CATALYTIC METHANOL DISSOCIATION

Yuri Aleinikov, Valentin Fainberg*, Alina Garbar, Marcel Gutman, Gad Hetsroni,
Yury Shindler, Leonid Tartakovsky, and Yoram Zvirin

Faculty of Mechanical Engineering, Technion - Israel Institute Of Technology
* Conference Lecturer

ABSTRACT

Results of the methanol dissociation study on copper/potassium catalyst with alumina support at various temperatures are presented. The following gaseous and liquid products of the catalytic methanol dissociation are obtained: hydrogen, carbon monoxide, carbon dioxide, methane, and dimethyl ether. Formation rates of these products are discussed. Activation energies of corresponding reactions are calculated.

BACKGROUND

Methanol is widely considered as a "clean" alternative fuel for gasoline and diesel engines, mainly due to the potential of reducing substantially engine exhaust emissions and of improving fuel economy. It is available in many regions and can be efficiently and economically produced in large quantities from a variety of feedstocks, including natural gas, coal and biomass. Some disadvantages of liquid methanol as fuel (heat of vaporization is higher and heat of combustion is lower than those of gasoline and diesel fuel) may be overcome by using heat of exhaust gases for previous methanol evaporation and catalytic conversion to gaseous products.

Methanol dissociation is investigated today, because it is a promising hydrogen source for propulsion systems. Methanol dissociates in the presence of a catalyst into hydrogen and carbon monoxide. Several catalysts on base of palladium [1], copper/chromium [2], or copper/potassium [3] have been proposed for methanol decomposition into CO and H_2.

Methanol dissociation products have a 20% higher heating value than liquid methanol since the reaction is endothermic. It gives fuel economy improvement and CO_2 reduction because the energy needed for the reaction is supplied by waste heat recovery of exhaust gases. High hydrogen content (above 30 vol.%) of the dissociated methanol allows much leaner combustion than that of liquid methanol or gasoline, resulting in a sharp reduction of NO_x formation and additional decrease in CO_2, CO, and hydrocarbon emissions. Methanol dissociation also leads to the reduction of particulate emission from diesel engines.

Using products of the on-board methanol dissociation as a fuel for an internal combustion engine makes it possible to benefit from hydrogen-enriched gaseous fuel, to eliminate the known problems of on-board hydrogen storage and to prevent very high expenses related to the use of fuel cells [4].

The main goal of this research is to investigate selectivity of methanol dissociation on the cheap and active catalyst $CuCl-KCl/Al_2O_3$ into different gaseous products: hydrocarbons, ethers, aldehydes, carbon oxides, and hydrogen. Understanding of these processes allows optimization of a catalytic reformer and possibility to adapt its operation performance to different applications, e.g. internal combustion engines (ICE) and fuel cells [5].

One of the practical aspects of this investigation is a search of an appropriate temperature regime and flow range relevant for the engine operation regime. Laboratory experiments enable us to derive guidelines for optimal design and performance of full-size catalytic reactors (reformers) for methanol dissociation.

EXPERIMENTAL

A laboratory unit for the investigation of methanol decomposition was designed and assembled (Fig. 1). The unit enables us to study the process of dissociation using various temperatures, methanol volume velocities and catalysts.

At the first stage of the investigation, a copper-potassium catalyst was used. It was prepared by impregnating alumina granules with an aqueous solution of CuCl and KCl.

GC analysis of gaseous and liquid samples was carried out on the gas chromatograph VARIAN 3600 with software VARIAN STAR on PC. Each sample was injected 3 - 5 times under different conditions; the difference between the values was less than 3 %.
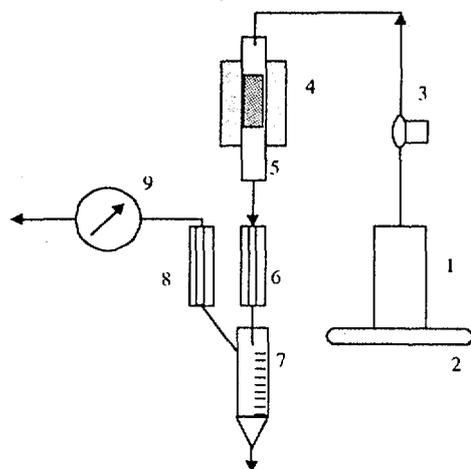
The results of the first series of the experiments are presented in Table 1. One can see that the applied catalyst allows to achieve a relatively high degree of methanol dissociation (91%) at temperatures >530°C.

