8. SUMMARY AND CONCLUSIONS

This report outlines work that has been conducted in order to gain insight into the processes occurring on a molecular level on the surface of supported ruthenium and silver-ruthenium bimetallic catalysts during the hydrogenation of carbon monoxide. The results presented here confirm the findings of others that:

1. the hydrogenation of carbon monoxide over ruthenium catalysts takes place with an activation energy of approximately 24 kcal/mol;
2. *in situ* ^{1}H-NMR measurements of hydrogen surface coverages during reaction support the accepted model of surface reaction-limited kinetics during CO hydrogenation; and
3. the addition of silver to ruthenium dramatically affects the specific activity of the catalyst, even though silver does not adsorb either reactant.

In addition, this study presents the following previously unreported findings:

1. addition of as little as 3% Ag to Ru/SiO_2 lowers the apparent activation energy to about 18 kcal/mol;
2. the presence of silver inhibits the kinetics of hydrogen adsorption, and thus affects the kinetics of the surface reaction, accounting for observed decreases in ruthenium activity;
3. the kinetics of hydrogen adsorption is structure-sensitive, occurring more rapidly at low-coordination sites; and
4. the portal site mediated adsorption model accurately describes the results of the present study and those of others.

Besides partially explaining the differences in observations of Ag-Ru and Cu-Ag adsorption studies, the implications of this study may also help resolve controversy surrounding the inconsistent results of reaction surface sensitivity studies examining CO hydrogenation. While the catalytic hydrogenation of CO may indeed be structure insensitive, the fact that this study suggests that the adsorption of hydrogen is structure sensitive may explain the inconsistency of experimental results where hydrogen adsorption is assumed to be at equilibrium and occurring much more rapidly that the surface reaction. In fact, this study shows that, under certain circumstances, adsorption effects may affect the kinetics of surface reactions and thus responsible for apparent surface reaction sensitivity. Finally, the general model of portal site mediated adsorption can be extended to include reaction systems other than the hydrogenation of CO, such as ethane hydrogenolysis where the effects on adsorption equilibrium kinetics may be different.

APPENDIX

Nomenclature

α	reaction order of hydrogen
β	reaction order of carbon monoxide
ΔG°	Gibbs free energy difference between transition state and ground state
ΔH°	enthalpy difference between transition state and ground state
ΔS°	entropy difference between transition state and ground state
ΔG_{ads}	Gibbs free energy of adsorption
ΔH_{ads}	heat of adsorption
ΔS_{ads}	entropy of adsorption
θ	surface coverage
a	hydrogen molecularity of rate determining step
b	carbon monoxide molecularity of rate determining step
c	arbitrary constant
c_i	hydrogen surface coverage constant for *i*th term of mechanism
d_i	carbon monoxide surface coverage constant for *i*th term of mechanism
E_a	activation energy
$E_{a,obs}$	observed, or apparent, activation energy
h	Planck's constant, 6.624×10^{-27} erg-s
i	step *i* of a mechanism
k	rate constant

k'	Boltzmann's constant, 1.3805×10^{-16} erg/molecule-K
K''	pseudo equilibrium constant between ground and transition states
$k_{barrier}$	number of transition state molecules reacting per unit time
K_H	hydrogen equilibrium constant
K_i	equilibrium constant of step i in a mechanism
n	total number of steps in a mechanism
P	partial pressure
r	rate of reaction
R	universal gas constant, 8.314 J/mol-K
T	absolute temperature, K

