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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⁻¹. 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 C₉ 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/γ-Al₂O₃ 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, MoO₃/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 Na₂O 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 H_2PtCl_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 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/ Al_2O_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 (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 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

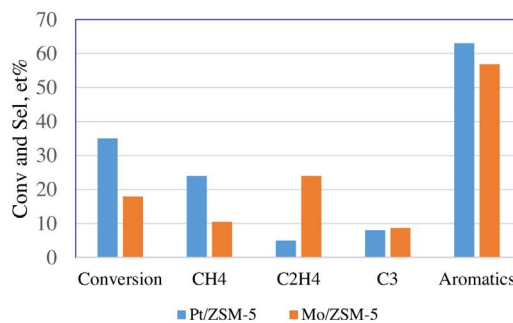


Fig. 1. Conversion and product distribution. Ethane aromatization over 0.5% Pt/ZSM-5 and 2.5% Mo/ZSM-5 catalysts (600 °C, 0.1 MPa, GHSV = 1000 h^{-1}).

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 C_9+ aromatics. The distribution of benzene, toluene, xylenes (BTX) and C_9+ within aromatics is shown in Fig. 2. Although ethane conversion, selectivity to C_1 – C_3 and C_9+ aromatics are different for Pt and Mo promoted ZSM-5 catalysts, the distribution of BTX and 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

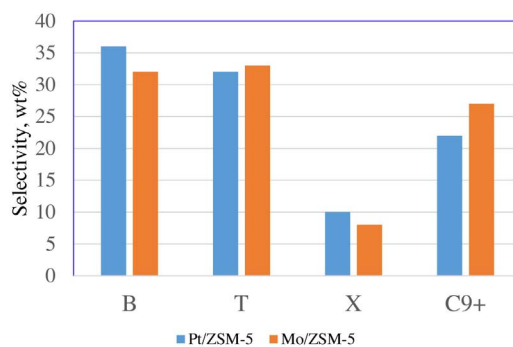


Fig. 2. Selectivity of BTX and C_9+ in aromatics product. Ethane aromatization over 0.5% Pt/ZSM-5 and 2.5% Mo/ZSM-5 catalysts (600 °C, 0.1 MPa, GHSV = 1000 h^{-1}).

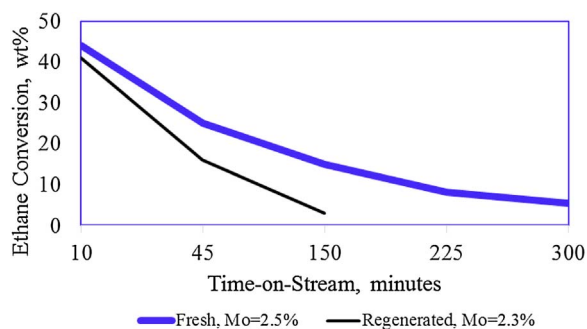


Fig. 3. Time-on-stream activity of 2.5%Mo/ZSM-5 catalyst (650 °C, 0.1 MPa, GHSV = 1000 h⁻¹).

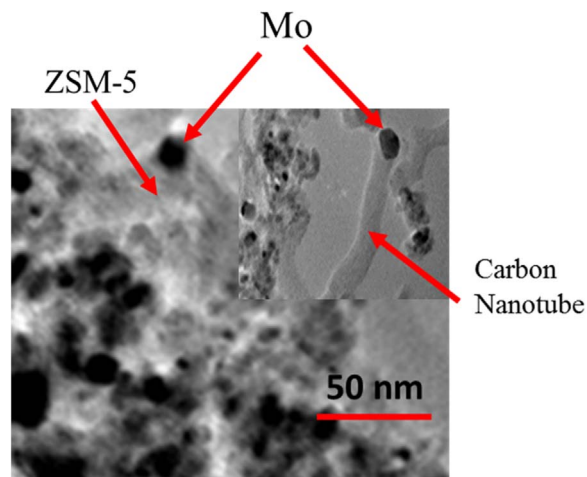


Fig. 4. SEM image of spent Mo/ZSM-5 catalyst after ethane dehydroaromatization reaction at 650 °C, 0.1 MPa, 12 h reaction time. Coke formation and metal leaching are observed.

