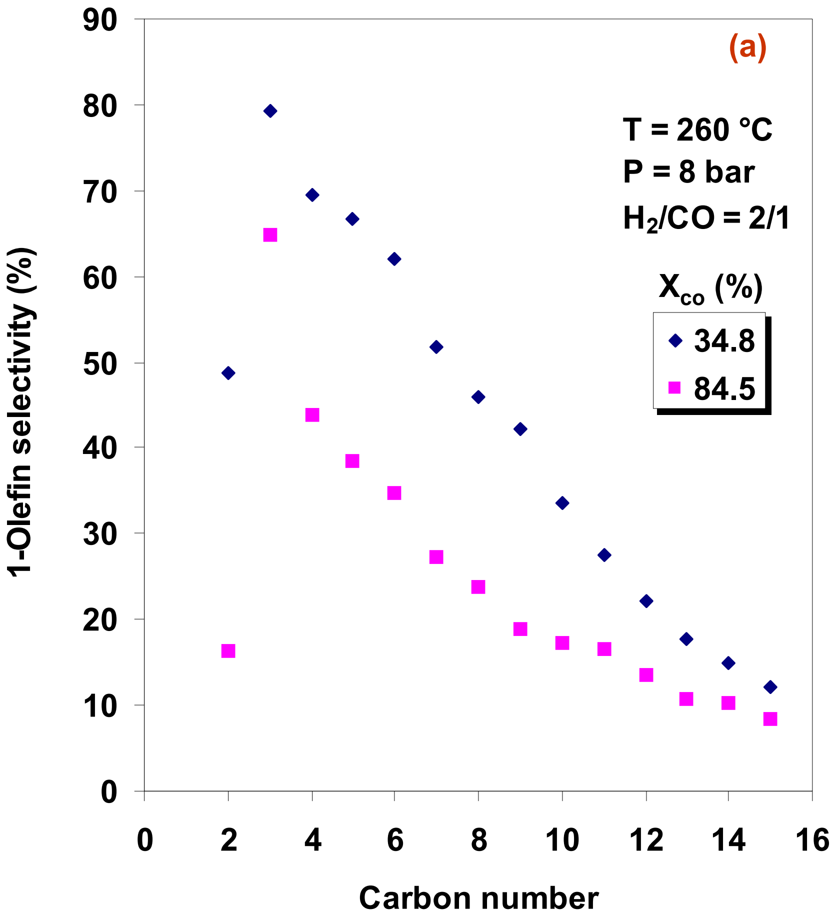

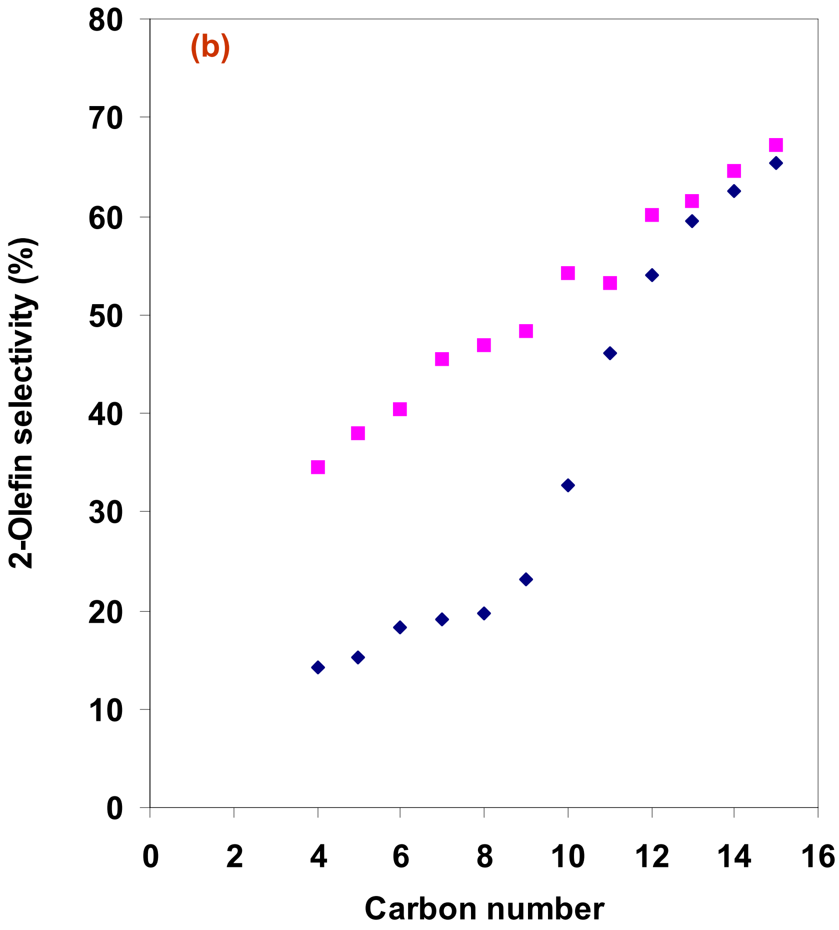

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