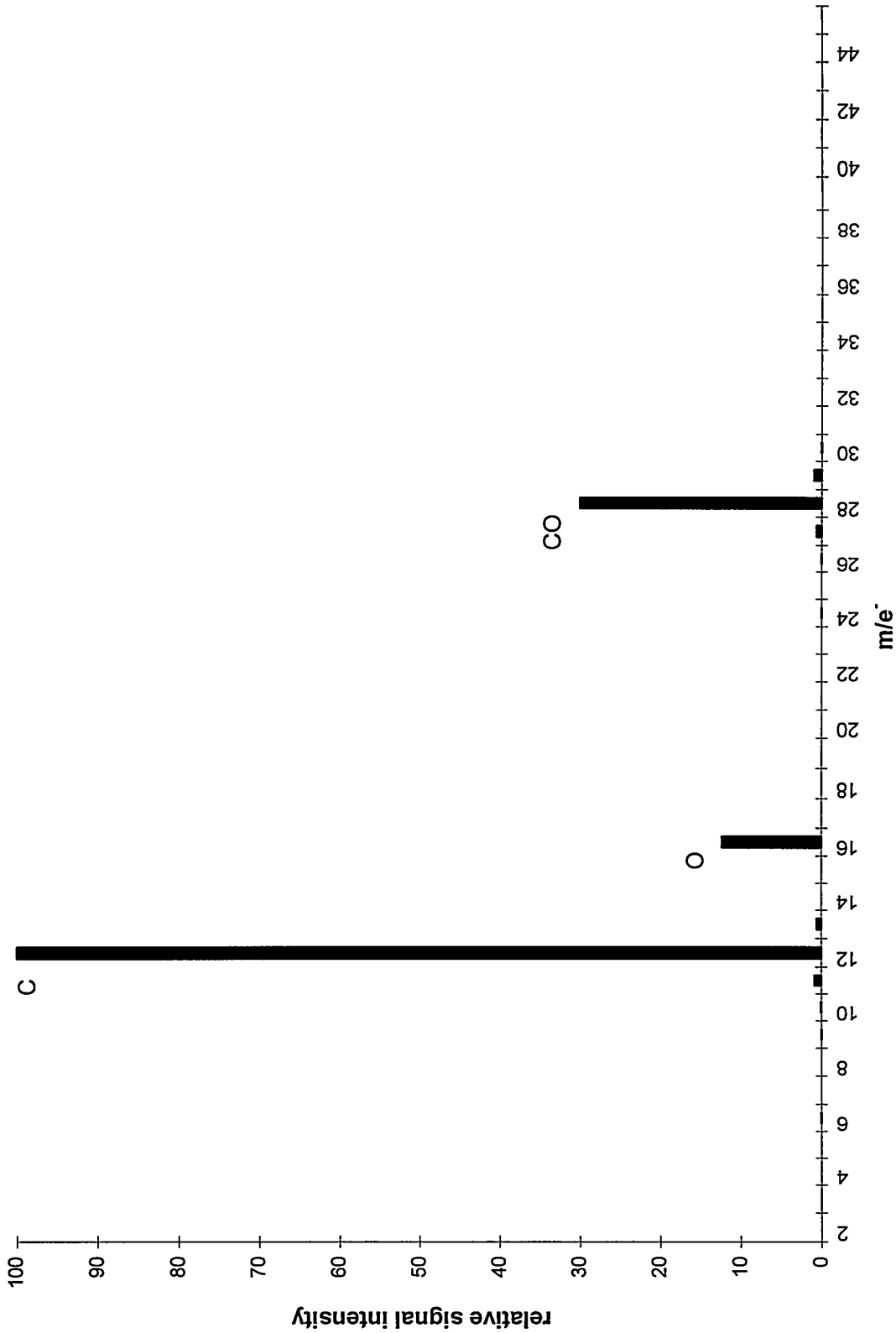

Figure 17. Mass spectra for carbon monoxide

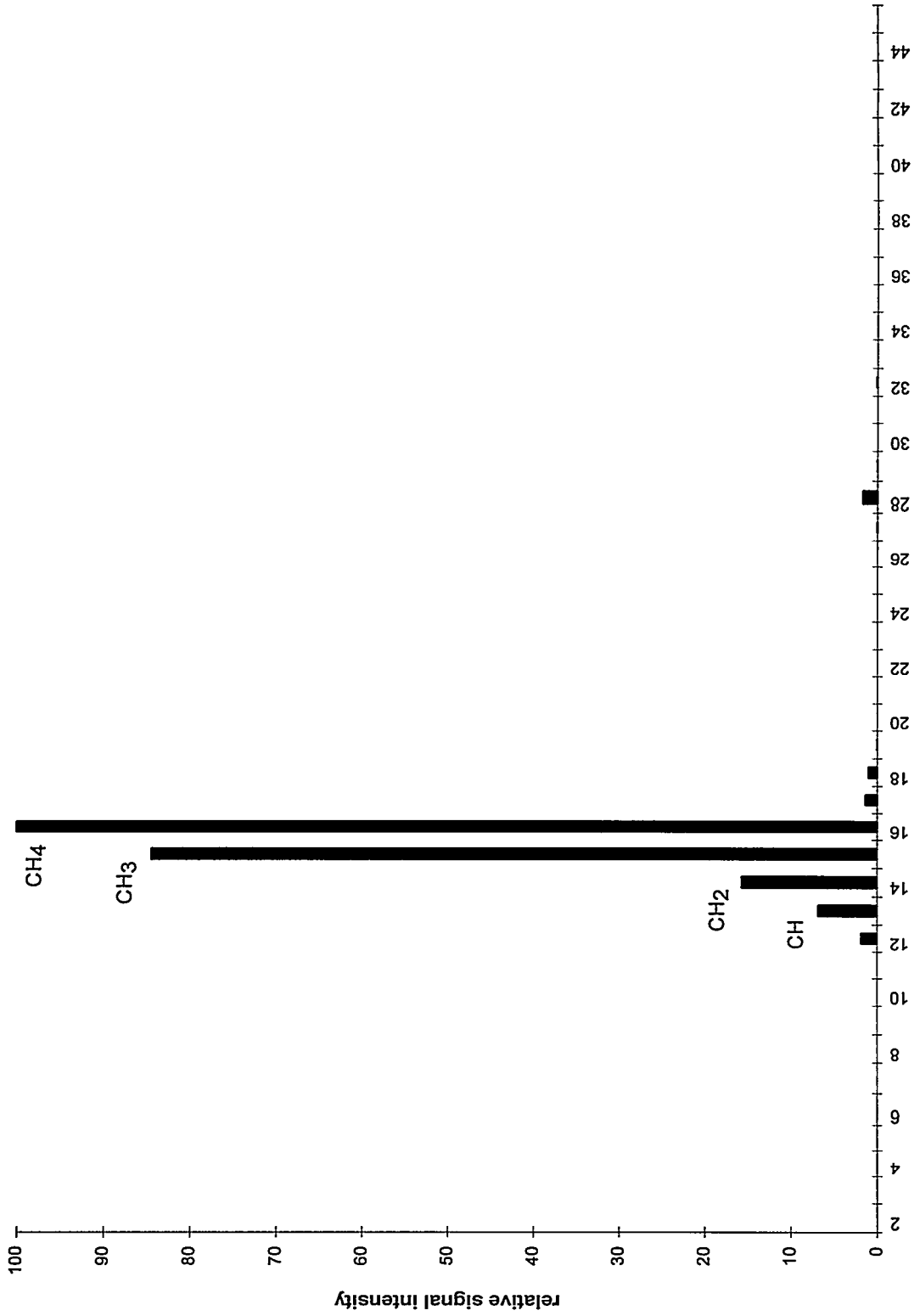

