

Table 1
Detailed reaction mechanism for steam reforming of methane.

Reaction	A (cm. mol. s)	β	E_a (kJ mol ⁻¹)
1. H ₂ + Rh(s) + Rh(s) → H(s) + H(s)	1.000 × 10 ⁻⁰²³	0.0	0.00
2. H(s) + H(s) → H ₂ + Rh(s) + Rh(s)	3.000 × 10 ⁻²¹	0.0	77.80
3. O ₂ + Rh(s) + Rh(s) → O(s) + O(s)	1.000 × 10 ⁻⁰²³	0.0	0.00
4. O(s) + O(s) → O ₂ + Rh(s) + Rh(s)	1.300 × 10 ⁻²²	0.0	355.20
5. CH ₄ (s) → CH ₄ + Rh(s)	8.000 × 10 ⁻⁰⁵⁴	0.0	0.00
6. CH ₄ + Rh(s) → CH ₄ (s)	2.000 × 10 ⁻¹⁴	0.0	25.10
7. H ₂ O + Rh(s) → H ₂ O(s)	1.000 × 10 ⁻⁰¹³	0.0	0.00
8. H ₂ O(s) → H ₂ O + Rh(s)	6.000 × 10 ⁻¹³	0.0	45.00
9. CO ₂ + Rh(s) → CO ₂ (s)	1.000 × 10 ⁻⁰⁵⁴	0.0	0.00
10. CO ₂ (s) → CO ₂ + Rh(s)	3.000 × 10 ⁻⁰⁶⁸	0.0	21.70
11. CO + Rh(s) → CO(s)	5.000 × 10 ⁻⁰³⁴	0.0	0.00
12. CO(s) → CO + Rh(s)	1.000 × 10 ⁻¹³	0.0	133.40
$\theta_{CO(s)}$			50.0 ^b
13. H(s) + O(s) → OH(s) + Rh(s)	5.000 × 10 ⁻²²	0.0	83.70
14. OH(s) + Rh(s) → H(s) + O(s)	3.000 × 10 ⁻²⁰	0.0	37.70
15. H(s) + OH(s) → H ₂ O(s) + Rh(s)	3.000 × 10 ⁻²⁰	0.0	33.50
16. H ₂ O(s) + Rh(s) → H(s) + OH(s)	5.000 × 10 ⁻²²	0.0	110.90
17. OH(s) + OH(s) → H ₂ O(s) + O(s)	3.000 × 10 ⁻²¹	0.0	100.80
18. H ₂ O(s) + O(s) → OH(s) + OH(s)	3.000 × 10 ⁻²¹	0.0	171.80
19. C(s) + O(s) → CO(s) + Rh(s)	5.000 × 10 ⁻²³	0.0	97.90
20. CO(s) + Rh(s) → C(s) + O(s)	3.700 × 10 ⁻²¹	0.0	169.00
$\theta_{CO(s)}$			50.0 ^b
21. CO(s) + O(s) → CO ₂ (s) + Rh(s)	1.000 × 10 ⁻²⁰	0.0	121.60
$\theta_{CO_2(s)}$			50.0 ^b
22. CO ₂ (s) + Rh(s) → CO(s) + O(s)	5.000 × 10 ⁻²¹	0.0	115.30
23. CO(s) + H ₂ (s) → C(s) + OH(s)	3.700 × 10 ⁻²¹	0.0	142.76
$\theta_{CO(s)}$			50.0 ^b
24. C(s) + OH(s) → CO(s) + H(s)	3.700 × 10 ⁻²⁰	0.0	25.54
25. CO(s) + H(s) → HCO(s) + Rh(s)	5.000 × 10 ⁻¹⁹	0.0	108.90
26. HCO(s) + Rh(s) → CO(s) + H(s)	3.700 × 10 ⁻²¹	0.0	0.00
$\theta_{CO(s)}$			-50.0 ^b
27. HCO(s) + Rh(s) → CH(s) + O(s)	8.000 × 10 ⁻²³	0.0	59.50
28. CH(s) + O(s) → HCO(s) + Rh(s)	3.700 × 10 ⁻²¹	0.0	167.50
29. CH ₄ (s) + Rh(s) → CH ₃ (s) + H(s)	5.500 × 10 ⁻²⁰	0.0	61.00
30. CH ₃ (s) + H(s) → CH ₄ (s) + Rh(s)	3.700 × 10 ⁻²¹	0.0	51.00
31. CH ₃ (s) + Rh(s) → CH ₂ (s) + H(s)	3.700 × 10 ⁻²⁴	0.0	103.00
32. CH ₂ (s) + H(s) → CH ₃ (s) + Rh(s)	3.700 × 10 ⁻²¹	0.0	44.00
33. CH ₂ (s) + Rh(s) → CH(s) + H(s)	3.700 × 10 ⁻²⁴	0.0	100.00
34. CH(s) + H(s) → CH ₂ (s) + Rh(s)	3.700 × 10 ⁻²⁴	0.0	68.00
35. CH(s) + Rh(s) → C(s) + H(s)	3.700 × 10 ⁻²¹	0.0	21.00
36. C(s) + H(s) → CH(s) + Rh(s)	3.700 × 10 ⁻²¹	0.0	172.80
37. CH ₄ (s) + O(s) → CH ₃ (s) + OH(s)	1.700 × 10 ⁻²⁴	0.0	80.34
38. CH ₃ (s) + OH(s) → CH ₄ (s) + O(s)	3.700 × 10 ⁻²¹	0.0	24.27
39. CH ₃ (s) + O(s) → CH ₂ (s) + OH(s)	3.700 × 10 ⁻²⁴	0.0	120.31
40. CH ₂ (s) + OH(s) → CH ₃ (s) + O(s)	3.700 × 10 ⁻²¹	0.0	15.06
41. CH ₂ (s) + O(s) → CH(s) + OH(s)	3.700 × 10 ⁻²⁴	0.0	114.50
42. CH(s) + OH(s) → CH ₂ (s) + O(s)	3.700 × 10 ⁻²¹	0.0	36.82
43. CH(s) + O(s) → C(s) + OH(s)	3.700 × 10 ⁻²¹	0.0	30.13
44. C(s) + OH(s) → CH(s) + O(s)	3.700 × 10 ⁻²¹	0.0	136.00