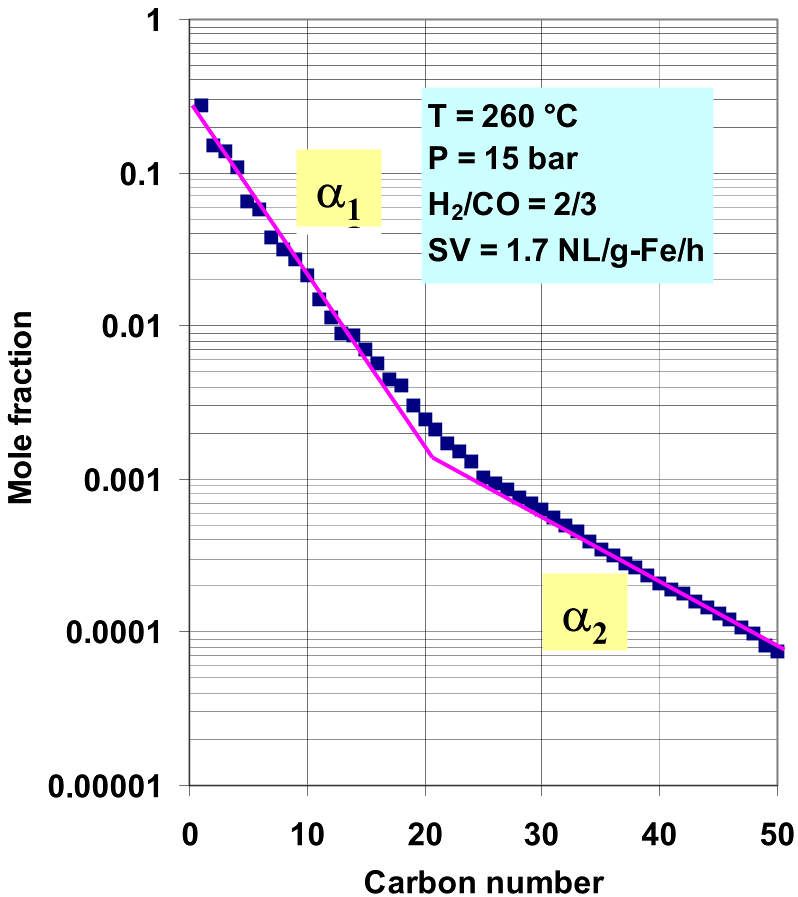
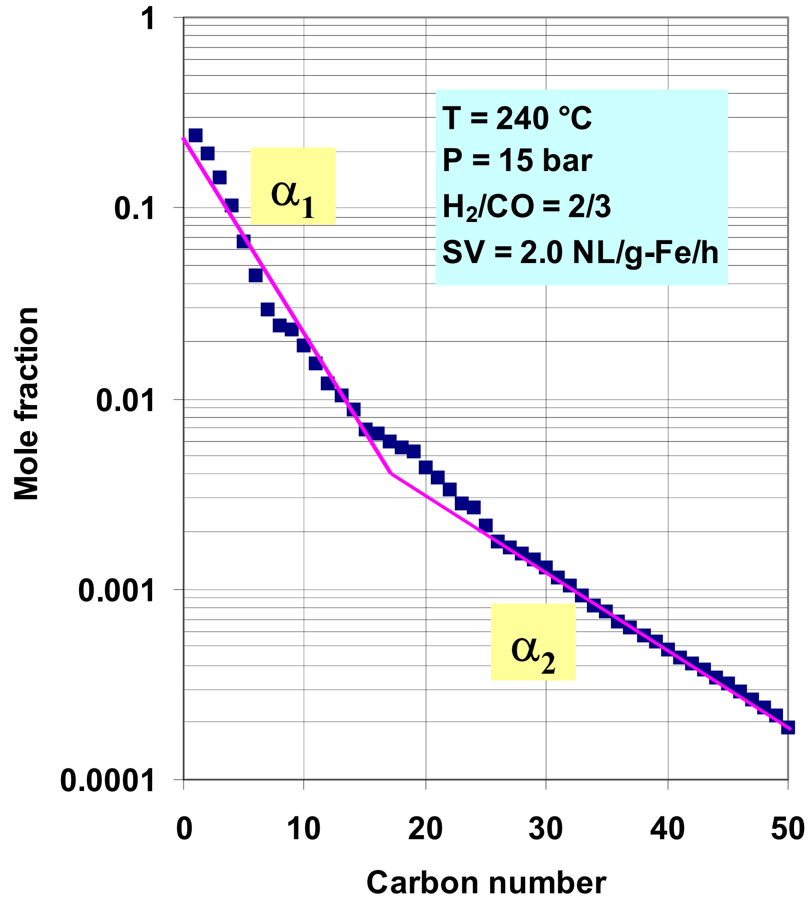
Carbon Number Product Distributions (ASF Plots)





