

1 *Supplemental Information*

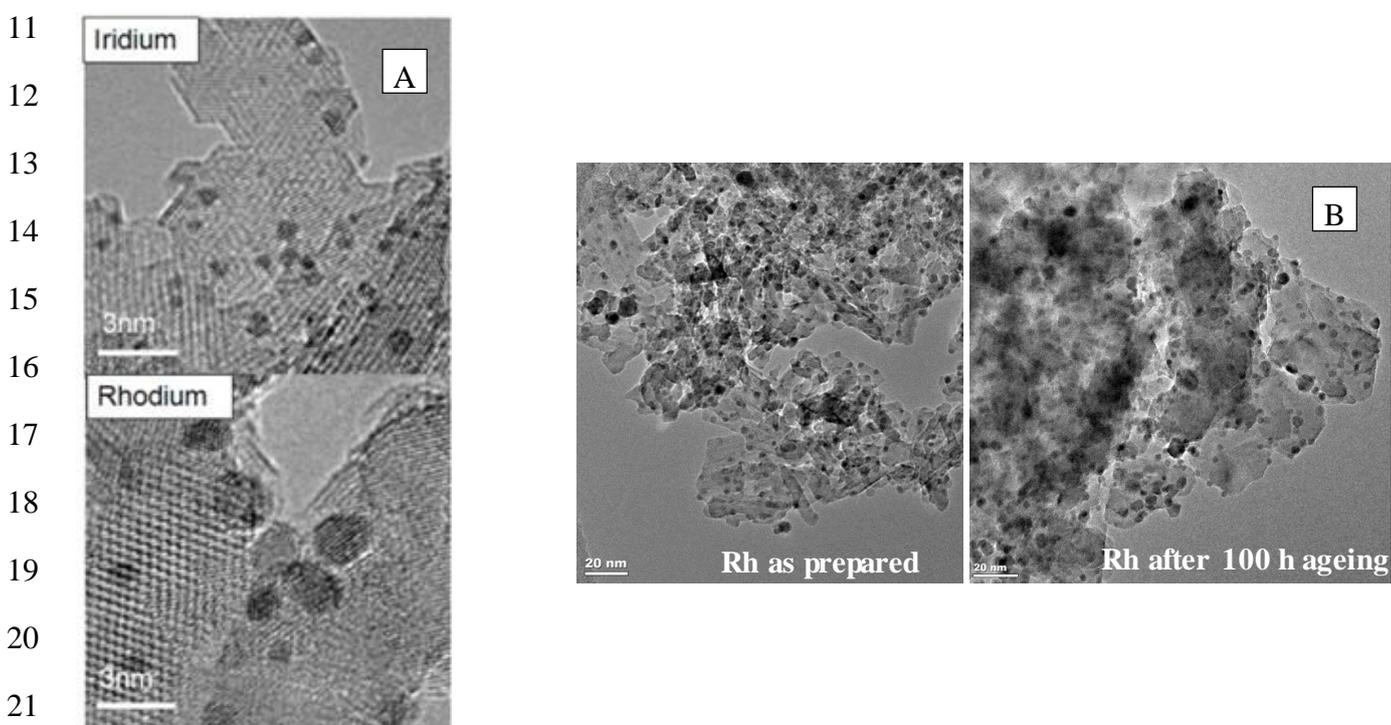
2 **Methane and Ethane Steam Reforming over**
3 **MgAl₂O₄-supported Rh and Ir Catalysts: Catalytic**
4 **Implications for Natural Gas Reforming Application**

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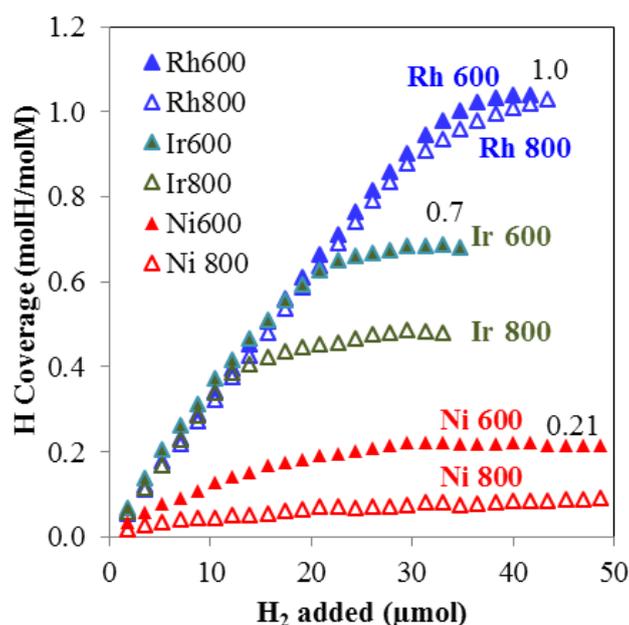
10 **1. TEM characterization**