Figure 18. Mass spectra for methane

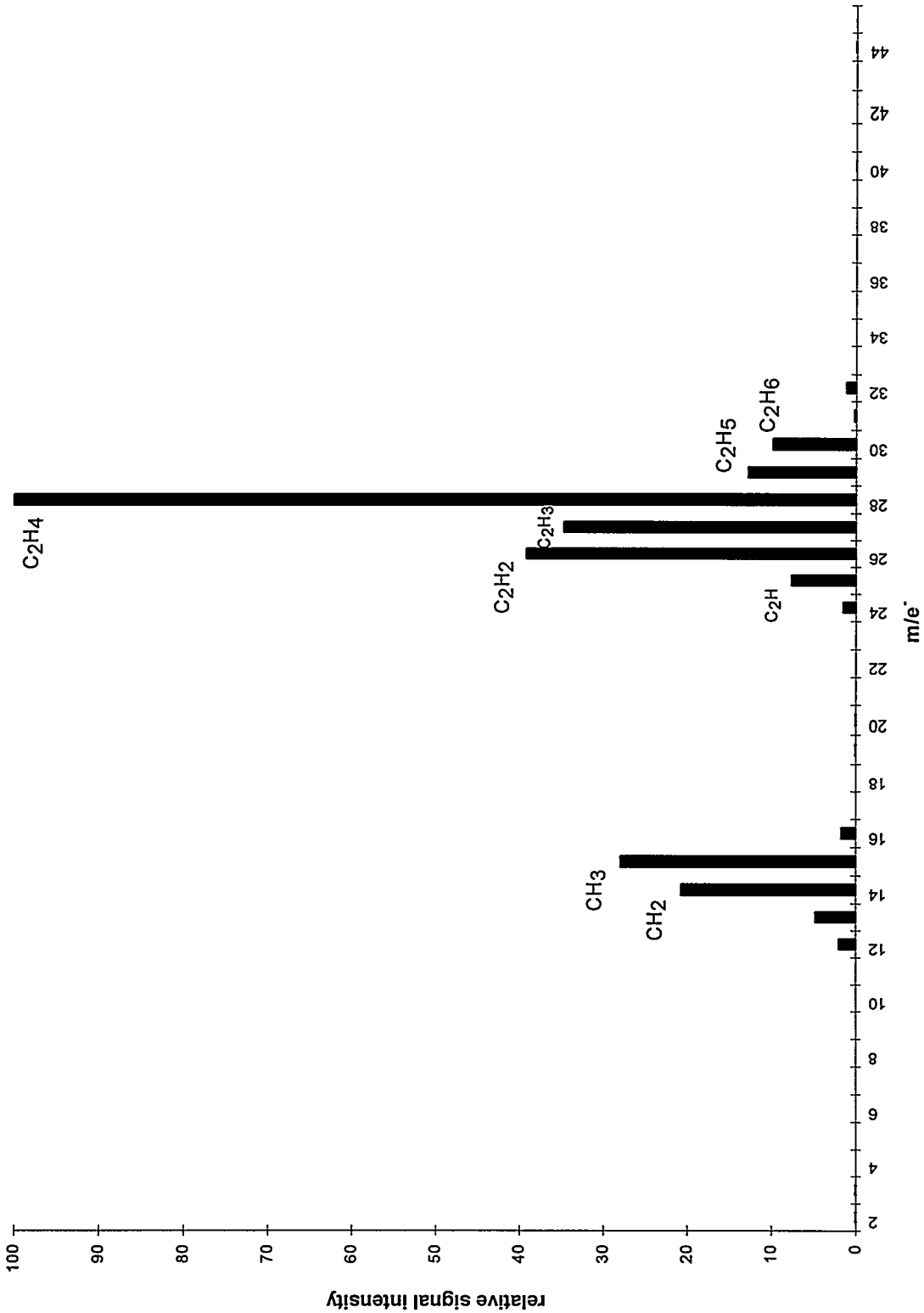

Figure 19. Mass spectra for ethane

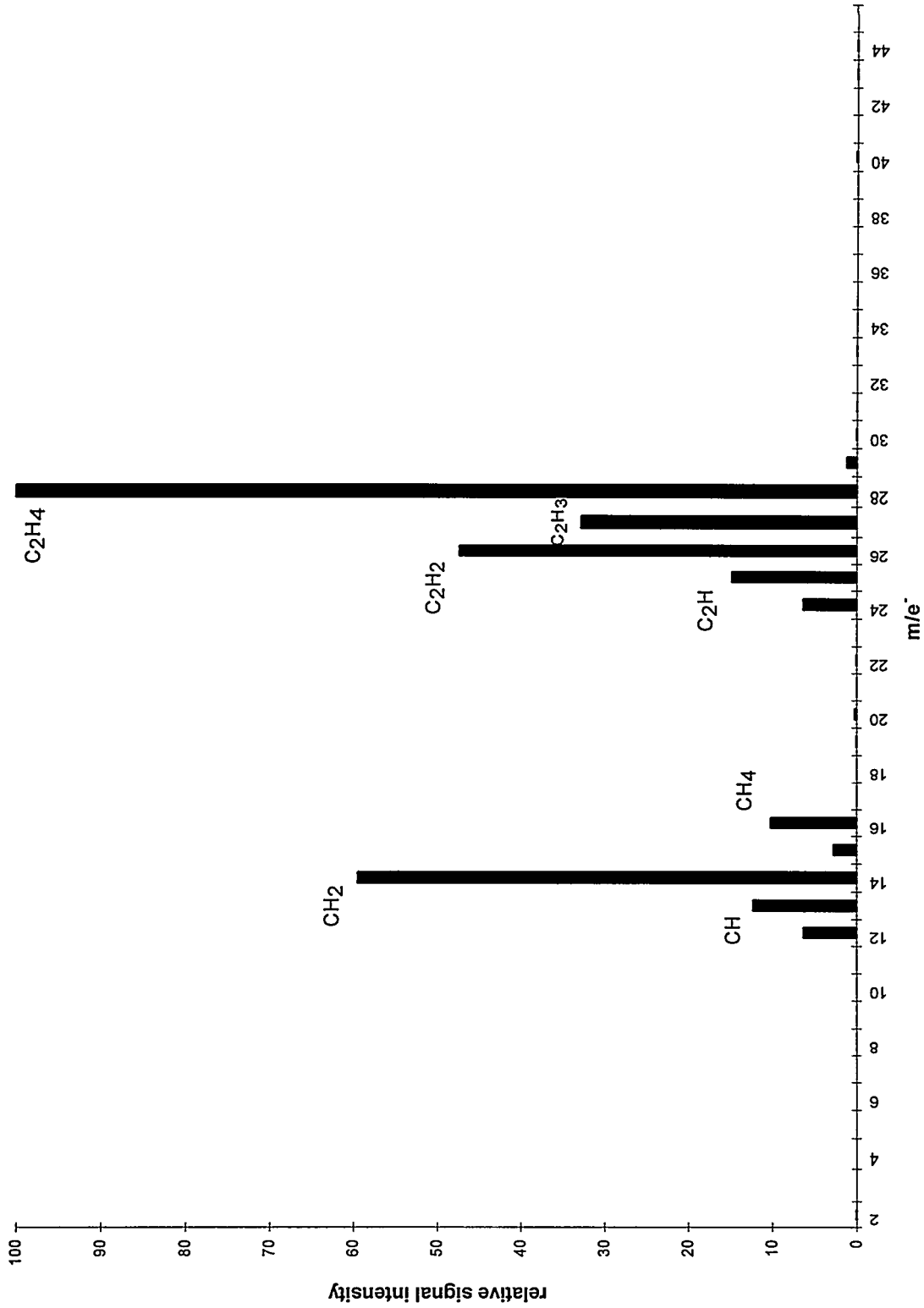

