Journal Club 2011/11/10 Tatsuaki Matsubara

Selective, Room-Temperature Transformation of Methane to C1 Oxygenates by Deep UV Photolysis over Zeolites

Sastre, F.; Fornés, V.; Corma, A.; García, H.

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1. Introduction

1-1. Methane (CH_4) as natural gas

- CH_4 is the principal component of most natural gas and widely used.
  - Home and industrial heating
  - Producing synthesis gas for methanol production
  - Feeding gas for Fischer-Tropsch units
- *Problems:* - Difficulty to transport from reserves.
  - Needs high energy to convert.

➔ It would be on much interest to convert CH_4 into liquid fuels, particularly methanol and C1 oxygenates in mild condition.

1-2. Conversion of CH_4 to MeOH

- Currently industrial processes:

(1) Indirect oxidation to MeOH and Fischer-Tropsch process [1]

$$CH_4 + H_2O \xrightarrow[> 700\ ^\circ C]{cat.} CO + 3H_2 \xrightarrow[240\text{–}260\ ^\circ C]{50\text{–}100\ atm} CH_3OH + H_2 \quad (1)$$

$$\xrightarrow[heat]{Fe\ or\ Co} \text{hydrocarbons} \quad (2)$$

- Recently developed in laboratories:

(2) α-oxygen

$$N_2O \xrightarrow[250\ ^\circ C,\ 0.8\ Torr]{Fe\text{-doped zeolite}} N_2 + (O)_\alpha \quad (3)$$

$$CH_4 + (O)_\alpha \xrightarrow[rt]{} (CH_3OH)_\alpha \quad (4)$$

- $(O)_\alpha$ is activated oxygen.
- Initial treatment (O_2, 550 °C, 0.8 Torr) is required.

Is it possible to convert CH_4 into MeOH under mild conditions?

1-3. This Work

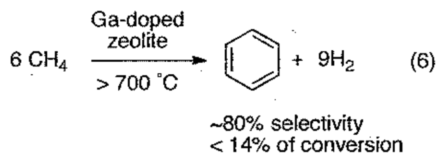
- *Concept*: General ability of radicals to readily activate CH_4 under mild conditions

$$\text{"In"}^\bullet + CH_4 \xrightarrow{-\text{"In"H}} CH_3^\bullet \xrightarrow{H_2O} CH_3OH \quad (5)$$

- Original photocatalytic process:
  - Deep UV irradiation (< 200 nm) of CH_4 over *zeolite*

What is zeolite? - Microporous, aluminosilicate materials

- Previous method of conversion of CH_4 with zeolite:



- Various kinds of structure can be synthesized. (194 frameworks are identified until 2010)
- Zeolite beta was employed:
  (1) Especially large pore (5–7 Å)
  (2) High Si/Al ratio

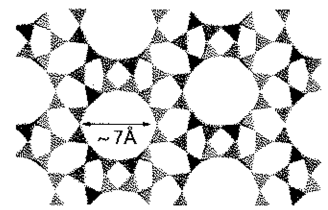


Figure 1. The structure of zeolite-beta

- *Implementation*: Generate silyloxy radicals by deep UV irradiation over zeolite

$$\equiv Si\text{–}OH \xrightarrow[(\lambda < 200\ nm)]{h\nu} \equiv Si\text{–}O^\bullet + H^\bullet \quad (7)$$

$$2 \equiv Si\text{–}O^\bullet + CH_4 \longrightarrow \equiv Si\text{–}OCH_3 + \equiv Si\text{–}OH \quad (8)$$

$$\equiv Si\text{–}OCH_3 + H_2O \longrightarrow \equiv Si\text{–}OH + CH_3OH \quad (9)$$

- Deep UV irradiation should give hydrogen atom and silyloxy radical. [2]
- Hydrogen atom from CH_4 should be abstracted to form silylmethyl ether. (eq. 7, 8)
- Microporus structure of zeolite is expected to capture CH_4, preventing CH_3 radicals from side reactions toward hydrocarbons.

