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## Upgrading of stranded gas via non-oxidative conversion processes

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### ABSTRACT

Ethane aromatization was carried out using metal promoted ZSM-5 catalysts. Desired products including ethylene and aromatics were obtained over Pt and Mo promoted ZSM-5 zeolite under reaction conditions of 600 °C, 0.1 MPa and GHSV = 1000 h<sup>-1</sup>. Results indicated that aromatics were formed via ethylene intermediate. Although ethane conversion and selectivity to aromatics were influenced by metal promoters, the distribution of benzene, toluene, xylenes and C<sub>9</sub> aromatics depends mainly on the shape selective property of the ZSM-5. Ethane aromatization catalyst deactivated over time due to carbon deposition and metal leaching. Although oxidative regeneration could recover 90% activity, the catalyst deactivated even faster after regeneration. For the purpose of economic comparison between direct and indirect natural gas conversion, the performance of edge coated Co-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Fischer-Tropsch synthesis catalyst was presented. Even with capital savings on downstream refining, indirect natural gas conversion shows lower internal rate of return (IRR), largely because of higher capital and operating costs in syngas production.

### 1. Introduction

There are abundant gas resources worldwide which are either physically or economically stranded. These gases include flaring gas in shale oil field, refinery off-gas, coal-bed methane, shale gas in geographically disadvantaged locations, etc. A recent study identified approximately 450 Tcf of natural gas stranded in fields greater than 50 Bcf that can be produced and gathered for less than 0.50 U.S. \$/million Btu [1]. Upgrading of these gases to value-added liquid products could reduce the demand on crude oil in the United States. Typically, stranded gases contain mainly methane but flaring gas from Bakken, North Dakota, contains over 20% ethane and propane [2]. As described in Table 1, in some regions of the United States, the price of ethane is actually lower than natural gas [3].

Indirect conversion of natural gas to liquid products (GTL) via syngas route has been commercialized but it requires huge capital investment. Shell's Pearl GTL plant is the world's largest source of gas-to-liquids products, capable of producing 140,000 barrels of GTL products each day. According to Shell, capital cost of the project is \$18–19 billion [4]. Direct conversion of natural gas without going through syngas route has been under investigation in the past 5 decades, but no commercial processes are practiced to date. A large number of studies have been published on the subject over the past 50 years.

This study emphasizes the upgrading of undervalued ethane and propane into aromatics and olefins. The high value chemicals that zeolite catalysts used for aromatization reaction of short chain paraffins consist mostly of the ZSM-5 [5]. Report indicates that ZSM-5 possesses shape selective and acidic properties [6]. For the aromatization of ethane, ZSM-5 modified with transition metals have been reported [7–9]. High activity and selectivity of metal-promoted ZSM-5 for ethane aromatization was reported [10]. As regards the formation of aromatics, MoO<sub>3</sub>/ZSM-5 proved to be the most active catalyst [11–16]. Other transition metals used as promoters include gallium [17]. However, the catalytic activity decreased dramatically with time on stream. In order to be commercially viable, an economical and scalable catalyst regeneration procedure is necessary for direct conversion of stranded gas.

This study is focused on catalytic conversion of short-chain paraffins to aromatics and olefins. Meanwhile, different approaches in upgrading of stranded gases including technical and economic feasibilities are compared.

### 2. Experimental

Non-oxidative ethane conversion catalysts were synthesized using H-form ZSM-5 zeolite obtained from Zeolyst International. The Si/Al ratio of the H-ZSM-5 is 30 and the content of Na<sub>2</sub>O was lower than

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**Table 1**

Regional Gas Price.

Gas price is March 2016, cited from Ref. [3].

Product	Price Unit	Gulf of Mexico	Europe	Asia	Appalachian Basin
Natural Gas	\$/MMBtu	2.50	6.30	8.20	0.87
Ethane	\$/gal	0.19	0.49	0.60	0.04
Propane	\$/gal	0.41	0.72	0.87	0.10
Isobutane	\$/gal	0.66	0.64	0.93	0.40
n-Butane	\$/gal	0.66	0.64	0.93	0.25
Gas Condensate	\$/gal	1.06	1.25		0.90

0.05%. The metal promoters Pt, Mo were introduced using soluble salts including  $\text{H}_2\text{PtCl}_6$  and ammonium molybdate (para) tetrahydrate as the precursors. Incipient wetness technique was used to impregnate metals on zeolite surface. After desired amount of metal-containing salt was introduced onto zeolite surface, the sample was dried at 110 °C for 12 h and calcined in air at 450 °C for 3 h. The ethane dehydration reaction was carried out in a laboratory fixed-bed reactor system under the reaction conditions of 0.1 MPa pressure, temperature of 500–650 °C, and gas hourly space velocity of 1000–1500  $\text{h}^{-1}$ . A quartz tubular reactor with 10 mm ID was packed with 70–100 mesh catalyst. Generally, 0.5 g of catalyst was installed in the reactor. Products were analyzed by on-line gas chromatograph with Porapak QS column. Mass spectroscopy instrumentation was employed to measure product concentration.