Figure 20. Mass spectra for ethene

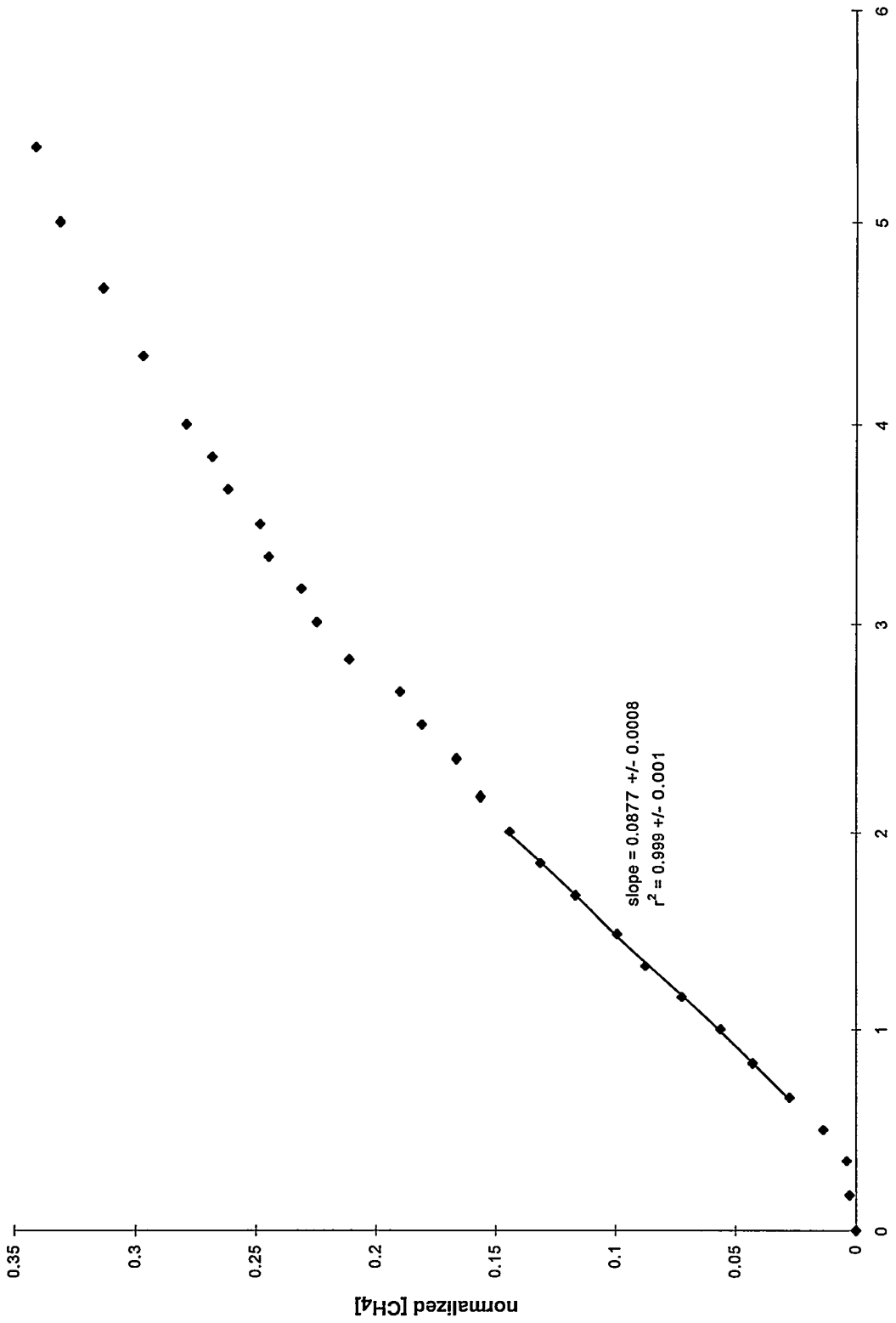

Figure 21. Methane formation over 4% Ru/SiO_2 (400 K, 460 torr)