2. Results and Discussion

2-1. Design and Synthesis of Zeolites

- 4 types of zeolite beta were synthesized following the reported procedures. (Table 1) [3]

Table 1. Synthesized zeolites and their nature

zeolite	Si/Al	pore size (Å)	surface area (m^2/g)	pore volume (cm^3/g)	population of silanol groups[a]
silica	only Si	no micropores			100
beta (Si, F)	only Si	7.1 x 6.6	481	0.22	20
beta (Al, F)	22		503	0.23	22
beta (Si, OH)	only Si		490	0.22	33
beta (Al, OH)	22		540	0.24	30

[a] Relative population of silanol groups

2-2. Deep UV Photolysis

- Methanol and other C1 oxygenates were obtained *only in the presence of O_2*.

zeolite beta (Al, F) — 1 h, rt; 165 nm UV; 0.5 atm:

$$\xrightarrow{CH_4/N_2} \text{hydrocarbons} + H_2$$

$$\xrightarrow{CH_4/\mathbf{O_2}} CH_3OH + \text{C1 oxygenates} \quad (10)$$

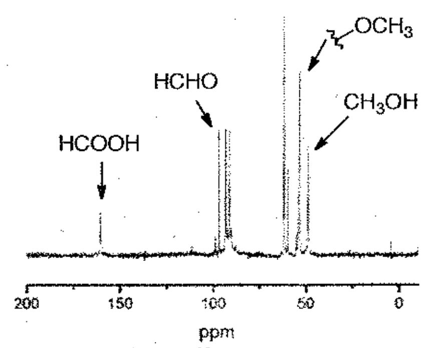


Figure 2. MAS ^{13}C NMR of zeolite after UV irradiation

2-3. Effect of the Nature of the Zeolite Catalysts

Table 2. Product Distribution

Reaction Condition:

$$CH_4 \xrightarrow[\text{5 min, rt, 0.5 bar, 185 nm-UV}]{\text{Silicates, 20 vol\% } O_2} \text{Products} \quad (11)$$

solid	silanol groups[a]	total conversion	absorption rate	products released to the gas phase (%)			products absorbed in the silicate (%)		
				C_2	H_2	CH_3OH	HCHO	HCOOH	CH_3OH
silica gel	100	0.5	0.85	54.2	29.1	--	19.6	28.3	52.1
beta (Si F)	20	**0.86**	99	--	20.7	79.3	23.8	25.5	50.7
beta (Al F)	22	**1.63**	> 99	--	100	--	25.8	24.4	49.8
beta (Si OH)	33	**2.01**	> 99	--	100	--	21.2	30.8	48.0
beta (Al OH)	30	**1.66**	98	84.2	15.8	--	16.4	28.7	54.9
no catalyst	0	0.49	0	73.5	3.8	5.1	23.9	25.8	50.3

[a] Relative population of silanol groups

- Photolysis over silica gel gives the lowest conversion of the series, though the amount of silanol groups is much larger on the amorphous silica catalyst.
  - ➢ Zeolite structure is advantageous to convert CH_4.

- Micropore in zeolite may be able to capture CH_4 molecule ➔ Prevent side reactions.
  - Good selectivity toward C1 oxygenates (> 98% selectivity), although beta (Al OH) showed a hydrocarbon generation.

☆<u>The larger the number of internal silanol groups, the higher the catalyst activity (higher total conversion).</u>
➔ Silanol groups are actually involved in CH_4 conversion.

- CH_4 conversion increases with the amount of photocatalyst (Table 3).

Table 3. CH_4 conversion as a function of the amount of beta zeolite

mass photocatalyst (g)	total conversion	products released to the gas phase (%)			products absorbed in the silicate (%)		
		C_2	H_2	CH_3OH	HCHO	HCOOH	CH_3OH
0.1	1.8	--	100	--	23.9	25.8	50.2
1	3.9	--	100	--	25.4	24.3	50.3
2	6.2	--	100	--	17.7	25.8	56.5
1[a]	**13**	**32.15**	**53.12**	**--**	**36**	**22.5**	**40.5**