Arrhenius parameters for the rate constant written in the form: $k = AT^{\beta} \exp(-E_a/RT)$. Total surface site density is $\Gamma = 2.77 \times 10^{-13}$ mol/cm².

^a Sticking coefficient.
^b Coverage dependent activation energy.

the adsorption of ethane, propane, and butane Eq. (14) was used.

$$\dot{s}_{C_nH_m} = A_k \cdot T^{\beta} \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot c_{C_nH_m}^a \cdot c_{vacancy}^b \quad (14)$$

The activation energy and the reaction orders, *a* and *b*, are given in Table 3. We observed a similar behavior in steam reforming of the single components ethane, propane, and butane (for instance, Figs. 4, 5 and 13), consequently, the rate constants lie in a narrow range. The pre-exponential factor is calculated using Eq. (11) [23] assuming a sticking probability of $S_i^0 = 0.006$. The activation energy is expected to be in the order of 50 kJ/mole corresponding to the activation energy for the removal of the first hydrogen atom [30] and is considered to be similar for all alkanes. $\beta = 0$ since no additional temperature dependency is expected. Butane conversion is a bit lower (Figs. 8 and 14). The final value of the parameters were obtained through comparison of experimentally derived and numerically predicted conversion and selectivity in SR of the single

Table 2
Experimental conditions ($p = 1-1.05$ bar).

Feed	T [°C]	S/C	Catalyst (cps)
Methane	460–840	2.2	Rh/umicore (600)
Methane	450–835	2.8	Rh/umicore (600)
Methane	520–845	3.3	Rh/umicore (600)
Methane	425–610	3.5	Rh/umicore (600)
Methane	445–695	3.6	Rh/umicore (600)
Methane	425–845	4	Rh/umicore (600)
Methane	420–820	2.7	Rh/umicore (900)
Methane	420–770	3.3	Rh/umicore (900)
Methane	415–705	3.5	Rh/umicore (900)
Methane	425–950	3.8	Unloaded (600)
Ethane	345–900	2.5	Rh/umicore (900)
Ethane	275–760	4	Rh/umicore (900)
Ethane	540–910	2.5	Unloaded (600)
Propane	335–750	2.5	Rh/umicore (900)
Propane	270–780	4	Rh/umicore (900)
Propane	680–1015	4	Unloaded (600)
Butane	420–720	2.5	Rh/umicore (900)
Butane	320–825	4	Rh/umicore (900)
Butane	540–960	4	Unloaded (600)
Natural gas	240–750	2.5	Rh/umicore (900)
Natural gas	250–750	4	Rh/umicore (900)
Natural gas	540–820	2.5	Unloaded (600)

components. The adsorbates then participate in the detailed mechanism of the C₁-chemistry, Table 1.

4.2. Gas-phase reactions

The reactions in the gas phase are included in the simulations applying the mechanism of Quiceno et al. [22]. This mechanism has been developed for oxidation processes of methane, ethane, propane and butane. It consists of 765 reactions among 63 species in the gas phase.

5. Results

The steam-to-carbon ratio (S/C), which is the total number of water molecules divided by the total number of carbon atoms in the feed gas, serves as parameter to describe the feed composition. For propane, for example, S/C 3 means 9 molecules of water per molecule propane. For natural gas, an average carbon content per molecule was calculated based on the gas composition. The S/C calculation also accounts for the amount of CO₂ contained in the natural gas.

Conversion, selectivity and yield are calculated as follows:

$$X_i = \frac{y_{i0} - y_{i,e}}{y_{i0}} \quad (15)$$

$$S_{CO} = \frac{x_{CO}}{x_{CO} + x_{CO_2} + x_{CH_4}}, \quad S_{CO_2} = \frac{x_{CO_2}}{x_{CO} + x_{CO_2} + x_{CH_4}}, \quad S_{CH_4} = \frac{x_{CH_4}}{x_{CO} + x_{CO_2} + x_{CH_4}} \quad (16)$$

$$S_{H_2} = \frac{x_{H_2}}{x_{H_2} + 2 \cdot x_{CH_4}} \quad (17)$$

$$P_p = X_i \cdot S_p \quad (18)$$

Table 3
Rate constants for the decomposition of ethane, propane and butane.

	E_a	<i>a</i>	<i>b</i>
C ₂ H ₆	51	0.6	0.87
C ₃ H ₈	50	0.63	0.85
C ₄ H ₁₀	49	0.495	0.94

$$\dot{s}_{C_nH_m} = A_k \cdot T^{\beta} \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot c_{C_nH_m}^a \cdot c_{vacancy}^b$$