22 **Figure S1.** (A) TEM analysis of 5Ir/MgAl₂O₄ (top) and 5Rh/MgAl₂O₄ (bottom) catalysts used in this
23 study. (B) effect of ageing on Rh/MgAl₂O₄ catalyst. (950 °C) under H₂.

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25 2. Hydrogen uptake over metal supported catalysts (Rh, Ir, Ni supported catalysts)

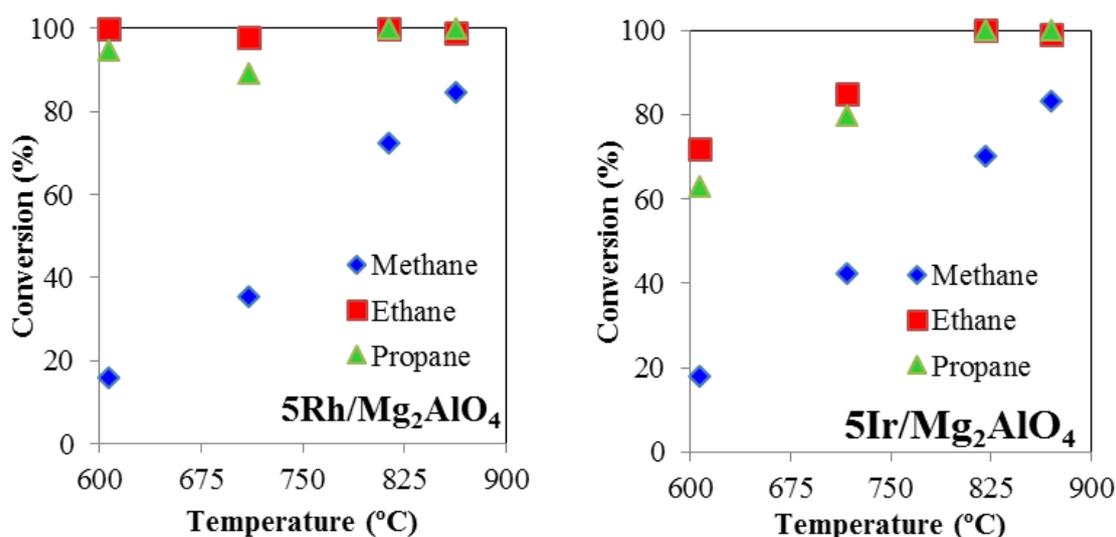


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27 **Figure S2.** Hydrogen uptake at 600 and 800 °C. Evolution of hydrogen uptake is calculated as H
 28 coverage (per mole of metal surface) vs H₂ pulsed. Volumetric pulse hydrogen adsorption
 29 measurements were carried out at 600 °C and 800 °C. First, 50 mg of the sample was reduced at 850
 30 °C for 16 h using H₂ (flow 10% in N₂, 100 mL/min) and purged for 4 in pure N₂. After ramping at the
 31 adsorption temperature, 5% Hydrogen/Ar is pulsed using a 100 µl loop with 1 minute intervals
 32 between injections.

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34 3. Conversion of natural gas simulant components

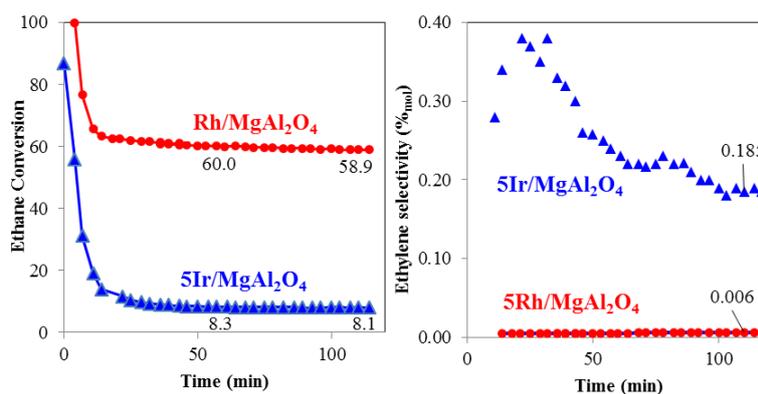


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36 **Figure S3.** Conversion of the individual components of a simulant natural gas mixture. Butane
 37 conversion was complete. Reaction conditions: S/C:1.5, t = 4.5 ms, 1h TOS, Simulant gas feed (94.5%
 38 methane, 4% ethane, 1% propane, 0.5% butane) was supplied by Matheson.