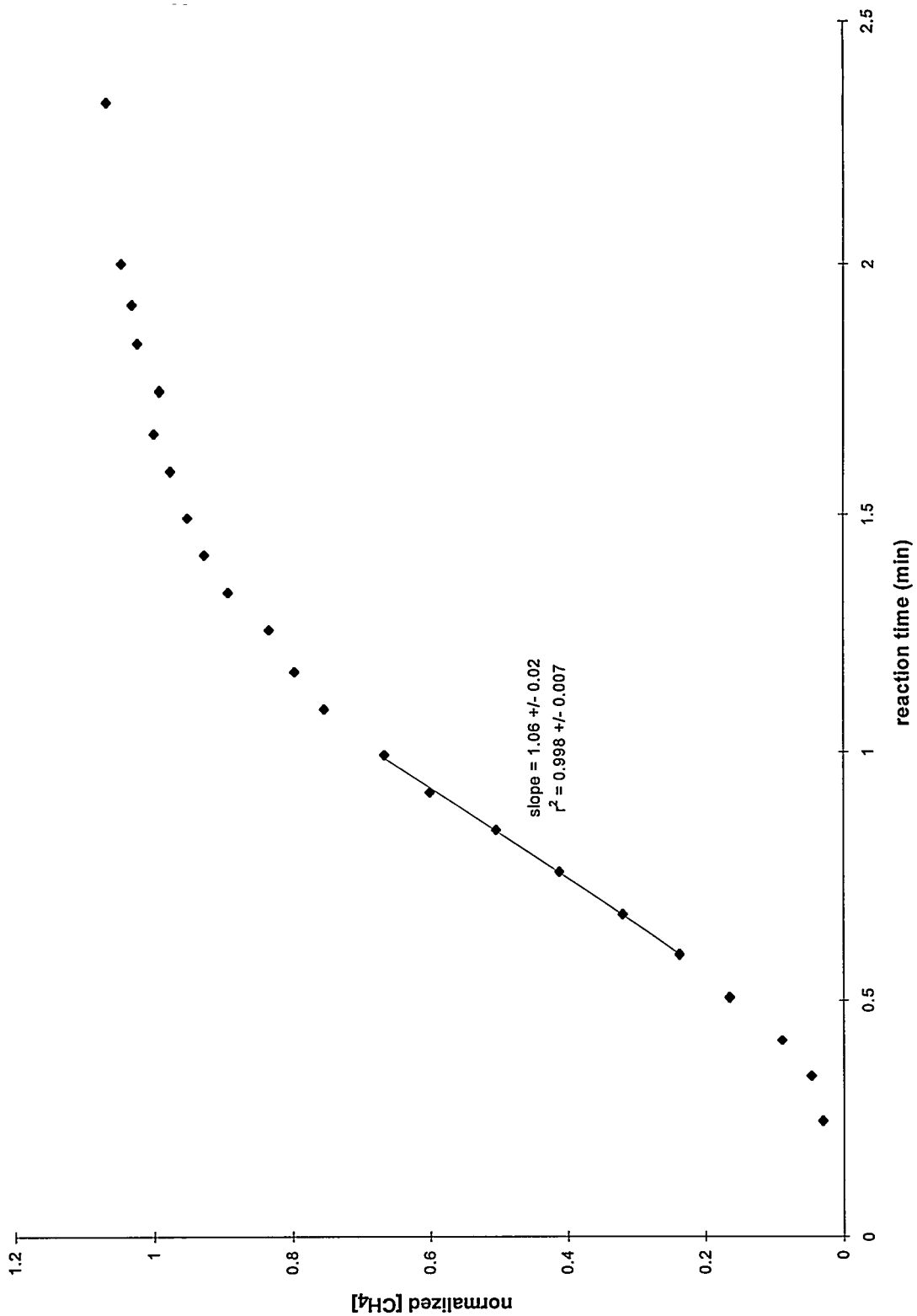

Figure 22. Methane formation over 4% Ru/SiO_2 (473 K, 460 torr)