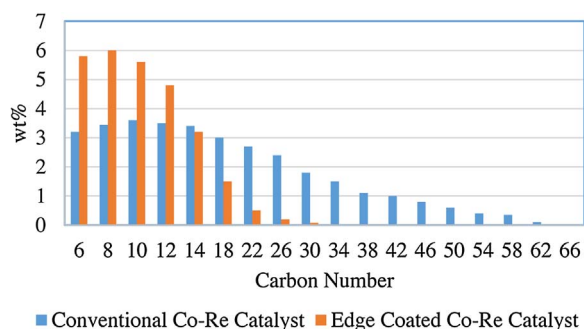


Fig. 5. Product distributions of different Fischer-Tropsch catalysts.

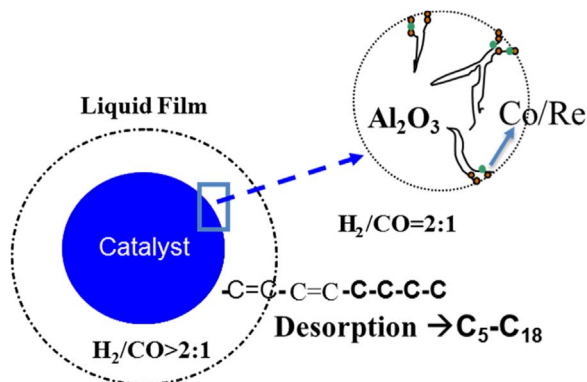


Fig. 6. Illustration of edge-coated Co-Re/ γ -Al₂O₃ catalyst (220 °C, 400 psig, H₂/CO = 2:1).

Table 2
Major Assumptions for Cost Comparison.

	Indirect	Direct
Plant-wide carbon efficiency	73%	75%
Catalyst cost	\$3/bbl	\$5/bbl
Plant life	20 years	20 years
Plant location	U.S. Gulf Coast	U.S. Gulf Coast
Construction time	36 months	36 months
CAPEX estimate	Refs. [4] and [25]	Major savings are from elimination of syngas production unit, and a hydrocracker
Operation and Maintenance	7% CAPEX	7% CAPEX

time on stream behavior at 650 °C of Mo/ZSM-5 is shown in Fig. 3. The conversion of ethane starts at 45% then decreases continuously, reaching a value of 5% after 5 h. An examination of the Mo/ZSM-5 catalyst after aromatization reaction revealed the deposition of carbon on the catalyst surface. Similar phenomena was observed on MoC/ZSM-5 catalysts [19,21]. The amount of coke increased with the increase of reaction time. Literature data has shown that coking on ethane aromatization catalyst is inevitable. The catalyst was regenerated by using 2% oxygen to burn off the carbon deposit. Then re-reduced and tested in the same reactor. As shown in Fig. 3, the regenerated Mo/ZSM-5 regained 90% activity of the fresh catalyst but the conversion of ethane declines much faster than the fresh catalyst. The Mo content of the regenerated catalyst is 2.3 wt%, slightly less than fresh catalyst which is 2.5 wt%. The slight loss of Mo content cannot explain the loss of activity.

SEM analysis was carried out to elucidate catalyst deactivation mechanism. As shown in Fig. 4, Mo was found on the tip of carbon nanotubes over the spent catalyst. Some Mo has already leached out from ZSM-5 surface becoming ineffective to catalyze ethane aromatization reaction. Because leached Mo was not anchored on zeolite surface, they were sintered during oxidative regeneration. Although Mo content on regenerated Mo/ZSM-5 catalyst didn't seem to change, the metal dispersion decreased and redox function diminished, therefore the regenerated catalyst tended to deactivate faster. In order to maintain catalytic activity, the regeneration cycle time should be shortened. That is, before Mo is leached out from catalyst surface, the catalyst should be put on regeneration. Multi-reactor swing operation has been practiced commercially in propane dehydrogenation (PDH) plant [22]. The PDH catalyst regeneration strategy can be utilized in ethane dehydroaromatization.