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40 4. Ethane conversion over Rh and Ir catalyst at 600 °C



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42 **Figure S4.** Ethane reforming conversion vs time on stream at 600 °C. Reaction conditions: S/C = 2.75,
 43 9 mg of catalyst. $\tau = 28.3$ ms, 35 sccm ethane, 80 sccm N₂, 9 mg of catalyst.

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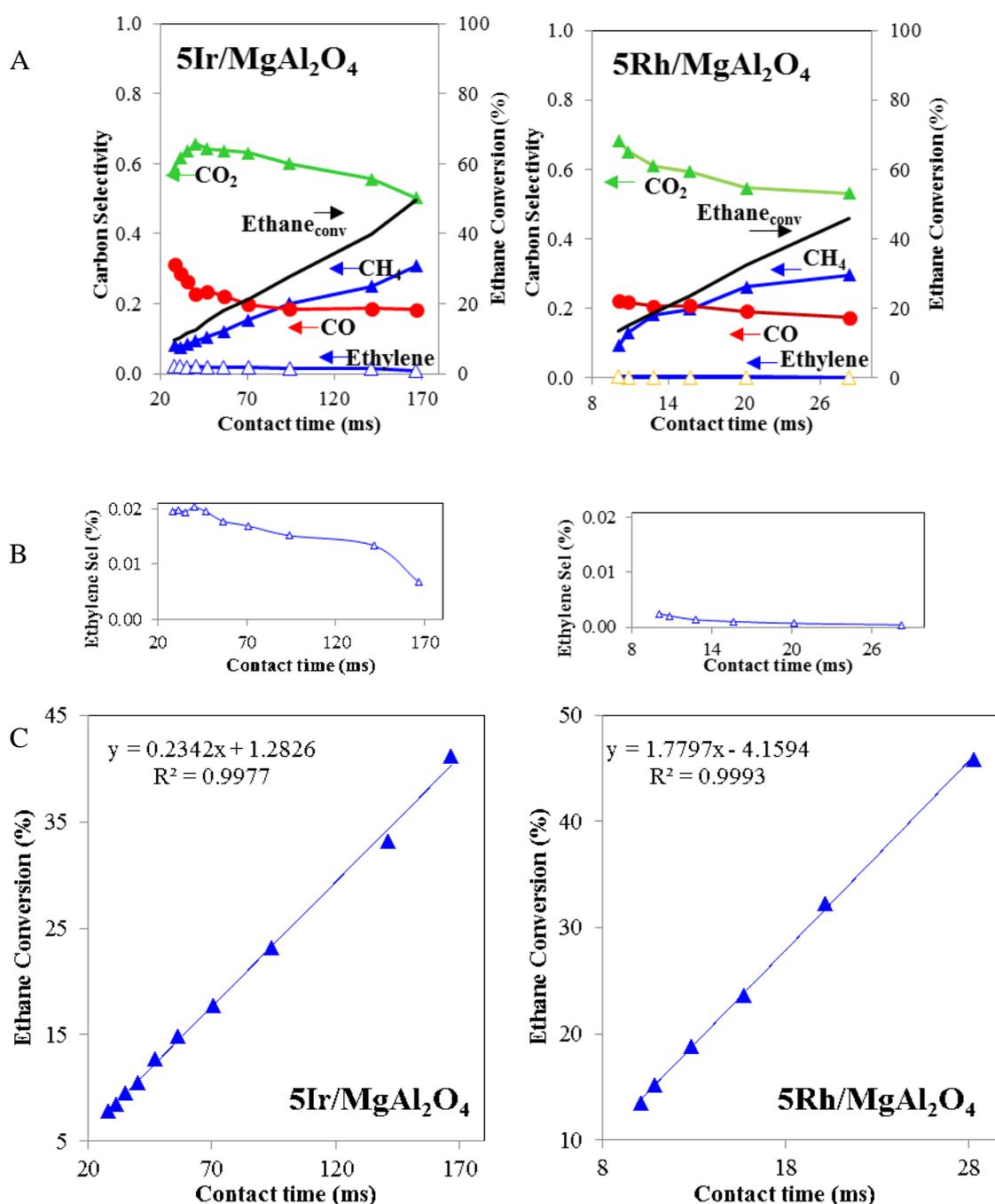
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47 **Table S1.** Deactivation check experiments for the Ir catalyst under ethane reforming experiments
 48 shown in Figure S4. Fresh catalyst was tested for methane activity before ("initial") and after reaction
 49 with ethane to check for deactivation ("final").