Two chain growth probabilities – "double alpha" phenomenon α_1 for lower MW products and α_2 for higher MW products ($\alpha_1 < \alpha_2$).

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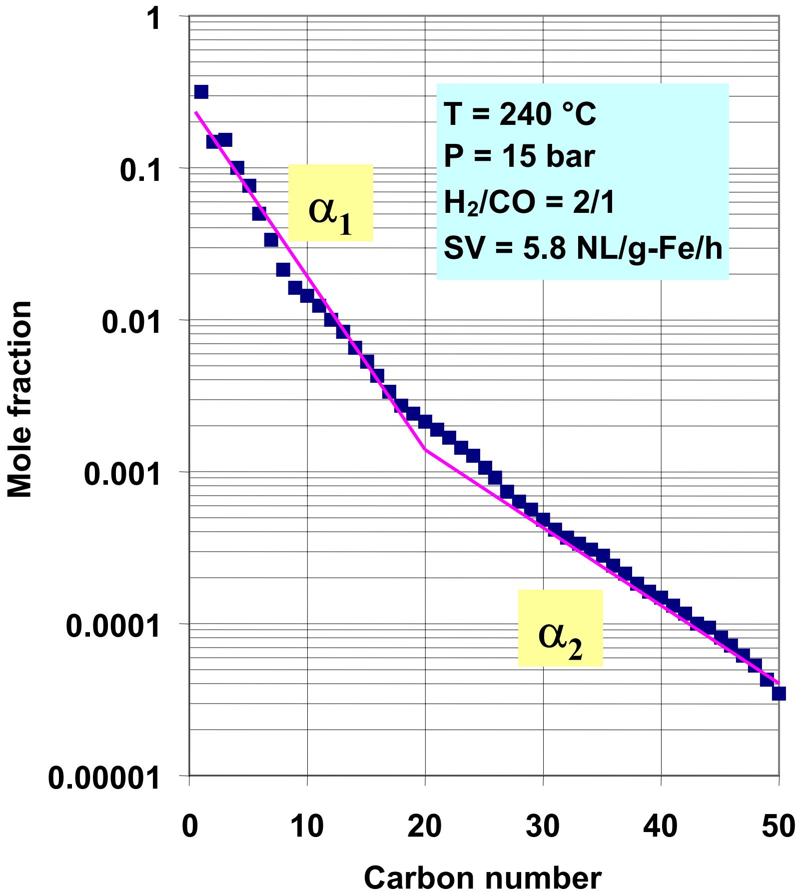

