Reaction coupling of ethylbenzene dehydrogenation with nitrobenzene hydrogenation

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The chemical equilibrium for the coupling of ethylbenzene dehydrogenation with nitrobenzene hydrogenation, to produce styrene and aniline simultaneously, has been calculated on the basis of the Soave–Redlich–Kwong equation of state. The dehydrogenation of ethylbenzene in the presence of nitrobenzene over the catalysts γ-Al_2O_3, ZSM-5, activated carbon and platinum supported on activated carbon has been carried out at 400 °C. The effects of Pt loading and the pretreatment of the catalysts have been investigated. It has been revealed that the conversion of ethylbenzene can be greatly improved by the reaction coupling due to the elimination of the hydrogen produced in the reaction by the hydrogenation of nitrobenzene. Platinum supported on the activated carbon has been suggested as a suitable catalyst. The best results with ethylbenzene conversion of 33.8% and styrene selectivity of 99.2% were obtained over Pt(0.02 wt%)/AC at 400 °C. Moreover, such process is also energetically favored since the necessary process heat to drive the ethylbenzene dehydrogenation can be provided by the coupling with the exothermic nitrobenzene hydrogenation reaction.

KEY WORDS: reaction coupling; ethylbenzene dehydrogenation; nitrobenzene hydrogenation; Pt/AC catalysts.

1. Introduction

Styrene is one of the most important basic chemicals and mainly used as the monomer of synthetic polymers. It is commercially produced by the dehydrogenation of ethylbenzene on iron oxide catalysts at 600–700 °C, just below the temperature where thermal cracking becomes significant [1]. Due to its high endothermic and volume-reducing character, a large amount of superheated steam is used to supply heat, lower the partial pressure of the reactant to shift the reaction equilibrium to the product, and avoid the formation of carbon deposits to prolong the life of catalyst. However, much of the latent heat of steam is lost at the gas–liquid separator instead of being reclaimed. Thus, it is highly desirable to develop new processes and catalysts that can lower the reaction temperature and water/ethylbenzene ratio.

Reaction coupling is an effective approach to improve the equilibrium conversion in the dehydrogenation reactions [2]. Several investigations on reaction coupling were carried out in the dehydrogenation of ethylbenzene in the presence of carbon dioxide instead of steam [3–11]; these combined the ethylbenzene dehydrogenation together with reverse water–gas shift reaction. It is estimated that the energy required for producing styrene in the coupling process is 1.9×10^8 cal per ton, compared with 1.5–1.9×10^9 cal in the current commercial process [7]. In addition, CO_2 was found to be able to suppress the catalyst deactivation. Therefore, the new processes that could be energy-saving and environmental friendly have been attracting increased attention. Since the commercial Fe–Cr–K catalyst does not work effectively in such coupling systems, a variety of new catalysts were reported [3–11].

However, reverse water–gas shift is also an endothermic reaction. For the reaction coupling, the provision of the necessary process heat by a concurrent exothermic reaction is favorable to drive the ethylbenzene dehydrogenation. Thus, the oxidative dehydrogenation of ethylbenzene at lower reaction temperatures has attracted considerable attention [12–16], in which oxygen was used as the hydrogen acceptor and water was formed as a by-product. More recently, a process involves the combination of the endothermic dehydrogenation of ethylbenzene to styrene with the strongly exothermic hydrogenation of nitrobenzene to aniline has been investigated.

Aniline is one of the most significant key compounds in aromatic chemistry. Many commodity chemicals, including cyclohexylamine, benzoquinone, alkylanilines etc., are manufactured from aniline. Aniline is mainly produced from the catalytic hydrogenation of nitrobenzene at 300–475 °C in a fixed bed. Bautista and coworkers [1] studied the gas-phase catalytic hydrogen transfer reaction between ethylbenzene and nitrobenzene, to produce styrene and aniline, at 360–460 °C on amorphous $AlPO_4$, SiO_2, Al_2O_3, and sepiolite, as well as on the nickel supported catalysts. The influence of Cu as a second metal was also studied. It was found

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that the ethylbenzene conversion under oxidative conditions was always comparatively higher than that in non-oxidative conditions, and the best results were obtained when amorphous $AlPO_4$ was used as the catalyst. Moreover, nitrobenzene played an important role as hydrogen acceptor, not only shifting the ethylbenzene dehydrogenation equilibrium but also restricting the secondary reactions by lowering the level of available hydrogen, especially when supported metals were used as catalysts.