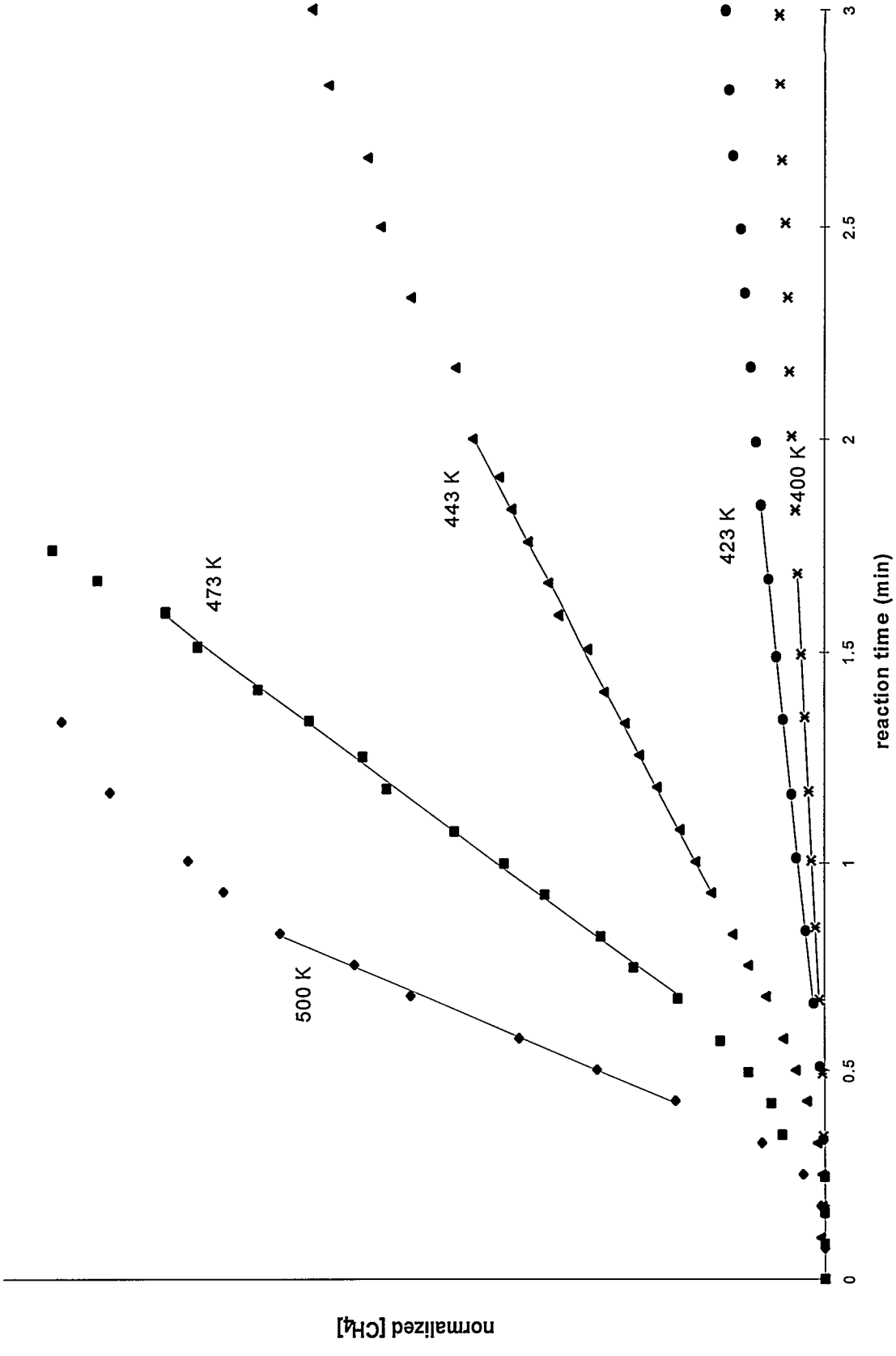

Figure 23. Methane formation over 3% Ag-Ru/SiO_2 (460 torr)

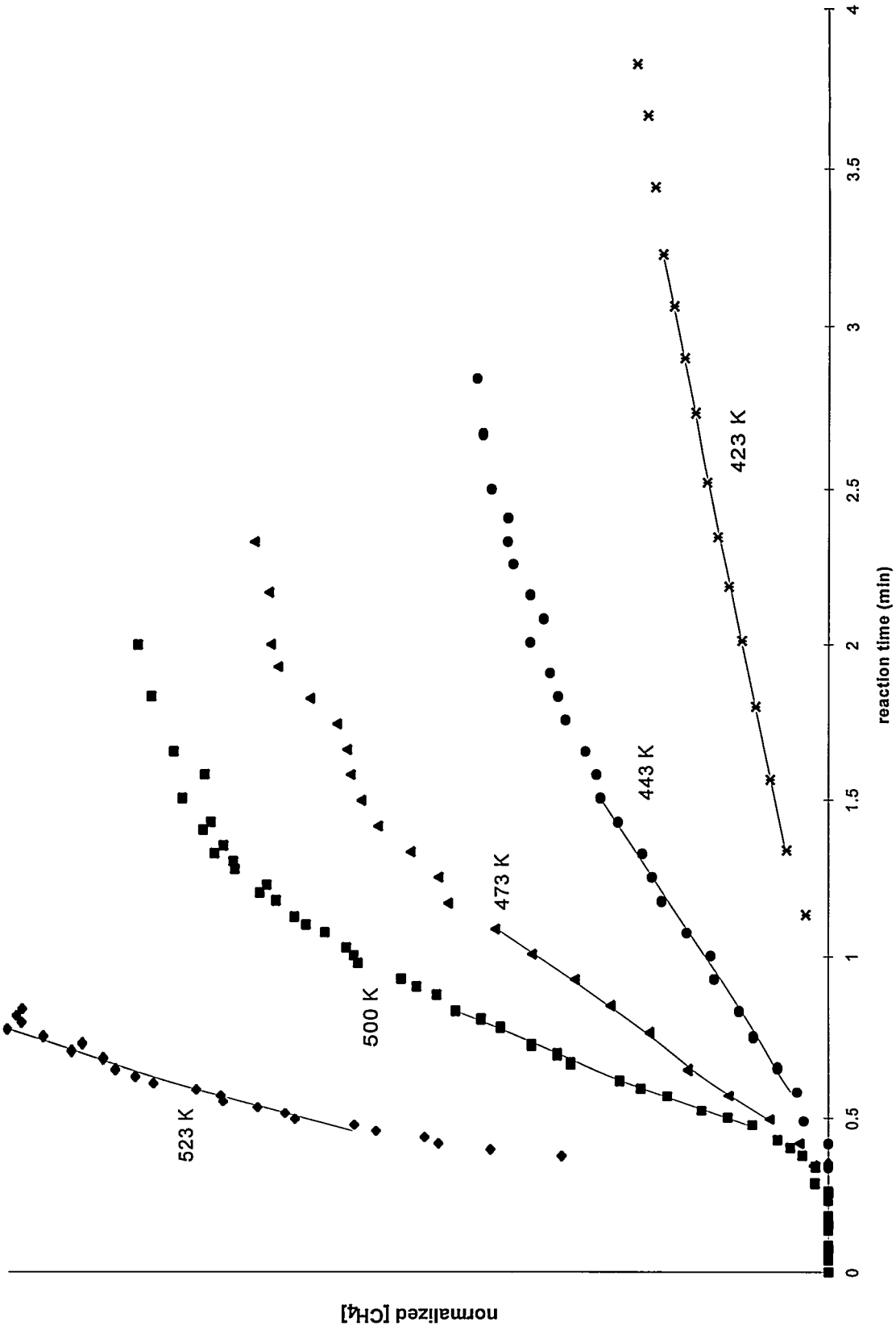

Figure 24. Methane formation over 10% Ag-Ru/SiO_2 (460 torr)

