Beneficial Use of Natural Gas with Novel Catalysts

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Abstract: Because of recent situation of resources and energy, we focused on catalytic reactions related to natural gas, and especially on FT process among them, through which process we can make fuels and/or petrochemical substrates. We developed catalysts which are zeolites including metal oxides and succeeded to gain much higher selectivity of products with our novel catalysts than conventional catalysts. This high selectivity would be derived from pore size of zeolites.
Keywords: Zeolite, FT process, Selectivity of products

1. Introduction

We focused on natural gas that has been low price without volatility of that price since shale gas revolution[1]. Among those catalytic reactions related to natural gas, FT process is one of the most appropriate way to use natural gas beneficially. Through this process, natural gas can be changed to petrochemical substrates (~C5) and also to fuels (C6~). Although this process would be useful, this process has a big problem for industrial application. That is low selectivity of products. Therefore, after the FT process, decomposition process and/or purification process are needed as an extra process. If this problem would be solved, it could be possible that those operations are skipped and that advantageous effect would be huge. To achieve the problem, we developed the catalysts which were zeolites including metal oxides being active for FT process.

2. Experimental

Catalysts written in Table 1 were prepared. After reduction treatment with hydrogen of these catalysts, they were used for FT process. Conditions of tests are shown as below. (Table 1) We used Ru/Al_2O_3 as conventional catalysts for this process. Zeolites including CoOx and zeolites including FeOx are our developed catalysts.

Table 1. Conditions of tests

No	Catalyst	Reaction gas	GHSV	Reaction temperature	Conversion rate	Selectivity of propylene
1	Ru/Al_2O_3	H_2/CO (2/1) mixed gas	2860 /h	523 K	56 % at 573 K	3.5 % at 523 K
2	Zeolites including CoOx				-	23 % at 523 K
3	Zeolites including FeOx				-	16 % at 523 K

3. Results and discussion

As a result of experiments, much higher selectivity of products was gained than conventional catalysts. (Figure 1) Additionally, the ratio of olefin was higher than the conventional one. (Table 2) This result is amazing because olefin is very useful for industrial application compared to paraffin as petrochemical substrates. Especially, a good yield of propylene was given. (Figure 2) This beneficial result was brought by small pore of zeolites. We compared the pore size of zeolites and the molecular size of hydrocarbons, and found out pore size of zeolites matched with molecular size of propylene. (Table 3) It was suggested that the high selectivity of hydrocarbons was derived from confinement space of zeolites.

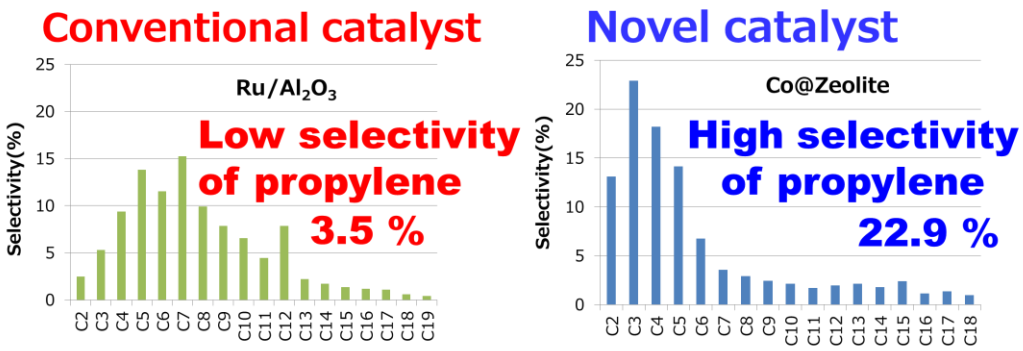

Figure 1. Selectivity of products

Table 2. Ratio of olefin

	Ratio of olefin (%)	
Number of carbon	Zeolites including CoOx	Zeolites including FeOx
C3	97.7	100.0
C4	74.9	69.7
C5	79.8	55.5
C3~C5	83.2	78.7

Catalyst	Selectivity of propylene
CoOx@MFI	22.9 %
FeOx@MFI	15.8 %
Ref)Ru/Al_2O_3	3.5 %

Figure 2. Selectivity of propylene

Table 3. Pore size of zeolites and size of products

Classification		Size (nm)
Pore size of zeolites		0.5 - 0.6
Molecular size of hydrocarbons	Methane	0.26
	Ethylene	0.39
	Propylene	0.52
	Butene	0.65
	Pentene	0.78
	Hexene	0.91

4. Conclusions

This result suggested that propylene can be directly, effectively produced from syngas, and it would be possible that decomposition and purification needed for conventional FT process are skipped. So we think this result could be important industrially. And this result suggested to be derived from the pore size of zeolites, so desired products could be gained by changing the pore size of zeolites. So this result is also academically exceptional.

References

1. International Energy Agency, World Energy Outlook 2017.