

# Effect of Catalyst Acidity on Thermal Cracking and Catalytic Cracking of Ethylene at High Temperature and Pressure

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**Abstract**—In this work, the effect of catalyst acidity on the thermal cracking vs. catalytic cracking of ethylene reactant to olefins and paraffin products at temperature 723 K and 25 atm was investigated over Silica-supported tungsten, zeolite, and gamma alumina. Silica was used as an inert bed for investigating the thermal cracking of ethylene. Catalyst acidity was determined using means of Ion-Exchange-Titration and Ammonia Temperature Programmed Desorption (NH<sub>3</sub>-TPD). It has been found that thermal cracking over an inert silica bed exhibited much higher contribution to ethylene cracking than those of catalytic cracking over gamma alumina, zeolite, and silica-supported tungsten, respectively. One of discovered interesting point is that the paraffin product is mainly contributed from only catalytic cracking in which high acidity resulting in high paraffin yield.

**Keywords**— Thermal cracking, Catalytic cracking, Ethylene

## I. INTRODUCTION

ETHYLENE has been one of the important chemicals for industry used for various applications such as the reactant for dimerization, oligomerization, polymerization, metathesis, and alkylation [1]-[5]. For the reaction having the involvement of ethylene that needs high reaction temperature (more than 473 K), the formations of methane, ethane, propane, butane, and so on have been found and reported as a cause from cracking reaction [6]. However, this has been still in doubt the true reaction mechanism to convert the ethylene to these paraffin [1]. Thus, clear understanding regarding

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this doubt will be an importance for industry to avoid the ethylene cracking side reaction.

In this work, the first objective was focused on the comparison effect between thermal and catalytic cracking of ethylene. Silica-supported tungsten, zeolite, and gamma alumina were used to investigate the effect of catalytic cracking as a function of catalyst acidity while inert silica bed was used to represent the thermal cracking at the same WSHV with those of catalytic cracking. Product distribution from each thermal and catalytic cracking was also elucidated.

## II. EXPERIMENTAL

### A. Catalyst Preparation

Inert silica is Davisil Grade 646 which was supplied from Sigma-Aldrich, Gamma alumina was prepared by the calcination of Boehmite at temperature 823 K while Zeolite-Y was supplied from Tosoh. The silica-supported tungsten was prepared by incipient wetness impregnation of an aqueous solution of ammonium metatungstate hydrate (Aldrich, 99.9 %).

### B. Characterization

The total acid content of catalysts was measured by temperature programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD), using a Micromeritic Chemisorb 2750 automated system. The catalyst was heated and the TPD profile was detected by TCD detector and analyzed with a ChemiSoft TPx software and ammonia effluent was kept by boric acid solution (20g/dm<sup>3</sup>) and finally titrated with a 0.01 N aqueous HCl solution the result was prepare with the acidity from the areas of the desorption profiles. The number of bronsted acid sites was also estimated by using a method involving an aqueous Ion-Exchange-Titration of the catalyst H<sup>+</sup> ions with Na<sup>+</sup> ions, followed by titration of the resulting solution.

### C. Reaction Testing

The catalyst sample was placed at the center of stainless steel tubular reactor with inner diameter (ID) of 7.5 mm. The catalyst was pretreated at 823 K under mainly nitrogen atmosphere. The reaction condition was as follows: pressure 25 atm, temperature 723 K. Feed composition is ethylene: nitrogen atomic ratio = 1:1. Product analysis was performed using an online-GC which is Agilent Technologies GC

system 7820 A gas chromatograph equipped with a column of packed 10% silicone SE-30 (3.02 m with 0.53 mm ID) and a flame ionization detector using helium as the carrier gas (7 cm<sup>3</sup>/min).

### III. RESULTS AND DISCUSSION

Fig. 1 shows the NH<sub>3</sub>-TPD over silica-supported tungsten, zeolite, gamma alumina, and inert silica revealing that silica-supported tungsten exhibits highest acidity, then the zeolite, gamma alumina, and silica respectively. The result from NH<sub>3</sub>-TPD is also in good agreement with that of Ion-Exchange-Titration which summarized in the Table 1. Inert silica exhibits very low acidity confirming that it could be used for representing the thermal cracking.