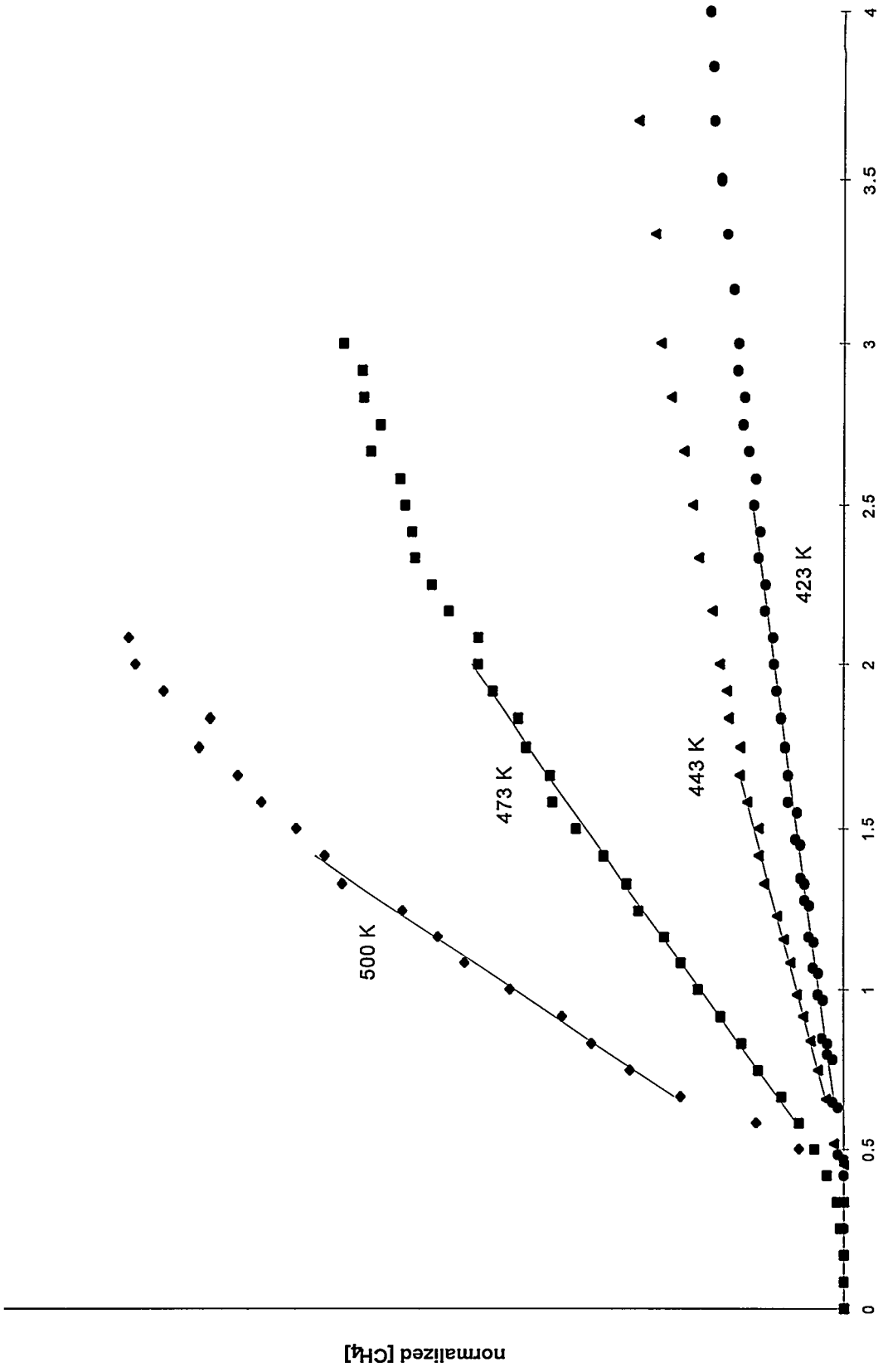

Figure 25. Methane formation over 20% Ag-Ru/SiO_2 (460 torr)