The degree of the dissociation and the volume velocity of the reaction increase rapidly with the temperature. Hydrogen, carbon monoxide, carbon dioxide, dimethyl ether (DME), water and methane are present among the products of the methanol dissociation. Other hydrocarbons and ethers, aldehydes or alcohols are practically absent. The reaction of methanol dehydration into DME prevails under studied conditions.

The products obtained are formed according to the following reactions:

$$CH_3OH \rightarrow 1/2\ (CH_3)_2O + 1/2\ H_2O \quad (1)$$

$$CH_3OH \rightarrow H_2 + 1/3\ (CH_3)_2O + 1/3\ CO_2 \quad (2)$$

$$CH_3OH \rightarrow CO + 2\ H_2 \quad (3)$$

$$CH_3OH \rightarrow H_2 + 1/2\ CH_4 + 1/2\ CO_2 \quad (4)$$

A quantitative analysis of the methanol dissociation products allowed to appreciate a contribution of each of these stechiometric reactions - routes of the methanol dissociation - to the process (Table 2).

Both of the two first reactions produce DME. The total contribution of the routes (1) and (2) is reduced with increase of temperature, despite the rise of the second route's contribution.

Three last reactions produce hydrogen. These reactions are characterized by a high energy of activation, therefore the volume of hydrogen significantly grows at high temperatures.

Figure 1. Laboratory unit for methanol dissociation: 1- methanol vessel; 2- balance; 3 - peristaltic pump; 4 - tube oven; 5 - reactor with a catalyst; 6 - water cooler; 7 - receiver; 8 - ice cooler; 9 - gas meter.

Analysis of the liquid products was performed by using column DB-5 (l = 60 m, d = 0.32 mm), employing helium carrier gas with rate of 1 ml/min, and an injector with a split ratio of 1:100. The column temperature was constant at 30°C.
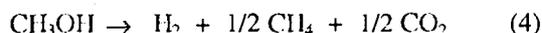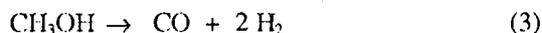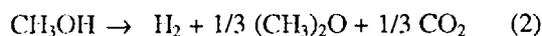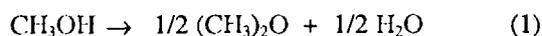
Calibration was made by using of internal standard method with ethanol as a standard. The calibration curve was built on the base of seven chromatograms.

For more complete determination of the gas components, four regimes of the GC work were used. Calibration curves for some of the components (hydrogen, methane, carbon monoxide and carbon dioxide) were built by using external standards. Response factors for others were taken from the paper [6].

Table 1.
Product Composition and Degree of Methanol Dissociation at Various Temperatures

Experiment number	I	II	III
Catalyst temperature, °C	472	504	531
Volume rate of dissociation, h⁻¹	4024	5003	9306
Degree of methanol dissociation, %	36.3	52.4	91.2
Product composition, mole %:			
H_2	4.2	22.3	33.9
CO	1.8	6.6	11.1
CH_4	0.1	0.4	0.8
$(CH_3)_2O$	16.2	16.0	23.7
CH_3OH	61.4	38.1	6.1
CO_2	0.7	2.8	3.8
H_2O	15.6	13.6	20.7

Table 2.
Contribution of different routes at various temperatures to the total methanol dissociation process and their energies of activation

Route	Contribution, %			E act.,
	472 °C	504 °C	531 °C	KJ
(1)	89	64	65	42.6
(2)	5	19	16	150.8
(3)	5	15	17	178.9
(4)	1	2	2	185.5

The contribution of the last route is minimum under all studied conditions, but the rate of methane formation grows at high temperatures (Table 3).

Table 3.
Formation rates of the methanol dissociation products at various temperatures.