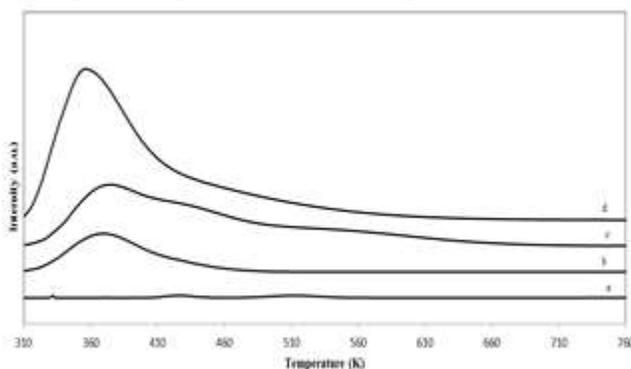


Fig. 1: NH<sub>3</sub>-TPD of (a) silica, (b) gamma alumina, (c) zeolite, and (d) silica-supported tungsten

TABLE I  
ACIDITY SUMMARY FROM NH<sub>3</sub>-TPD AND ION-EXCHANGE TITRATION

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Zeolite-Y	SiO <sub>2</sub> -supported tungsten
Acidity from NH <sub>3</sub> -TPD* (μmol NH <sub>3</sub> /g-catayst)	0.1	20.9	53	202
Acidity from NH <sub>3</sub> -TPD** (μmol NH <sub>3</sub> /g-catayst)	0.25	18.8	46.5	182
Acidity from ion exchange (μmol H <sup>+</sup> /g-catayst)	0.04	5.25	40.95	115.5

\* acidity from area of NH<sub>3</sub> TPD

\*\* acidity from titration of H<sub>3</sub>BO<sub>3</sub> with HCl

Fig. 2 shows the catalytic cracking conversion at 723 K and 25 atm of ethylene to those of methane, ethane, propane, and butanes over the silica-supported tungsten, zeolite, and gamma alumina compared with the thermal cracking through an inert silica bed. It reveals surprisingly that thermal cracking over inert silica bed exhibited much higher contribution to ethylene cracking than those of catalytic cracking over silica-supported tungsten, zeolite, and gamma alumina, respectively. Increase high level of acidity gave less contribution to ethylene cracking, only approximately 10% incremental of the cracking conversion compared with that of thermal cracking over inert silica bed which contributed the

ethylene cracking up to 30%.

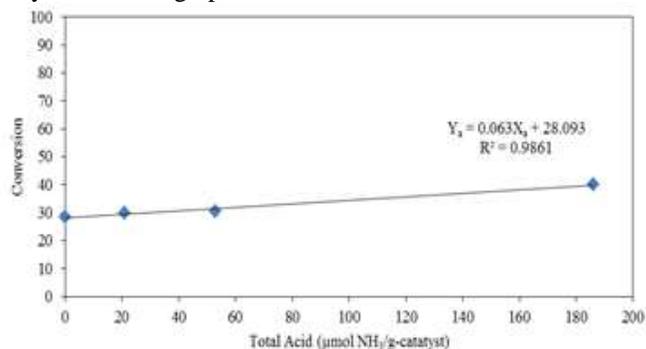


Fig. 2 Ethylene cracking conversion over various catalyst acidities

Fig.3 shows the paraffins yield from the cracking of ethylene at 723K and 25 atm over silica-supported tungsten, zeolite, and gamma alumina compared with the thermal cracking through an inert silica bed. The observed paraffins products are methane, ethane, propane, and butanes revealing surprisingly that product paraffins formation mainly contributed from the catalytic cracking in which higher level of acidity gave also higher paraffins yield from ethylene cracking whereas the thermal cracking over an inert silica bed causes mainly the formation of product olefins like propene and butenes.

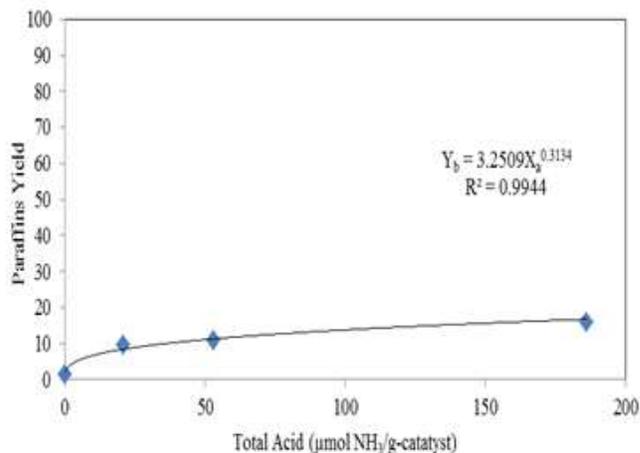


Fig.3: Paraffins yield from ethylene cracking over various catalyst acidities

### IV. CONCLUSION

Catalytic cracking of ethylene under high temperature and pressure (723 K and 25 atm.) over various acid catalysts was investigated in order to compare with the thermal cracking using an inert silica bed to keep the same reaction WSHV. It was surprisingly found that thermal cracking of ethylene exhibited much higher contribution to ethylene cracking than those of catalytic cracking over silica-supported tungsten, zeolite, and gamma alumina, respectively. Moreover, the formation of paraffin from the ethylene cracking was found to be mainly contributed from the catalytic cracking whereas thermal cracking caused only the formation of olefins product.

#### ACKNOWLEDGMENT

The authors would like to thank SCG Chemicals, the financial supports from Chulalongkorn University.

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