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Reactivation of an industrial spent catalyst as an environmental waste by ultrasound assisted technique for using in styrene production

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ABSTRACT

In this study, the regeneration of a commercial spent catalyst for the ethylbenzene (EB) dehydrogenation was investigated and successfully utilized for styrene monomer (SM) production as a powerful catalyst. The spent catalyst as an environmental waste was regenerated in three steps: decoking of the spent catalyst, phase changing of the decoked catalyst and potassium injection to the phase changed catalyst. The spent catalyst was decoked by oxygen-nitrogen mixtures and crystalline phase change was achieved by water treatment. The potassium deficiency of the spent catalyst was compensated in an aqueous solution of 10 wt.% K_2CO_3 (99%, Merck) by ultrasound energy assisted technique for the first time. Evaluation of the catalyst activity showed that the styrene yield of the regenerated catalyst assisted by ultrasound energy was increased about 3.1% compared to that of fresh ones. The results also revealed that the spent catalyst could be rejuvenated to some extent of activity which can reproduce comparable performance and stability of fresh catalyst that is environmentally and economically beneficial.

1. Introduction

Catalysts are complex materials and about more than 80% of chemical process are carried out in the presence of a catalyst [1]. Worldwide catalyst market in the oil and gas industry was about 6259.3 kilotons in 2013 and is estimated to reach 7803.4 kilotons in 2020 [2]. The catalyst consumption in Iran is estimated about 22.5 kilotons in 2015 with a significant increase in demand expected in the future [3].

The catalysts gradually deactivate with time and needed to be replaced or regenerated. If the catalyst regeneration is not possible, the spent catalysts are disposed as the solid waste, causing adverse environmental impacts. The surveys show that about 280 tons of ethylbenzene dehydrogenation spent catalysts are annually disposed into environment in Iran. The discarded spent catalysts form toxic metal compounds that can be widely distributed in the environment [4]. Thus, the proper management of the spent catalysts are important from both economic and environmental points of view. The four common methods to solve the environmental problems of the spent catalysts are as follows: regeneration of the spent catalysts; recovering the precious metals; using in the different chemical processes and finally treating and producing the new catalyst.

Among the chemical processes, the ethylbenzene dehydrogenation is one of the most studied processes that occurs in the presence of a catalyst [5,6]. Styrene is produced essentially as a result of ethylbenzene dehydrogenation along with benzene (BZ) and toluene (TOL) [7] as well as minor by-products as shown in the following reactions [8,9].

$$\underset{EB}{C_6H_5-C_2H_5} \overset{Cat.}{\leftrightarrow} \underset{SM}{C_6H_5-C_2H_3} + H_2 \quad \Delta H = 124.9\ kJ\ mol^{-1} \tag{1}$$

$$\underset{EB}{C_6H_5-C_2H_5} \rightarrow \underset{BZ}{C_6H_6} + C_2H_4 \quad \Delta H = 106.5\ kJ\ mol^{-1} \tag{2}$$

$$\underset{EB}{C_6H_5-C_2H_5} + H_2 \rightarrow \underset{TOL}{C_6H_5-CH_3} + CH_4 \quad \Delta H = -57.1\ kJ\ mol^{-1} \tag{3}$$

The catalysts for ethylbenzene dehydrogenation are mainly composed of iron oxide and potassium as a promoter (about 10 wt. %) along with molybdenum and cerium [10]. Deactivation of ethylbenzene dehydrogenation catalyst can occur depending on

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Nomenclature

Symbols used

a	Activity (−)
F_i	Molar flow rate of component i (mol h^{-1})
$-r_A$	Styrene production rate at t = t (kmol $kgcat^{-1}$ h^{-1})
$-r_{AO}$	Styrene production rate at t = t_0 (kmol $kgcat^{-1}$ h^{-1})
S_i	Selectivity of component i (−)
Y_{SM}	Styrene yield (−)
X_{EB}	Ethylbenzene conversion (−)
ΔH	Heat of reaction (kJ mol^{-1})

the coke formation, potassium migration, Fe_2O_3 reduction to Fe_3O_4 and physical degradation [11,12]. Baghalha and Ebrahimpour [13] and Shiji et al. [14] studied the structural change and performance of the spent catalyst compared to fresh catalyst using several characterization methods including XRD, SEM and XRF. Furthermore, the catalyst deactivation process has been modelled by Haghlesan et al. [15] on an industrial scale.

Generally, deactivation of ethylbenzene dehydrogenation catalyst are considered as potassium migration out of the catalyst pellet duo to the temperature gradient resulting from the endothermic nature of the reaction [16,17]. Catalyst deactivation as a result of potassium migration was also studied by Matsui et al. [18] in a differential reactor at constant temperature.

