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Stepwise methane steam reforming: a route to CO-free hydrogen

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A method for the production of clean hydrogen is demonstrated. The process consists of two steps involving the decomposition of methane to CO-free hydrogen and surface carbon in the first step followed by steam gasification of this surface carbon in the second step. This process can be operated in cycles and could be an excellent hydrogen source for fuel cells and other devices or processes requiring CO-free hydrogen.

Keywords: methane decomposition, Ni/zirconia, steam gasification

In order to utilize hydrogen as a primary fuel for fuel cells, it is highly desirable to develop processes which produce hydrogen free of impurities, particularly carbon monoxide. Steam reforming, partial oxidation and autothermal reforming [1–3] of methane are well-developed processes for the production of hydrogen, however, carbon monoxide is formed as a by-product in all these processes. CO can be further converted to CO_2, but it is difficult to remove the last traces of CO which are capable of poisoning the electrode of a typical fuel cell.

In this study, a stepwise process for the production of CO-free hydrogen is demonstrated. This two-step process involves the catalytic decomposition of methane to produce CO-free hydrogen and surface carbon in the first step followed by the steam gasification of the surface carbon in the second step:

$$\begin{array}{ll} CH_4 \rightarrow C^* + 2H_2 & \text{step I} \\ C^* + H_2O \rightarrow H_2 + CO_2 + CH_4 & \text{step II} \\ \quad (C^* \text{ is surface carbon}) & \end{array}$$

In these GC-pulse experiments, essentially all (10–20% of a monolayer equivalent) of the surface carbon formed in the first step is removed by water in the second step. Thus the catalyst retains its initial activity for methane decomposition through many cycles. The carbon monolayer equivalents (MLE) were estimated from the specific metal surface area, assuming one monolayer to correspond to a $C/Ni_{surface}$ ratio of 1.0. In order to avoid the formation of graphitic or inactive carbon, the reaction sequence was carried out at temperatures <650 K [4].

The decomposition of methane has been studied quite extensively with respect to fundamental dynamical studies [5] as well in methane homologation investigations [6–8]. The decomposition of methane has been considered as a method to obtain hydrogen [9,10], but not in a reversible, cyclic process as demonstrated here. The amount of CO-free hydrogen formed in the first step varied from 1.00 to 1.34 moles per mole of methane reacted, depending on the reaction conditions. Hydrogen is produced in the second step of the reaction as well in a mixture of gases (primarily CH_4 and CO_2). This mixture can be separated or simply methanated and returned to step I.

The catalyst selected for these studies was Ni supported on zirconia, based on the work of Lunsford et al. [11] that addressed step II of this reaction sequence. The Ni/zirconia (88% Ni) catalyst was prepared by co-precipitation of the hydroxides from a basic solution of the nitrate salts [11,12]. The resulting gel was filtered, washed with distilled water and then dried in air at 338 K. Following this the catalyst was oxidized in air for 2 h at 473 K and then at 673 K for 2 h. The oxidized catalyst was then reduced with H_2 in flowing He, at a flow rate of 20 ml/min for 30 min at 523 K and then at 723 K for 15–16 h. Two catalyst loadings were investigated, 100 and 200 mg. Since the results were essentially independent of catalyst loading, only these data for 200 mg are reported. Following the reduction step, the reactor was cooled to the desired reaction temperature under flowing He.

The Ni surface area was measured by CO pulse adsorption experiments carried out at room temperature assuming a CO/Ni ratio of 1.0. Prior to the Ni surface area determination, the catalyst was pre-reduced at 723 K for a period of 15 h in flowing H_2, then brought to room temperature in flowing helium. The analysis of CO was carried out on-line with a TCD. The exposed Ni surface area was determined to be 5.83 m^2/g.

The total reaction (cycle) involved two steps. In the first step, a (5% CH_4 in He) pulse of 1.65 ml was introduced to the catalyst via a He carrier gas. Following this, a 2 μl pulse of water was introduced in the heated zone of the catalyst reactor. Between cycles, the catalyst was maintained at 648 K under flowing H_2. Analysis of gases was carried out

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Table 1
Reaction cycles at 648 K for a catalyst loading of 200 mg.[a]

Cycle #	Step I		Step II		C deposited	C removed
	CH_4[b]	H_2	CH_4[c]	CO_2		
1	3.45	4.62	1.15	2.31	3.45	3.46
2	3.45	3.80	1.16	2.22	3.45	3.38
3	3.45	3.45	1.05	2.30	3.45	3.35
4	3.45	3.86	1.09	2.27	3.45	3.36
5	3.45	4.10	0.94	2.58	3.45	3.52
6	3.45	4.25	1.02	2.45	3.45	3.47
7	3.45	4.20	1.07	2.32	3.45	3.39
8	3.45	3.67	0.87	2.60	3.45	3.47
9	3.45	4.06	0.82	2.52	3.45	3.37
10	3.45	4.26	0.96	2.50	3.45	3.46
11	3.45	4.04	0.81	2.65	3.45	3.46
12	3.45	4.04	1.06	2.41	3.45	3.47
13	3.45	3.67	1.05	2.39	3.45	3.44

[a] All units in μmoles.
[b] μmoles of methane reacted in step I.
[c] μmoles of methane formed in step II.

via an on-line GC (with TCD) using He as a carrier gas (flow rate 30 ml/min). The sensitivity of H_2 was improved by converting it into water prior to the TCD. A $30' \times 1/8''$ Hayasep DB column was used for the separation of the gases. Unreacted water was trapped prior to the Hayasep DB column by a trap cooled by a slurry of acetone and dry ice.

As mentioned above, each reaction cycle consisted of two steps; several such cycles were repeated at a reaction temperature of 648 K. The results for several reaction cycles at 648 K with a catalyst loading of 200 mg are shown in table 1. From the table it is apparent that essentially all of the carbon deposited in step I was removed in the second step for each cycle. The quantity of carbon deposited in the first step corresponded to 13% of a MLE. The amount of CO-free hydrogen produced in each cycle varied from 1.00 to 1.34 μmoles per μmole of methane consumed. In step II the only products observed were hydrogen, methane and CO_2.

Surface carbon on Ni occurs in three forms [13]: (a) the highly reactive carbidic form, (b) the unreactive graphitic form, and (c) the amorphous form which has intermediate reactivity. Since almost the entire amount of carbon deposited in the first step can be quantitatively removed by water in step II, the surface carbon formed in step I is assumed to be of the carbidic or amorphous form.

HREEL studies carried out recently in our group investigating the decomposition of methane on ruthenium single crystals, indicated the presence of a methylidyne species on the Ru surface at temperatures up to 700 K [14]. If all the surface carbon in the present study were in the form of a methylene or a methylidyne species, 1–2 μmoles of atomic hydrogen per μmole of methane would be anticipated to remain on the surface. This is in good agreement with the results of table 1. Thus it is likely that the hydrogen remaining on the surface after the first step can be accounted for by the presence of a mixture of surface methylene and methylidyne species.

Studies involving the decomposition of methane on Ni single crystal using surface science techniques are currently underway to characterize more precisely the relevant surface species. Experiments are also in progress to more fully optimize the reaction conditions, e.g., temperature, carbon coverage, pressure, etc.

Production of CO-free hydrogen using stepwise, steam reforming of hydrocarbons has been demonstrated for the production of clean hydrogen for use in fuel cells and other devices or processes with CO-free hydrogen requirements. The hydrogen produced in the second step along with CO_2 can be utilized for other applications such as Fischer–Tropsch synthesis.

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