Fischer-Tropsch catalyst, containing 10% Co-3%Re/ $\text{Al}_2\text{O}_3$  was prepared by incipient wetness technique. The catalyst support  $\gamma\text{-Al}_2\text{O}_3$  (Sasol Puralox) was pre-treated at 500 °C in air for 2 h prior to the impregnation. The  $\gamma\text{-Al}_2\text{O}_3$  support has spherical shape and uniform particle distribution. An aqueous solution of cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (98% purity, Aldrich) and Perrhenic acid ( $\text{HReO}_4$ ) (Engelhard, 53.29 wt.% P.M.) was prepared. The solution containing desired amounts of Co and Re ions was used to introduce Co and Re onto  $\gamma\text{-Al}_2\text{O}_3$  support. After Co and Re were impregnated on  $\gamma\text{-Al}_2\text{O}_3$ , the sample was dried at 110 °C followed by calcination in the air at 400 °C for 3 h. Edge coating technique was adopted to selectively anchor Co and Re at pore mouths of  $\gamma\text{-Al}_2\text{O}_3$  support. The  $\gamma\text{-Al}_2\text{O}_3$  support was presoaked with propanol, then a solution containing Co and Re was impregnated onto the  $\gamma\text{-Al}_2\text{O}_3$ . The sample was quickly heated to 110 °C and dried at this temperature for 12 h followed by calcination at 450 °C for 3 h. Fixed-bed reactor was used to carry out syngas conversion under reaction conditions of 2–3 MPa pressure, temperature of 200–290 °C,  $\text{H}_2/\text{CO} = 2:1$ , and gas hourly space velocity of 5000–7200  $\text{h}^{-1}$ . Generally, 0.5 g catalyst was installed in the fixed-bed reactor. Prior to syngas was introduced, the Co-Re/ $\gamma\text{-Al}_2\text{O}_3$  catalyst was reduced by 10% hydrogen at 350 °C for 6 h.

### 3. Results and discussions

#### 3.1. Ethane aromatization over metal-promoted ZSM-5 zeolite

Experimental results obtained from aromatization of ethane over 0.5% Pt/ZSM-5 and 2.5% Mo/ZSM-5 are presented in Fig. 1. Pt modified ZSM-5 exhibits higher conversion and slightly higher selectivity to aromatics as well. Ethane dehydrogenation to form ethylene took place initially (Eq. (1)) then aromatics are formed via trimerization and cyclization of ethylene (Eqs. (2) and (3)). Compared with Pt/ZSM-5 catalyst, Mo/ZSM-5 catalyst produces more ethylene but less methane. Higher selectivity to methane is caused by hydrogenolysis of ethane. Another possible route for the methane production includes the hydrogenolysis of side-chains of toluene and xylenes. We also observed propylene C3 and small amount of C4 olefins. The reaction chemistry associated with the formation of propylene and butane are illustrated in Eqs. (6)–(8). Iwamoto and Kosugi reported the mechanism on the

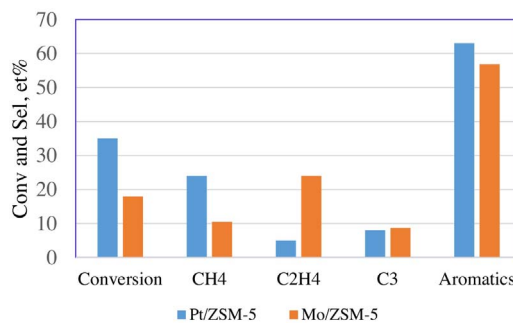
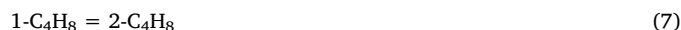
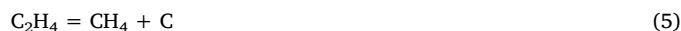


Fig. 1. Conversion and product distribution. Ethane aromatization over 0.5% Pt/ZSM-5 and 2.5% Mo/ZSM-5 catalysts (600 °C, 0.1 MPa, GHSV = 1000  $\text{h}^{-1}$ ).

conversion of ethylene to butenes over Nickel ion-loaded mesoporous silica catalysts [18]. In general, Eqs. (1)–(8) illustrate reaction stoichiometric formation of methane, ethylene, benzene, toluene, propylene and butenes [18,19].



The main liquid products from ethane conversion were benzene, toluene xylenes and  $\text{C}_9+$  aromatics. The distribution of benzene, toluene, xylenes (BTX) and  $\text{C}_9+$  within aromatics is shown in Fig. 2. Although ethane conversion, selectivity to  $\text{C}_1$ – $\text{C}_3$  and  $\text{C}_9+$  aromatics are different for Pt and Mo promoted ZSM-5 catalysts, the distribution of BTX and  $\text{C}_9+$  aromatics within aromatics fraction are similar. This is largely because aromatic selectivity is shape selective which is strongly associated with zeolite rather than metal promoters [20]. Literature report has shown that the structure of high Si/Al ratio zeolite affects the activity and selectivity of the metal promoted catalysts [20].

#### 3.2. Catalyst deactivation and regeneration

The stability of ethane aromatization catalysts is crucial to technology commercialization. General approach is to maintain catalytic activity and selectivity for desired products as long as possible. The

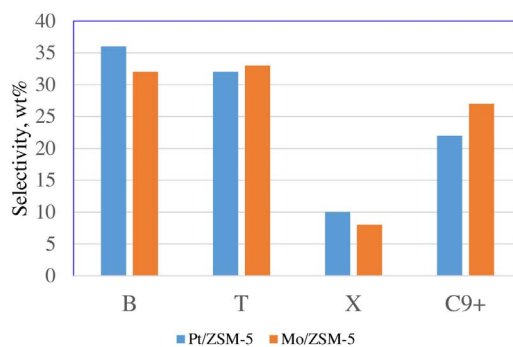


Fig. 2. Selectivity of BTX and  $\text{C}_9+$  in aromatics product. Ethane aromatization over 0.5% Pt/ZSM-5 and 2.5% Mo/ZSM-5 catalysts (600 °C, 0.1 MPa, GHSV = 1000  $\text{h}^{-1}$ ).

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