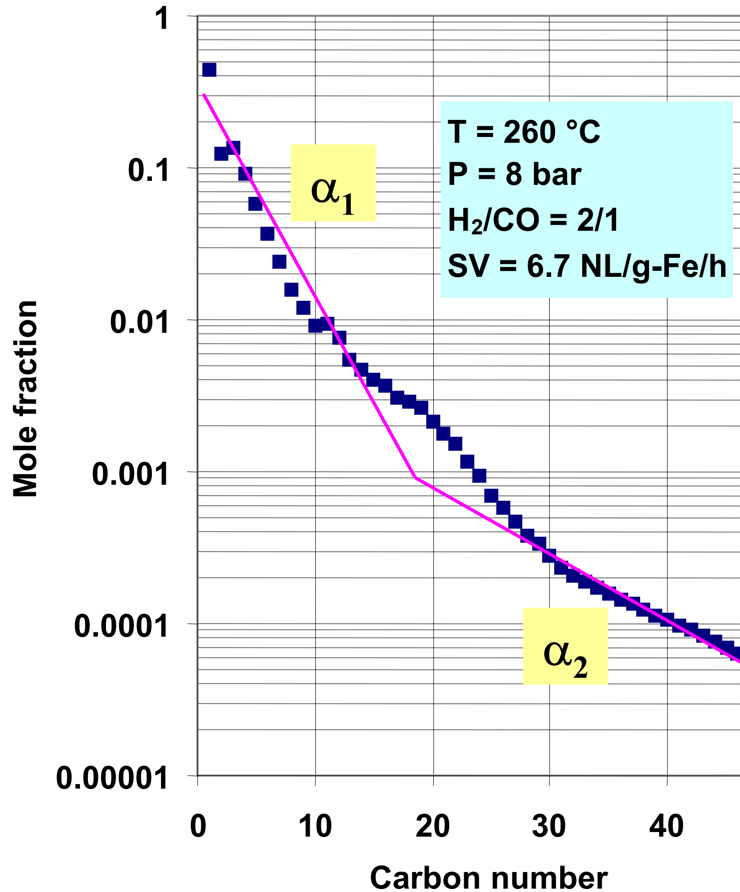

Two chain growth probabilities – "double alpha" phenomenon α_1 for lower MW products and α_2 for higher MW products ($\alpha_1 < \alpha_2$).

Conclusions/Summary

- **Catalyst deactivation was moderate in run SB-21903 (694 h on stream) but more severe in the other two tests (terminated at ~340 h).**
- **Deactivation did not have significant effect on hydrocarbon and olefin selectivities in runs SB-21903 & 26203. Lower methane and higher C_5^+ selectivity were obtained in SB-28603 at 340 h in comparison to results at 70 h on stream.**

Conclusions/Summary (Continued)

- **Decrease in usage ratio and increase in CO_2 selectivity with increase in conversion are consistent with a concept that the water-gas-shift (WGS) reaction is a consecutive reaction.**

- **The increase in the extent of WGS reaction (i.e. increase in CO_2 selectivity) with increase in temperature, or decrease in total pressure, or decrease in feed H_2/CO ratio are kinetic effects.**

Conclusions/Summary (Continued)

- **Decrease in 1-olefin content and increase in 2-olefin content with increase in conversion are consistent with a concept that 1-olefins participate in secondary reactions. 2-olefins are formed in part by secondary isomerization of 1-olefins.**

- **Secondary hydrogenation and isomerization of 1-olefins both increase with increase in partial pressure of hydrogen.**

Conclusions/Summary (Continued)

- **Gas residence time has significant effect on ethylene selectivity and selectivity of lower MW olefins olefins, but this effect is less pronounced for higher MW olefins (C_{10}^{+}). The residence time of high MW olefins is governed by VLE and the rate of liquid removal from the reactor.**

Conclusions/Summary (Continued)

- **Methane selectivity decreases (and that of C_5^+ hydrocarbons increases) with decrease in temperature, increase in pressure, and/or increase in partial pressure of CO.**

- **The effect of conversion (i.e. gas space velocity) on hydrocarbon selectivity (CH_4 and C_5^+) was relatively small and qualitative trends were not the same at different process conditions.**

- **Double "alpha" phenomenon for carbon number distribution was observed under different process conditions.**

Future Plans

- **Modification of kinetic models of Lox & Froment (1992) and Zimmerman, Bukur & Ledakowicz, (1992) incorporating findings from more recent studies on the mechanism of F-T synthesis;**