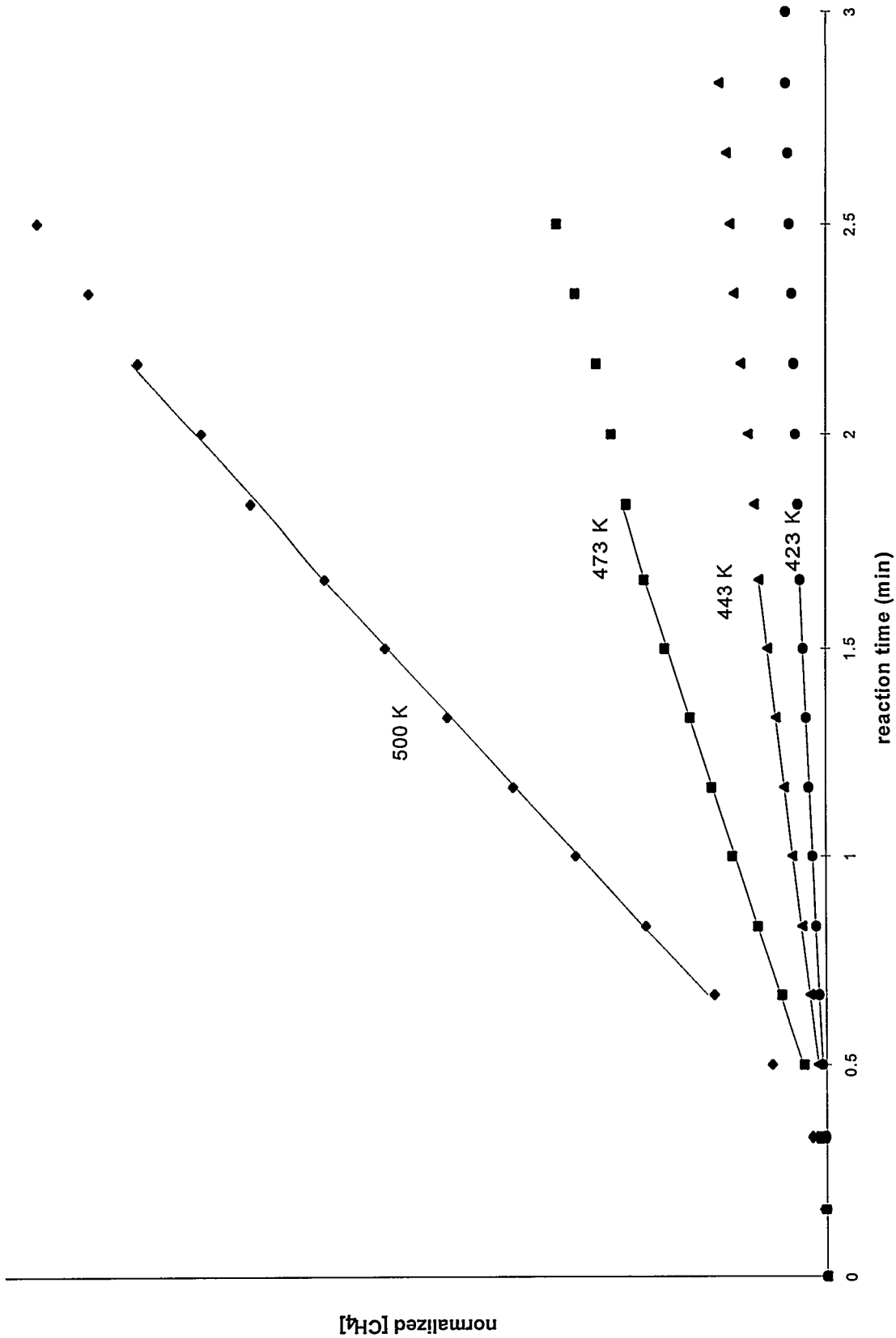

Figure 26. Methane formation over 30% Ag-Ru/SiO_2 (460 torr)

Table 6. Experimental design

experiment	catalyst	temperature (K)
1	4% Ru/SiO_2	473
2		400
3		443
4		443
5		423
6		400
7		473
8		423
9	3% $Ag\text{-}Ru/SiO_2$	473
10		423
11		400
12		443
13		423
14		473
15		400
16		443
17	30% $Ag\text{-}Ru/SiO_2$	400
18		443
19		473
20		423
21		500
22		443
23		400
24		443
25		500
26		423
27	4% Ru/SiO_2	500
28		500
29		400
30		473
31		423
32		443
33		400
34		443
35		423
36	3% $Ag\text{-}Ru/SiO_2$	423
37		473
38		443
39		500
40		400

Table 6. (continued)

experiment	catalyst	temperature (K)
41	3% Ag-Ru/SiO_2	423
42		400
43		500
44	10% Ag-Ru/SiO_2	500
45		423
46		473
47		400
48		443
49		500
50		443
51		400
52		443
53		473
54		523
55	20% Ag-Ru/SiO_2	500
56		473
57		443
58		523
59		423
60		500
61		443
62		473
63		423

Table 7. Statistical analysis of Ru/SiO_2 rate data

temperature (K)	slope	calibration factor	TOF[a]
400	0.0486	10.2	0.0949
400	0.0877	11.2	0.157
401	0.105	9.63	0.217
402	0.0493	10.3	0.0959
420	0.251	10.9	0.456
421	0.435	10.9	0.796
421	0.356	11	0.649
423	0.462	12	0.772
440	1.09	11.5	1.88
443	1.59	11.6	2.74
443	1.06	11.2	1.90
443	1.00	11.3	1.76

[a](10^{-3} mol CH_4 /mol Ru_s /sec)

Table 8. Statistical analysis of Ag-Ru/SiO_2 rate data

catalyst	temperature (K)	slope	calibration factor	TOF[a]	activation energy[b]
3% Ag	402	0.178	63.7	0.0302	17.6 +/- 1.2
	423	0.402	57.5	0.0973	
	446	1.22	110	0.222	
	473	3.12	85.9	0.727	
	501	11.7	138	1.70	
	502	5.39	30.3	3.55	
10% Ag	400	0.00533	5.26	0.0203	16.7 +/- 1.7
	425	0.0238	3.5	0.136	
	445	0.0767	4.33	0.354	
	472	0.169	2.57	1.31	
	503	0.316	3.91	1.61	
	523	0.397	2.02	3.91	
20% Ag	424	0.00637	14.7	0.00867	18.8 +/- 1.5
	430	0.0132	12.9	0.0203	
	445	0.0253	11.9	0.0424	
	445	0.0188	9.47	0.0397	
	474	0.0685	8.18	0.167	
	476	0.107	18.7	0.114	
	500	0.143	8.92	0.321	
30% Ag	401	0.00434	11.1	0.00785	18.7 +/- 0.6
	425	0.0206	11.2	0.0368	
	444	0.0552	11.3	0.0975	
	445	0.0251	6.27	0.0801	
	475	0.147	7.51	0.393	
	500	0.421	10.3	0.818	
	501	0.478	10.2	0.934	

[a](10^{-3} mol CH_4 /mol Ru_s /sec)
[b]kcal/mol