No deactivated production of hydrogen by pyrolysis of ethane over graphite-based catalysts using membrane-type reactors

Kazuhisa Murata,* Naotugu Ito, Takashi Hayakawa, Kunio Suzuki and Satoshi Hamakawa

National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan.
E-mail: kmurata@nimc.go.jp

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A system consisting of a graphite catalyst and an Ag-Pd membrane reactor was found to be effective for ethane decomposition to hydrogen and carbon, where the H_2/C ratio was approximately 1.5, in accordance with the stoichiometric ratio; catalyst deactivation was not observed during reaction, since the graphite-like carbons produced by the reaction, probably also catalyze the reaction in the temperature range of 800–1000 K.

Hydrogen is expected to be used as an energy source for fuel cells such as the proton-exchange membrane (PEM) type. At present, hydrogen is typically produced *via* steam reforming and/or partial oxidation of hydrocarbon fuel.[1] Alcohols are used as precursors to hydrogen.[2] In these cases, however, carbon monoxide is a co-product. Therefore, the current PEM fuel cells require complete elimination of CO (<1 ppm) from the hydrogen stream in order to prevent poisoning of the Pt catalyst of the cells. An alternative route is to directly decompose the hydrocarbons into hydrogen and carbon. In this case, no CO_2 is formed and the need for subsequent reactions, such as water–gas shift and CO oxidation, is eliminated. Metal oxide catalysts such as Ni/SiO_2 and Fe/Al_2O_3 are usually used for the decomposition reaction. However, over these catalysts, decomposition activity is reduced as the reaction proceeds, due to accumulation of carbon products at temperatures of 600–800 K. The undesirable formation of organic products (CH_4, C_2H_4, *etc.*) is also a significant problem.[3]

In the course of our research work on carbon-based catalysts,[4] we attempted decomposition of ethane to form hydrogen over metal-free carbon catalysts. We found that formation of hydrogen without deactivation was observed over a graphite catalyst over the temperature range 800–1000 K. The reaction was also found to be accelerated by elimination of *in situ* formed hydrogen through a Ag-Pd alloy tube. Now we report some of our results.

Commercially available carbon materials, such as activated carbon (Aldrich), C_{60} soots (MER Corp.) and graphite (Alfa) were dried at 493 K *in vacuo* for 3 h prior to use. The particle sizes of these materials were between 50–300 μ. Catalyst thus pretreated (1 g) was diluted with quartz sand (5 g)† and, for the fixed-bed reactor (FBR), placed in a quartz tube (12 mm inner diameter). An electric furnace was used for heating. The catalyst was pretreated in N_2 at 873 K for 3 h and then a premixed gas of nitrogen–ethane (2–20 vol% C_2H_6, 20 ml min^{-1}) was introduced at atmospheric pressure ($W/F = 125$ g h mol^{-1}).‡ For the Ag-Pd membrane reactor (PMR), a double-tubular type arrangement was used: the inner and outer tubes were Pd-Ag alloy (90Pd10Ag) (250 μ thick and 10 mm outer diameter) and quartz (1.5 mm thick and 19.5 mm inner diameter), respectively. The carbon catalysts were placed between the inner and outer tubes. The catalyst pretreatment was the same as that described above. The premixed gas was passed into the catalyst bed at atmospheric pressure ($W/F = 125$ g h mol^{-1}) and Ar gas (1500 ml min^{-1}) was fed through the inside of the Ag-Pd alloy tube at atmospheric pressure to remove permeated hydrogen. The organic and hydrogen products were analyzed by gas chromatography (GC) on Porapack Q and 5 Å molecular sieve columns, after 30 min on-stream at each temperature, and the yield of carbon was estimated by the mass balance of carbon [eqn. (1)].

$$C_2H_6 \rightarrow 3H_2 + 2C \qquad (1)$$

As shown in Fig. 1, pyrolysis of C_2H_6 occurred at 850–1050 K in the presence of activated carbon catalyst (AC Darco G-60, **1**), and hydrogen, carbon and a small amount of organic material (methane, ethylene, benzene *etc.*) were formed. Over all these runs, the carbon yield estimated from the mass balance was in good accordance with that calculated by weighing after the reaction. The C_2H_6 conversion was as low as 47% at 948 K in the case of the fixed bed reactor (FBR) (Fig. 1). In contrast, the C_2H_6 conversion was found to be enhanced by removal of hydrogen through the Ag-Pd membrane tube and, as a result, was over 90% at 948 K. In this case, over 90% of hydrogen formed was eliminated from the reactant gas *via* permeation into the argon. For comparison, the conversion in a quartz sand/PMR system was less than that for the catalyst **1**/FBR system. Also, the conversion in a PMR system without the argon flow