3.3. Edge-coated catalyst for indirect natural gas conversion

Indirect natural gas conversion via Fischer-Tropsch (F-T) synthesis has been commercially practiced. Products from conventional F-T catalyst usually contain a wide range of carbon distribution as shown in Fig. 5. Hydrocracking and isomerization reactions are necessary to convert these long chain paraffins to diesel and lube oils. Typically, the capital costs of downstream refining equipment are much more than F-T reactor itself. To minimize downstream hydrocracking process, edge coated catalyst is developed to restrict carbon chain growth by only coating Co-Re at the pore mouth (edge) of the catalyst support γ -Al₂O₃. This is largely because, on edge-coated catalyst, the liquid film surrounding the catalyst particles becomes thinner, therefore desorption rate is faster than chain growth rate [23]. As a result, edge-coated catalyst only allows carbon chain to grow until certain length, then desorption becomes dominant. The catalyst design concept is illustrated in Fig. 6. The side-by-side comparison between edge coated catalyst and conventional Co-Re catalyst is shown in Fig. 5. The benefit of using edge-coated catalyst for F-T synthesis is the significant

Table 3
Comparison of Direct and Indirect Natural Gas Conversion to Chemicals.

	Natural Gas Price \$/mmBtu	Crude Oil Price \$/bbl	Capex \$/daily bbl	IRR	Technology Status
Direct Conversion	1–2	30–90	~70,000	5–40%	R & D
Indirect Conversion	1–2	30–90	~160,000	0–17%	Commercialized

reduction on the requirement of a hydrocracker and elimination of a number of separation units.

Although progress has been made in catalyst and process innovations for F-T synthesis, the main obstacle of indirect natural gas conversion via F-T synthesis is the cost on syngas generation. The advantage of direct natural gas conversion is the elimination of syngas generation which is about 40% capital cost for a gas-to-liquid plant [24]. The economic comparison between direct and indirect natural gas conversion processes is discussed in the following section.

3.4. Cost comparison of direct and indirect natural gas conversion

The economic comparison of direct and indirect natural gas conversion process was made based on engineering feasibility study at FEL 1 level cost estimate methodology. Capital costs are developed for each major component based on the sizing developed in the process simulations. The estimate of capital costs, operating costs were based on Refs. [4] and [25] NETL reports that obtained a cost basis from an engineering firm's cost engineering data and method. No vendor quotes were obtained or detailed engineering was performed as part of this FEL-1 analysis. All costs were escalated to 2016 dollar values by using Chemical Engineering Plant Cost Index. The cost estimates reported are not definitive; having a reasonable range of accuracy (–15% to +35%). Additionally, there are certain project-specific risks and design choices that cannot be covered comprehensively in this analysis. Table 2 shows the assumptions made in cost comparison.

The economic performance is compared based on internal rate of return (IRR) of the two scenario. IRR is the discount rate at which the net present value of future cash flows is equal to the initial investment. IRR is an indicator of the profitability, efficiency, quality, or yield of an investment. The capacity of the plant is based on 100,000 bbl/day. During the sensitivity study, natural gas price is varied between \$1–2, and crude oil priced is varied from \$30–90/bbl. Certainly, at low crude oil price of \$30/bbl, none of these technologies will have commercial viability. However, when crude oil price increases and natural gas price remains low, the return on investment will be high. Especially, the direct route will create more economic impact on natural gas upgrading (Table 3).

4. Conclusions

Ethane aromatization over metal promoted ZSM-5 yields 40%

conversion, 60% selectivity to aromatics and 20% selectivity to ethylene at 600 °C and ambient pressure. Ethylene is the key intermediate for aromatics formation. Although direct natural gas conversion process appears to be more promising in terms of reduced numbers of process stages which is translated to huge savings on capital investment and operating cost. However, catalyst stability and regeneration are major obstacles to commercial applications. The future R & D should be focused on anchoring metal promoters in the crystal structure of zeolite to prevent metal leaching and sintering.

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