	Conversion		Time on Stream	Conditions
Initial	22.7% conversion	methane	30 minutes	$\tau = 30.2$ ms, S/C = 3 35 sccm Methane
Ethane reforming Experiment (Figure S4)	8.1% conversion	ethane	120 minutes (150 minutes total)	$\tau = 28.3$ ms, S/C = 2.75 35 sccm Ethane,
Final	23.1% conversion	methane	30 min (180 minutes total)	$\tau = 30.2$ ms, S/C = 3 35 sccm Methane

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51 5. Product distribution vs contact time



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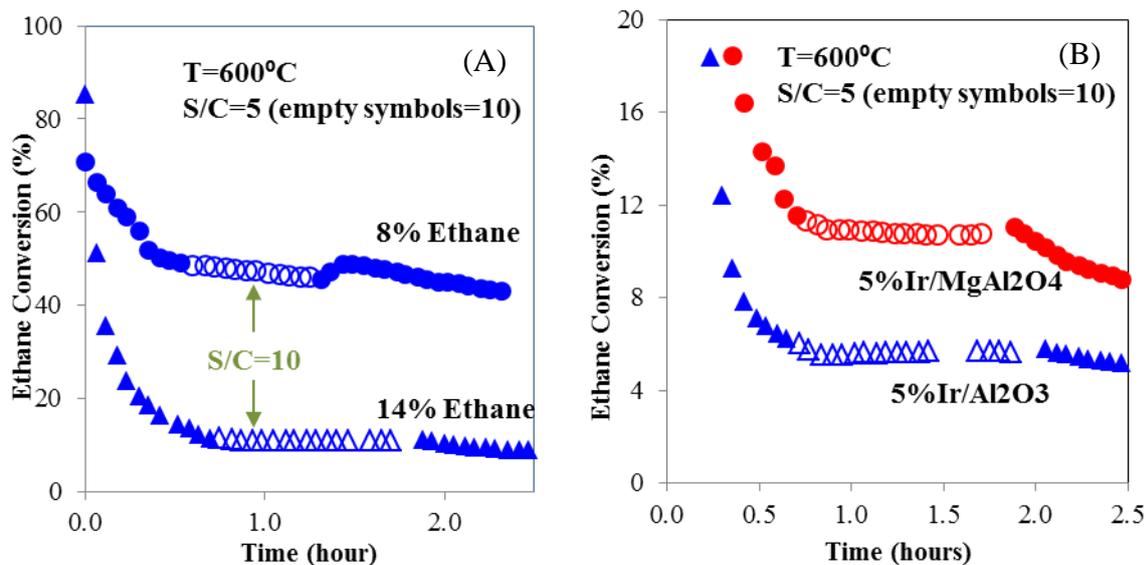
55 **Figure S5.** Ethane reforming conversion and carbon selectivity vs contact time (ms) for the reforming
 56 of ethane at 600 °C over MgAl₂O₄-supported Ir and Rh catalysts (A-top), ethylene selectivity (mol %)
 57 vs contact time (ms) (B-middle), and linear correlation for ethane conversion vs contact time, .
 58 Reaction conditions: S/C = 2.75, 9 mg of catalyst. Changes in contact time were achieved by changing
 59 gas flow over the same mass of catalyst in a continuous experiment. Each point corresponds to a
 60 steady state measurement after stabilizing for 1h. Ethane over iridium catalyst was changed from 35
 61 to 3.5 sccm. For the case of Rh, ethane flow was varied from 35 to 100 sccm.