Thus, previous research proved that the reaction behaviors could be improved greatly by coupling a dehydrogenation reaction with a hydrogenation reaction, an endothermic reaction with an exothermic reaction, and a reductive reaction with an oxidative reaction. However, considerable work is still necessary on the study of the intrinsic factors of such reaction coupling, screening of proper catalysts and optimization of the operating conditions before such process proves to be practical. In the present paper, the chemical equilibrium for the coupling reaction of ethylbenzene dehydrogenation with nitrobenzene hydrogenation, to produce styrene and aniline simultaneously, is calculated on the basis of Soave–Redlich–Kwong (SRK) equation of state. The dehydrogenation of ethylbenzene in the presence of the nitrobenzene over the catalysts γ-Al_2O_3, ZSM-5, activated carbon (AC) and platinum supported on AC is carried out at 400 °C under atmospheric pressure. The effects of Pt loading and the pretreatment of the catalysts are also investigated.

2. Thermodynamic analysis

The dehydrogenation of ethylbenzene (EB) to styrene (ST) can be expressed by

$$\begin{aligned} &C_6H_5\text{-}C_2H_5(\mathrm{EB}) \rightarrow C_6H_5\text{-}C_2H_3(\mathrm{ST}) + H_2 \\ &\Delta H^0_{298.15\,\mathrm{K}} = +117.6\,\mathrm{kJ\,mol^{-1}} \end{aligned} \tag{1}$$

and the hydrogenation of nitrobenzene (NB) to aniline (AN) can be written as

$$\begin{aligned} &C_6H_5\text{-}NO_2(\mathrm{NB}) + 3H_2 \rightarrow C_6H_5\text{-}NH_2(\mathrm{AN}) + 2H_2O \\ &\Delta H^0_{298.15\,\mathrm{K}} = -464.3\,\mathrm{kJ\,mol^{-1}}. \end{aligned} \tag{2}$$

The equilibrium constants for the two reactions are defined as follows:

$$\begin{aligned} K_1^0 &= K_{P,1} \cdot K_{\phi,1} \cdot (P^0)^{-1} \\ &= \left(\frac{x_{\mathrm{ST}} x_{\mathrm{H_2}}}{x_{\mathrm{EB}}}\right)_{\mathrm{eq}} \cdot \left(\frac{\phi_{\mathrm{ST}} \phi_{\mathrm{H_2}}}{\phi_{\mathrm{EB}}}\right)_{\mathrm{eq}} \cdot \left(\frac{P^0}{P}\right)^{-1} \end{aligned} \tag{3}$$

$$\begin{aligned} K_2^0 &= K_{P,2} \cdot K_{\phi,2} \cdot P^0 \\ &= \left(\frac{x_{\mathrm{AN}} x^2_{\mathrm{H_2O}}}{x_{\mathrm{NB}} x^3_{\mathrm{H_2}}}\right)_{\mathrm{eq}} \cdot \left(\frac{\phi_{\mathrm{AN}} \phi^2_{\mathrm{H_2O}}}{\phi_{\mathrm{NB}} \phi^3_{\mathrm{H_2}}}\right)_{\mathrm{eq}} \cdot \frac{P^0}{P}. \end{aligned} \tag{4}$$

Here ϕ_i is the fugacity coefficient, and x_i is the mole fraction of component i respectively. The value of K^0 can be calculated from the following thermodynamic relationships:

$$-\Delta_r G^0(T) = RT \ln K^0(T) \tag{5}$$

$$\frac{-\Delta_r G^0(T)}{T} = \frac{-\Delta_r G^0(T_{\mathrm{ref}})}{T_{\mathrm{ref}}} + \int_{T_{\mathrm{ref}}}^{T} \frac{\Delta_r H^0(T)}{T^2}\,\mathrm{d}T \tag{6}$$

$$\Delta_r H^0(T) = \Delta_r H^0(T_{\mathrm{ref}}) + \int_{T_{\mathrm{ref}}}^{T} \Delta C_p^0(T)\,\mathrm{d}T. \tag{7}$$

Using the heats of formation, entropies and heat capacities of each component, the equilibrium constant K^0 at different temperatures can be determined. The heats of formation, entropies and heat capacities of each component used in the present work are cited from reference [17].

The value of K_ϕ can be calculated on the basis of the Soave-modified Redlich–Kwong equation of state [18],

$$P = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)} \tag{8}$$

and the detailed calculation procedure has been described elsewhere [19].

Dehydrogenation of ethylbenzene to styrene is an endothermic and volume increasing reaction; high temperature and low pressure are favored for the conversion of ethylbenzene. Figure 1 gives the equilibrium conversion of ethylbenzene in the cases of simple dehydrogenation, N_2 dilution and the coupling with water–gas shift or nitrobenzene hydrogenation at different temperatures under 0.1 MPa. It can be seen that the conversion is quite low in the simple ethylbenzene dehydrogenation even at high temperatures, for example, only 3.5% at 400 °C and 70% at 690 °C. The conversion can be increased obviously by introducing nitrogen into the reaction system due to the decrease of the partial pressures of all the components in the system. The decrease of partial pressure for the components is one of the reasons for using large amounts of steam in the commercial process.