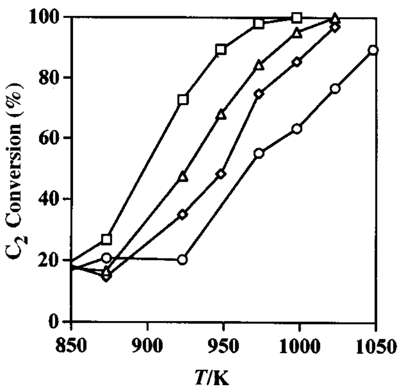

Fig. 1 Comparison of an Ag-Pd membrane reactor (PMR) with a fixed-bed reactor (FBR) for the ethane decomposition over activated carbon catalyst: catalyst = AC Darco G-60, W/F = 12 5 g h mol^{-1}, ethane: N_2 = 10 : 90. (□) PMR, (△) PMR without argon, (◇) FBR and (○) PMR without AC catalyst (quartz sand only).

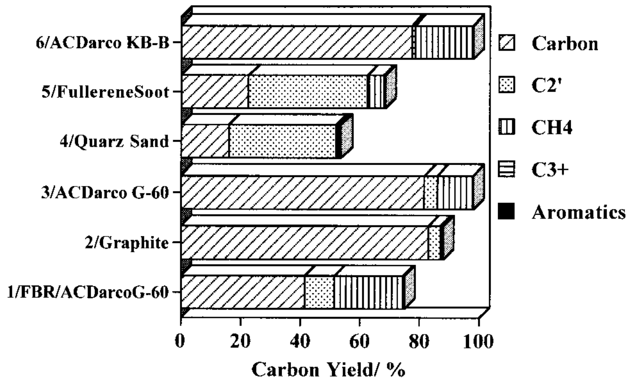

Fig. 2 Effects of carbon catalyst on the activity of ethane decomposition: T = 973 K, W/F = 125 g h mol^{-1}, ethane: N_2 = 10 : 90.

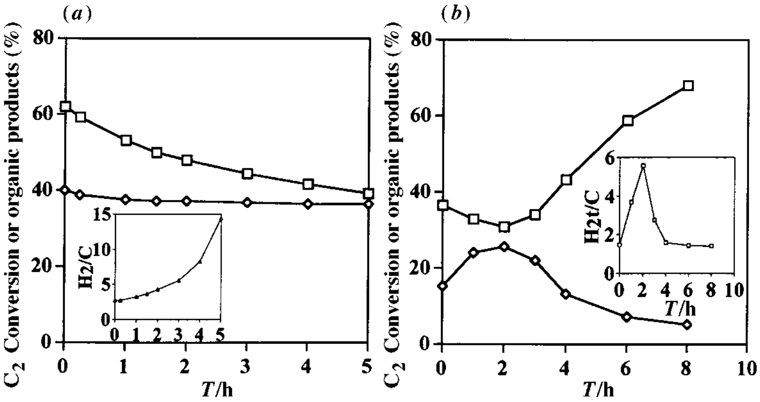

Fig. 3 Change in catalytic activity for the decomposition of ethane as a function of time. (*a*) System = AC Darco KB-B/fixed-bed reactor: (□) C_2 conversion, (◇) organic product yield. T = 923 K, W/F = 125 g h mol^{-1}, ethane: N_2 = 2 : 98. Inset: Plot of H_2/C molar ratio against time. (*b*) System = graphite/Ag-Pd membrane reactor: (□) C_2 conversion, (◇): organic products yield. T = 923 K, W/F = 125 g h mol^{-1}, ethane: N_2 = 2 : 98. Inset: Plot of H_2t/C molar ratio against time.

was between that of the PMR with argon and that of the FBR system.These findings indicate that the combined use of the carbon catalyst and the PMR system was very effective for C_2H_6 pyrolysis.