Product	Formation rate, mole/cm^{3}min			E act.,
	472 °C	504 °C	531 °C	KJ
CO	$1.42 \cdot 10^{-4}$	$5.28 \cdot 10^{-4}$	$1.09 \cdot 10^{-3}$	173.7
CO$_2$	$5.09 \cdot 10^{-5}$	$2.26 \cdot 10^{-4}$	$3.70 \cdot 10^{-4}$	170.1
CH$_4$	$8.33 \cdot 10^{-6}$	$3.47 \cdot 10^{-5}$	$7.41 \cdot 10^{-5}$	185.8
H$_2$	$3.37 \cdot 10^{-4}$	$1.77 \cdot 10^{-3}$	$3.33 \cdot 10^{-3}$	195.9
(CH$_3$)$_2$O	$1.24 \cdot 10^{-3}$	$1.27 \cdot 10^{-3}$	$2.33 \cdot 10^{-3}$	51.0

The formation rates were calculated on the formula:

$$W = 1/V * dN_A/d\tau ,$$

where V - volume of catalyst, dN_A - change in the number of moles of the product A during the passing of the methanol vapor through V, $d\tau$ - time of the methanol contact with catalyst.

The formation rate of all products increases by 2-10 times with increase in temperature from 470 to 530°C. The formation rate of DME at 472°C is significantly higher than that of: hydrogen (by 4 times), carbon monoxide (by 9 times), and of course carbon dioxide and methane. That is why DME prevails among the methanol dissociation products (Table 1). At high temperatures (500 - 530°C) the formation rate of hydrogen exceeds that of DME, and the formation rate of carbon monoxide is of the same order than that of DME. Therefore, gas volume increases and a degree of the methanol dissociation through one pass over the catalyst bed also significantly increases.

The effect of the temperature on the rate of the reactions (1-4) is shown in Figure 2, where the

values of the efficient reaction rate K$_{eff}$ were calculated to compare values of activation energy for different routes.
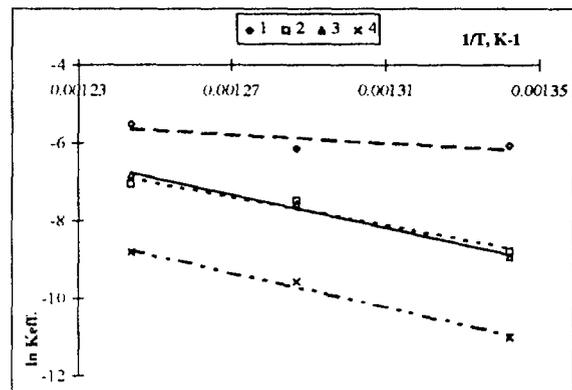

Figure 2. Reaction rate versus temperature.

The obtained results show that methanol can be a good source of various kind of chemicals and an environment-safe fuel and that an effective, non-expensive reactor for methanol dissociation can be developed.

REFERENCES

1. J.-J. Chen, et al., Spectroscopic Studies of Methanol Decomposition. Surface Science, 328, pp. 248-262, 1995.
2. Wu-Hsun Cheng, Deactivation and Regeneration of Cu/Cr Based Methanol Decomposition Catalysts. Appl. Catal. B., 7 (1 - 2), pp. 127-136, 1995.
3. A. Schmitz, D. Eyman and K. Gloer, Highly Active Methanol Dissociation Catalysts Derived from Supported Molten Salts. Energy and Fuel, 8, pp. 729-740, 1994.
4. L. Tartakovsky, Y. Aleinikov, V. Fainberg, A. Garbar, M. Gutman, G. Hetsroni, Y. Shindler, and Y. Zvirin. Hybrid Propulsion System Based on an ICE Fueled by Methanol Dissociation Products - General Concept. 31-st ISATA Conf., Duesseldorf, Germany, June 1998.
5. L. Tartakovsky, Y. Aleinikov, V. Fainberg, A. Garbar, M. Gutman, G. Hetsroni, Y. Shindler, and Y. Zvirin. General concept of a gas engine for a hybrid vehicle, operating on methanol dissociation products, ibid.
6. Dietz, W. A. Response Factors for Gas Chromatographic Analyses, J. Gas Chromatogr., 1967, vol. 5, page 68.