According to Mross's [19] findings, potassium addition (greater than 3 wt.%) to iron oxide hydrate prevents catalyst shrinkage and density reduction and also increases porosity of the catalyst. Serafin et al. [20] proposed that 0.25–5 wt.% addition of Cr to the catalyst could induce stability of potassium ferrite ($K_2Fe_{22}O_{34}$) active phase along with enhancement in activation energies of potassium desorption. According to Bieniasz et al. [21], catalyst deactivation inhibition in the presence of Cr, is owing to limitations of potassium diffusion from the bulk towards the surface.

Numerous studies have been conducted on the deactivation, regeneration and reusing of the spent catalysts [22–24]. In accordance with Patel's [25] study, the spent catalyst wastes of the hydroprocessing units are the major part of the refineries solid wastes. Solid catalyst wastes reduction and reuse methods are reviewed by Marafi and Stanislaus [26].

The regeneration of the ZSM-5 zeolite in catalytic pyrolysis of plastic wastes was performed by Lpez [27]. Moreover, Küntzel et al. [28] found that the steam treatment is more effective than hot gases injection for the zeolites regeneration. Villacampa et al. [29] surveyed the regeneration of a co-precipitated Ni/Al_2O_3 catalyst for the methane cracking process. They confirmed that hydrogen inhibits carbon formation and catalyst deactivation.

Many researchers have studied the regeneration of the ethylbenzene dehydrogenation catalyst and reported their findings in the patent publications. They were described their inventions generally, but not explained in details [30–32]. In other word, there is no comprehensive study about the regeneration and reusing of ethylbenzene dehydrogenation spent catalyst in literature.

Given the above considerations, the regeneration of an industrial spent catalyst is very essential. So, the main objective of our research is the regeneration of the ethylbenzene dehydrogenation spent catalyst which is of high importance from both economic and environmental aspects. An important part of the catalyst regeneration is the potassium injection to the spent catalyst which was performed in this work by ultrasound energy assisted for the first time. We believe that the results reported here, will be useful to reduce the environmental impacts of the spent catalyst.

2. Material and methods

2.1. Materials

In this study, an industrial spent catalyst for the ehtylbenzene dehydrogenation to styrene was used. The fresh and spent catalysts with a diameter about 3 mm and length of 4–6 mm, are BASF (S6-32) type and mainly contained of Fe_2O_3 and Fe_3O_4, respectively. The spent catalysts were downloaded from the industrial reactor which had been used for about 36 months under temperature range of 580–640 °C, Liquid hourly space velocity (LHSV) of 1 h^{-1} and steam to oil (ethylbenzene) ratio (S/O) of 1.3(wt./wt.).

K_2CO_3 (99%, Merck) solution at a concentration of 10 wt.% was used for the compensation of migrated potassium during catalyst deactivation.

In order to perform the catalytic tests, commercial ethylbenzene from benzene alkylation unit was used for styrene production [33]. The specification of ethylbenzene feed which was used in dehydrogenation reaction is tabulated in Table 1. Demineralized water was also used for steam generation.

2.2. Analysis and catalyst characterization

The crystalline phase of catalysts were characterized by X-ray diffractometer (XRD-Siemens D5000) with a Cu.Kα (λ = 0.154056 nm) monochromatic radiation at a voltage of 40 kV and a current of 30 mA. Diffraction patterns were obtained in the 2θ range of 20–80° at a scanning rate of 1.2° min^{-1}.

The elements content and surface spectroscopy were obtained by the scanning electron microscope (SEM-Tescan Mira3 FESEM) equipped by an energy dispersive X-ray spectroscope (EDX) for all catalysts. Moreover, the surface area and pore size distribution of fresh and spent catalyst were measured by BET methods using a Quantachrome NOVA 2000 apparatus.

2.3. Catalyst regeneration and performance devices

The spent catalyst was treated by potassium injection that assisted with ultrasonic energy. The ultrasonic process was performed using a BANDELIN SONOPULS apparatus with a frequency of 20 kHz, an effective output power of 80W and a probe diameter of 13 mm.

A laboratory scale fixed bed reactor (stainless steel, 200 mm length and 20 mm I.D.) which was placed inside an electrical furnace was used for decoking spent catalyst and activity determination. Water and ethylbenzene injection was carried out by a programmable two channel syringe pump. The reactor effluent was further cooled in the condenser and separated to liquid phase and non-condensable gases (off gases). The experimental setup used for ethylbenzene dehydrogenation and spent catalyst decoking is depicted in Fig. 1.

Table 1
Analysis of the ethylbenzene feed used for dehydrogenation.

Component	wt.%
Benzene	0.149
Toluene	0.051
Ethylbenzene	99.701
Diethylbenzene	0.001
C7-C8 non aromatics	0.060
C9 aromatics	0.038