Fig. 2 shows the effects of some carbon catalyst/PMR systems on the product yields at 973 K. The efficiency of pyrolysis (carbon yield) was in the order: **2**/graphite > **6**/AC Darco G-60 > **3**/AC Darco KB-B > **1**/AC Darco G-60/FBR > **5**/C60 soots > **4**/quartz sand. In the graphite catalyst, in particular, organic by-products were formed only in *ca.* 4% yield. In the activated carbons (**3** and **6**), the yield of organic products was *ca.* 15%, although their carbon yields were close to that on graphite. The use of a fixed-bed reactor (FBR) resulted in the formation of a larger amount of organic products (>35% yield) than that in a Pd-membrane reactor (PMR) (compare **1** and **6**). In the cases of C_{60} soots (**5**) and quartz sand (**4**), the dehydrogenation of ethane to form ethylene predominates over decomposition.

In order to shed more light on the characteristics of carbon catalyst/PMR systems, the effects of the reaction parameters on the ethane decomposition were briefly examined. The effect of the flow rate of the argon on the activity was found not to be significant under the conditions employed, provided the flow rate is above 100 ml min^{-1}. This suggested that the rate of hydrogen permeation was, in general, greater than that of ethane decomposition over the carbon catalyst under the conditions employed. The ethane conversion at 923 K increased with an increase in contact time (W/F = 25–125 g h mol^{-1}). As expected thermodynamically, lower ethane concentrations (2–20%) gave higher ethane conversions, over the temperature range from 773 to 973 K.

The mechanism of decomposition over the carbon catalysts is not clear. However, the reaction is promoted by the removal of the hydrogen formed (Fig. 1) and it seems likely that a material with a graphite-like nature is formed during decomposition, as shown by X-ray powder diffraction and H_2 temperature programmed desorption of the carbon formed, carried out by analyzing methane formed by hydrogenation of the carbon product. It is well-known that catalyst deactivation occurs as a result of the formation of graphite-like carbon[5] when metal-oxide catalysts are used in the temperature range 600–800 K. In fact, even with the activated carbon catalyst (**3**)/FBR system without metal, the ethane conversion at 923 K decreased as the reaction proceeded [Fig. 3(*a*)]; as a result, the H_2/C ratio increased due to the reduction of carbon formation and predominant formation of organic compounds [Fig 3(*a*), inset]. On the other hand, we found that the deactivation did not occur when graphite catalyst (**2**) was used, and the ethane conversion increased [Fig. 3(*b*)] as carbon was formed. In the initial stages, the H_2t/C ratio (the molar ratio of total amount of H_2 to carbon) was greater than 1.5 [the value given by stoichiometric ethane decomposition, see eqn. (1)] because of the formation of organic products (>20%). After 5 h, however, the ratio approached 1.5, and subsequently remained constant; this indicated that the decomposition reaction occurred predominantly. This is the first example of a catalyst not being deactivated even at high ethane conversion. It is possible that the graphite-like carbon produced by the reaction also efficiently catalyzes the reaction in the membrane reactor§ over the temperature range 800–1000 K. Further investigations are currently underway to elucidate the decomposition mechanism operative in the graphite/Ag-Pd membrane reactor system.

In summary, we have found that graphite is a very good catalyst for converting ethane to hydrogen in a Ag-Pd membrane system with high activity and no deactivation. We believe this to be an excellent procedure for hydrogen production for PEM fuel cells.

Notes and references

† In order to ensure a smooth gas flow, a weight ratio of graphite : quartz of 1 : 5 was used; the results were not affected by the amount of quartz.

‡ *W/F* = weight of catalyst (g) over flow rate (mol h^{-1}).

§ In these cases, both graphite and PMR are important. In fact, the minimum amount of organic products was formed in the graphite catalyst/PMR system, as can be seen from Fig. 2. In the graphite/PMR system, graphite-like carbon formed over the graphite surface would not undergo successive reaction such as methane formation from hydrogen and the carbon, because almost all of the hydrogen was eliminated from the graphite surface. Thus, it seems likely that the stable graphite-like carbon product could also catalyze the reaction. On the contrary, in the AC/FBR system, the carbon product could undergo many successive reactions, since hydrogen was still present over the surface. Thus, in this case, it seems unlikely that the carbon product could catalyze the reaction.

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