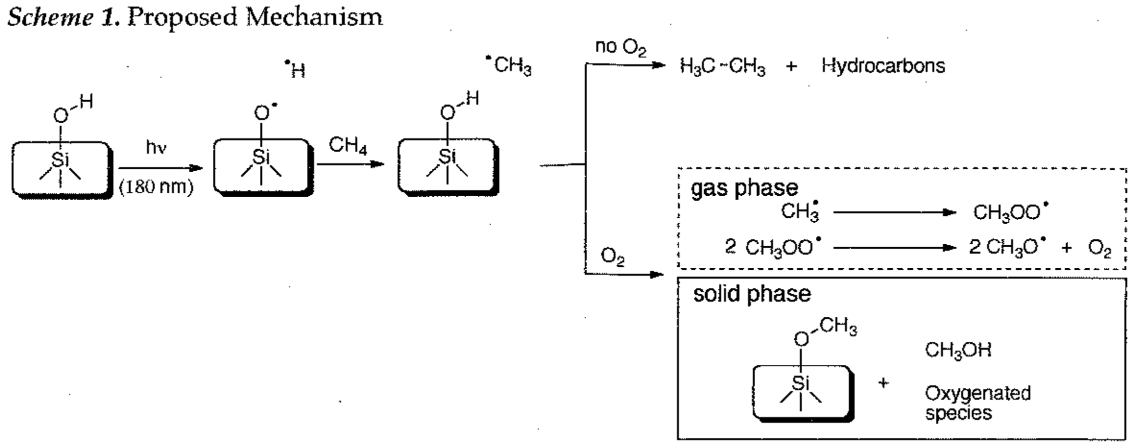
[a] After 1 h irradiation

☆<u>CH_4 conversion above 13% could be obtained in 1 h with selectivity over 99% toward oxygenated products.</u>

2-4. Reaction Mechanism

- UV irradiation may generate silyloxy radicals and hydrogen atom.
- The presence of oxygen is crucial to scavenge CH_3 radicals, stopping the formation of hydrocarbons (Scheme 1).

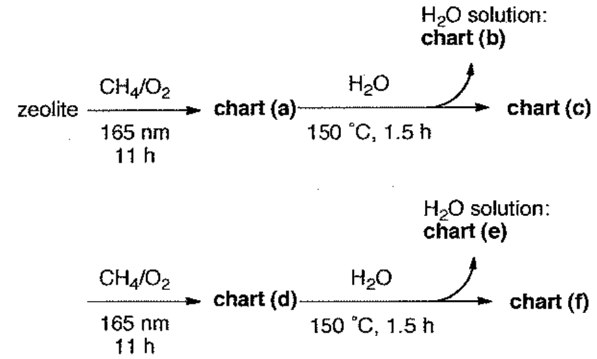
Scheme 1. Proposed Mechanism



2-5. Usability of this Method

- Energy consumption:
  7.16 Gcal mol^{-1} (13% conversion with 185 nm lamp, 60 min irradiation)
  cf.) 15.9 Gcal mol^{-1} (transformation of 1 mol of CH_4 to CO/H_2) [4]
- Two-step cycle was achieved (Scheme 3, Figure 2).

Scheme 3. Two-step cycle



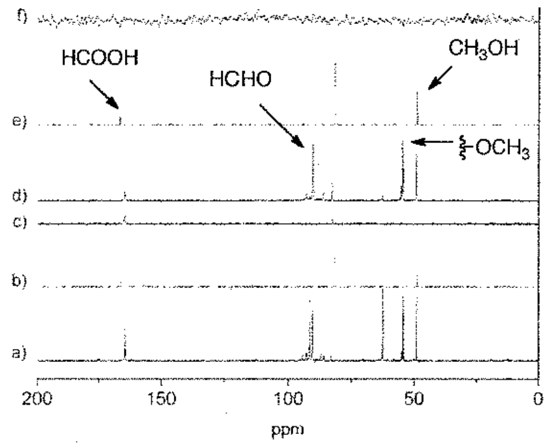


Figure 2. ^{13}C NMR of two-step cycle

- Zeolite can be reused (at least 3 times) without observing changes in the behavior of the material.
- Remaining water doesn't affect to the activity of zeolite.

3. Conclusions

- 13% conversion of CH_4 into C1 oxygenates has been accomplished with deep UV irradiation over zeolites at room temperature.
- Oxygen is crutial for the selectivity toward C1 oxygenates, over 95%.
- Estimated energy consumption is about one-half than the energy required for the conventional CH_4 steam reforming process.

4. References

1. Ismagilov, Z. R.; Matus, E. V.; Tsikoza, L. T. *Energy Environ, Sci.* **2008**, *1*, 526–541.
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