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65 6. Control experiments for ethane reforming

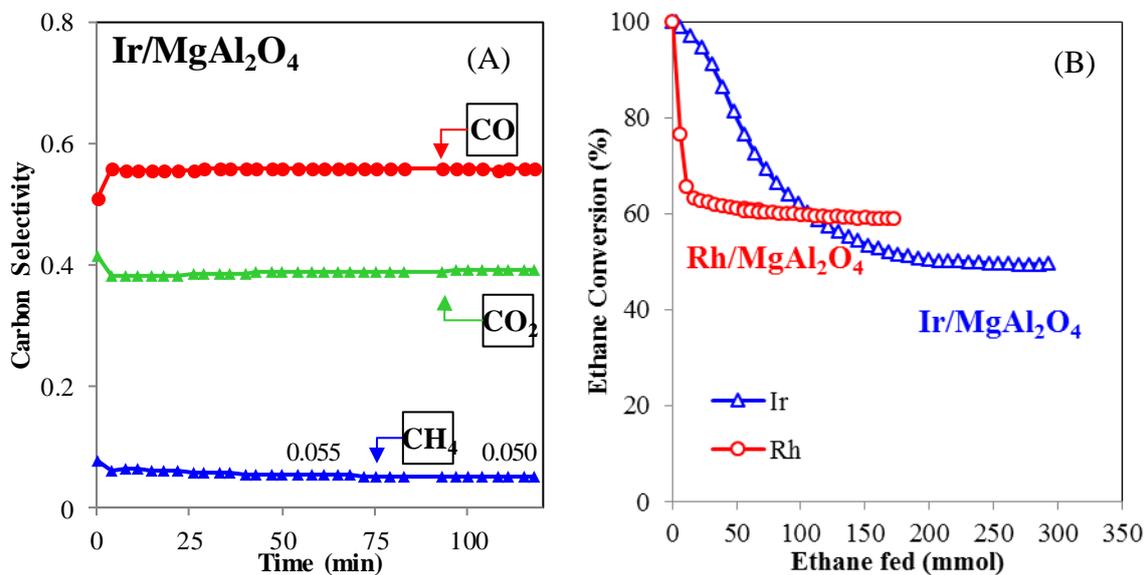


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67 **Figure S6.** Ethane reforming conversion over 5Ir/MgAl₂O₄ catalyst at 600 °C. (A) Ethane conversion
 68 vs time on stream at increase carbon/steam ratio (10 for empty symbols) at two different concentration
 69 of ethane in the gas (8 and 14 vol.%). (B) Ethane conversion vs time on stream comparing Ir activity
 70 over two different supports, MgAl₂O₄ (red) and Al₂O₃ (blue).

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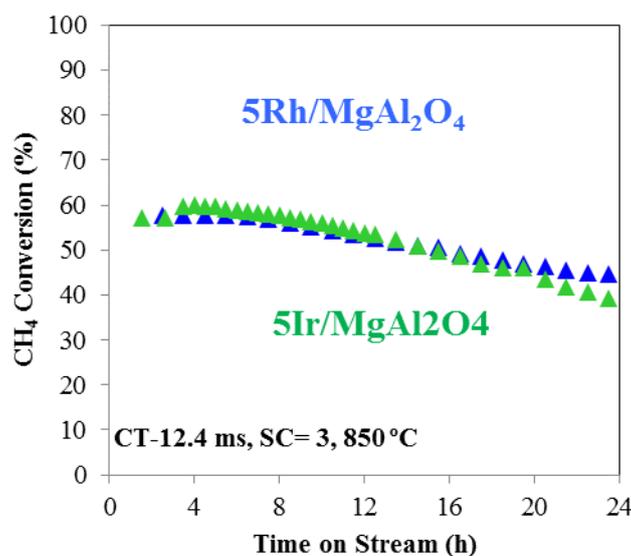


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74 **Figure S7.** (A) Product selectivity for ethane steam reforming over Ir at 600 °C (8.2% conversion). (B)
 75 Ethane conversion over Rh and Ir catalysts at 600 °C (S/C = 3 mol, τ = 28 ms (Rh), τ = 167 ms (Ir)).

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77 7. Additional catalyst durability experiments