- **Estimation of kinetic parameters from experimental data in STSR (formulation of reactor model, VLE calculations, parameter estimation, model discrimination based on statistical analysis and physico-chemical criteria).**

Acknowledgements

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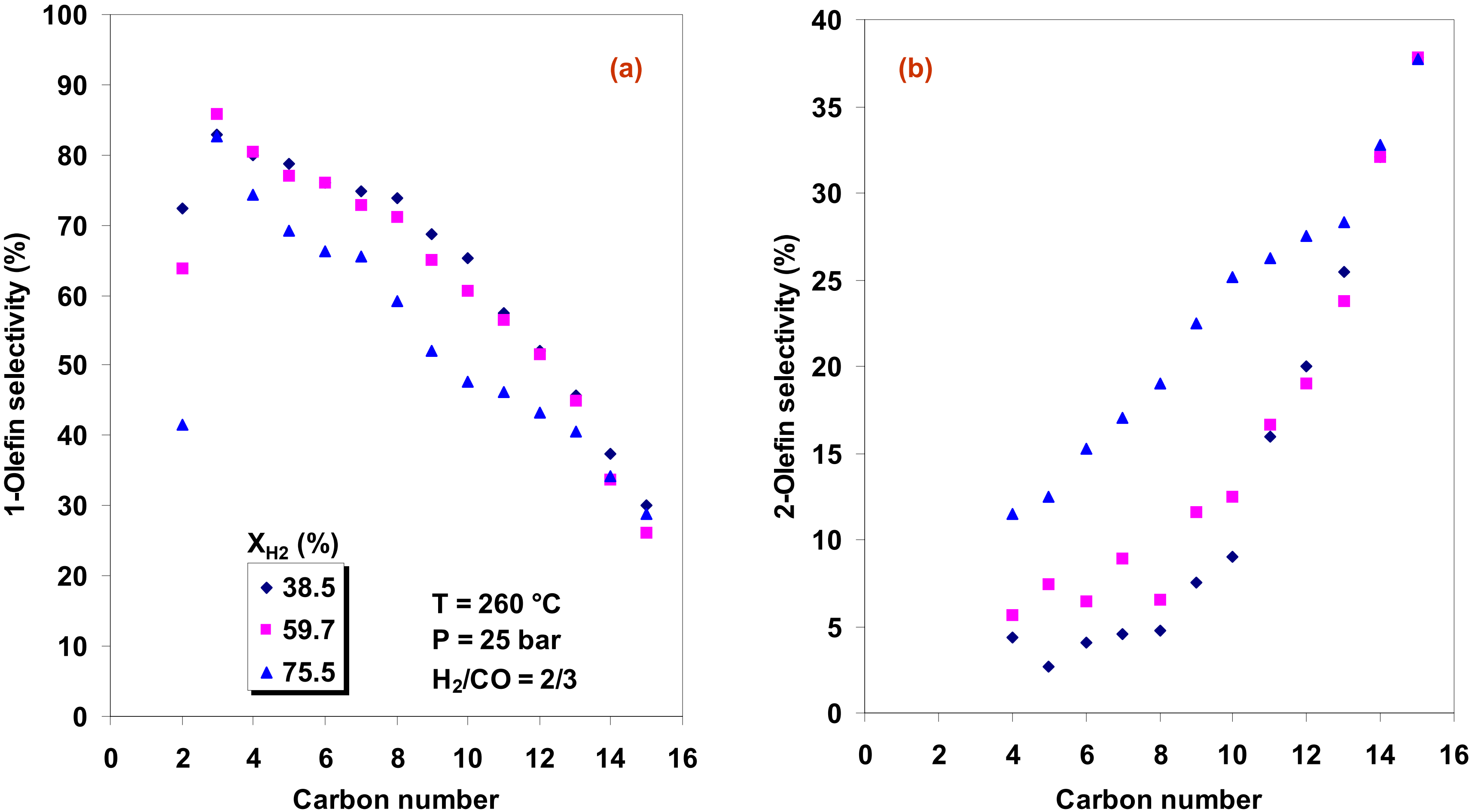
We are grateful to Dr. X. Wang for preparing figures and assistance with data analysis.

Effect of conversion (gas space velocity)



1-olefin content decreases whereas 2-olefin content increases with increase in conversion and MW weight (carbon number).