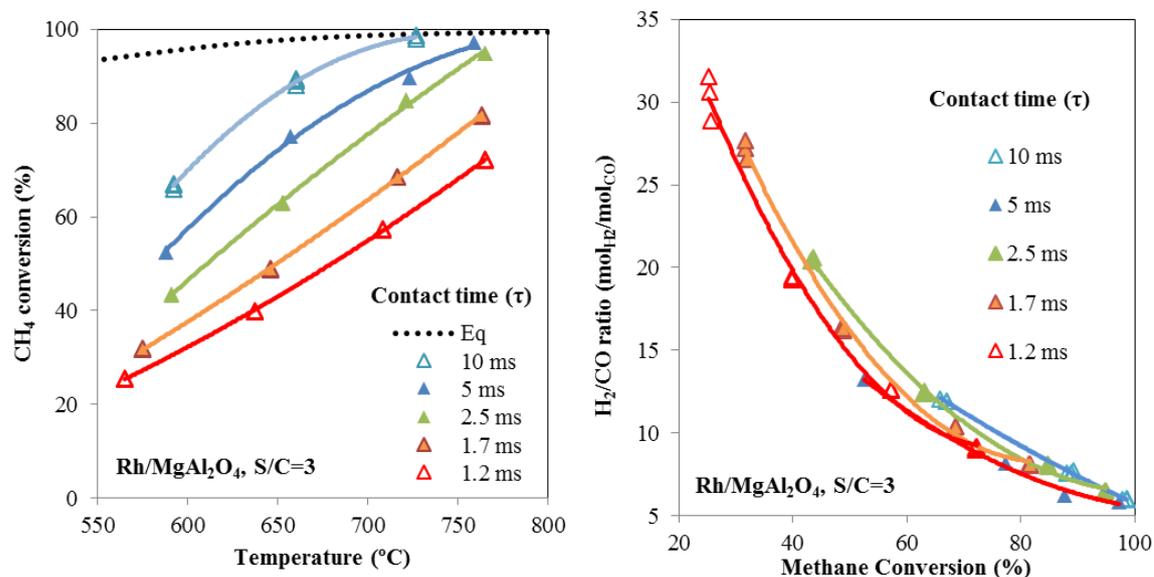


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79 **Figure S8.** Conversion vs time on stream for methane steam reforming over the Rh and Ir supported
80 catalysts at 850°C ($S/C = 3$ mol, $\tau = 12.4$ ms; Methane feed = 22.6 vol.%).

81 8. Steam reforming product over Rh/MgAl₂O₄ catalyst: H₂/CO ratio

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Figure S9. Methane conversion (A) and H₂/CO ratio for methane steam reforming products (B) over benchmark 5% Rh/MgAl₂O₄ catalyst. CH₄, S/C = 3, 9 mg of catalyst. 5% Rh MgAl₂O₄ catalyst reduced in-situ at 850 °C for 16h under flowing 10% H₂ in N₂.

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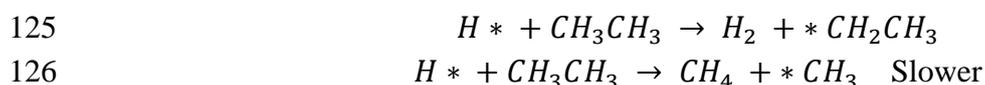
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105 MECHANISM SUMMARY

- 106 1- C–C bond is weaker than C–H bond.
- 107 2- Reforming reactions does not seem to have kinetic relevance.
- 108 3- C–C bond cleavage is sterically hampered. At least 2H must be removed before C–
- 109 C bond interacts with the metal.
- 110 4- Oxidative dehydrogenation (secondary route to ethylene) is very unlikely. Higher
- 111 amounts of steam do not affect ethane conversion rates.
- 112 5- Dehydrogenation is the first step
- 113
$$* + C_2H_6 \rightarrow 2 * CH_3$$
- 114 6- Methyl radical can lead to methane formation. Note that Rh is 30% selective to
- 115 methane. Also, deactivation is accompanied by a loss in Methane selectivity.
- 116 7- If not both, at least one of the carbons will form a methyl radical, this methyl
- 117 subtracts H from ethane forming an ethyl group and methane. Ethyl radical is
- 118 therefore the route to ethylene.
- 119 • Initiation (weakest bond breaks crating active surface species)
- 120 • Chain Transfer (one species creates another – less important)
- 121 • μ -propagation (monomolecular transformation)
- 122 • β -propagation (bi-molecular transformation, active species + reactant molecule)
- 123 • Termination (not shown)

124 In short,



- 127 8- C–C bond is stable until *CHCH* is formed (Iglesia 2014). C–C cleavage has
- 128 negative order with respect to H₂. This could mean that H is adsorbed preferably.
- 129 9- C1 species are not kinetically important and reforming reaction in not kinetically
- 130 important.

131 In this reaction mechanism, hydrogen capacity of the metal (stoichiometry), its adsorption

132 strength, and the coverage relative to other active species (C2, C1, O, CO) is likely to be important in

133 overall catalytic rate. Initiation and termination reactions are first order in chain mechanisms as well

134 as methane activation in reforming reactions. For Ir we found a low reaction order (0.3) indicating

135 that the slowest step is related to the creation (accumulation) to an adsorbed species (ethyl group).

136 Ethyl group formation is superseding the global reaction order.