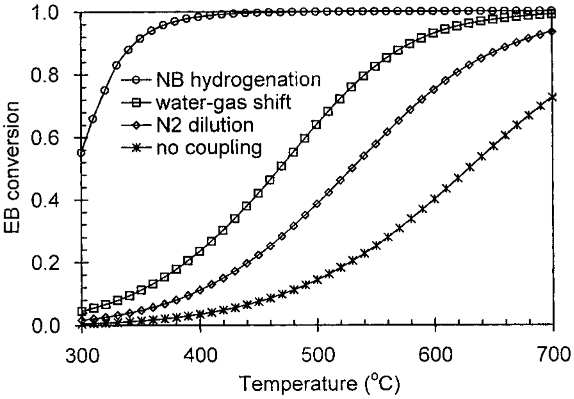

Figure 1. Comparison of the coupling of ethylbenzene dehydrogenation with different reactions at 0.1 MPa: the feed composition (in mole ratio) is EB : NB = 3 : 1 for coupling with nitrobenzene hydrogenation, EB : CO_2 = 1 : 10 for coupling with reverse water–gas shift and EB : N_2 = 1 : 10 for N_2 dilution.

However, this enhancement by dilution is limited, for example, the conversion of ethylbenzene is increased from 14.4% to 38.6% at 500 °C in the presence of nitrogen (mole ratio $EB:N_2 = 1:10$).

To enhance the conversion of ethylbenzene or reduce the operating temperature considerably, it is necessary to eliminate the hydrogen produced in the reaction by coupling it with hydrogen-consuming reactions. For the coupling with the water–gas shift reaction, the conversions are 63.9% and 82.4% at 500 °C and 550 °C, respectively, with the mole ratio CO_2/ethylbenzene being 10. However, for the coupling with nitrobenzene hydrogenation, the equilibrium conversion of ethylbenzene is as high as 98.5% even at 400 °C with the mole ratio ethylbenzene/nitrobenzene being 3. This proves the superiority of the reaction coupling over the dilution with nitrogen. Stoichiometrically, the molar ratio of ethylbenzene to nitrobenzene for the coupling reaction is 3. Therefore, ethylbenzene and nitrobenzene at molar ratio of 3 can be almost quantitatively transformed to styrene and aniline at 400 °C if a suitable catalyst is available.

Moreover, the hydrogenation of nitrobenzene is a strongly exothermic process while the reverse water–gas shift is endothermic. Thus, the coupling with nitrobenzene hydrogenation is also energetically favored, since the necessary process heat to drive the ethylbenzene dehydrogenation can be provided by the concurrent use of the exothermic nitrobenzene hydrogenation reaction. As a result, the whole coupling process is weakly exothermic ($\Delta H^0_{673.15\,\mathrm{K}} = -107.5\,\mathrm{kJ\,mol^{-1}}$).

3. Experimental

3.1. Catalyst preparation

γ-Al_2O_3, ZSM-5 ($Si/Al > 500$) as well as activated carbon (BET area, $942\,m^2/g$) were used as catalyst supports. Active component Pt was introduced by impregnation of the activated carbon (20–40 mesh) with an aqueous solution of chloroplatinic acid for 18 h, and then the catalysts were dried at 120 °C in air for 4 h. The catalysts were further treated by calcinations under N_2, reduction by H_2 or oxidation by air in the reactor prior to the reaction.

3.2. Catalytic tests

The catalytic tests were carried out in a stainless steel fixed-bed reactor (6.0 mm i.d.), and 200 mg catalyst was used for each run. Normally, the catalyst was treated in a nitrogen flow from room temperature to reaction temperature, and then switched to the mixture of the reactants (ethylbenzene and nitrobenzene in a molar ratio of 3:1). The reaction was operated at 400 °C under atmospheric pressure. The mixture of ethylbenzene and nitrobenzene was fed to the reactor by a microfeeder at a constant flow rate of 470 mg/h (~4.26 mmol/h). For the simple ethylbenzene dehydrogenation and nitrobenzene hydrogenation reactions, the test procedures were done in the same way except that the liquid reactant in the microfeeder was changed to pure ethylbenzene or nitrobenzene instead of the mixture.

In some cases, the catalyst was reduced by pure H_2 and/or oxidized by air in the reactor prior to the reaction. First, the catalyst was treated in a nitrogen flow from room temperature to reaction temperature, then reduced by H_2 for 2 h. After that, the catalyst was flushed by N_2 for 0.5 h before the reaction or the oxidation treatment. For the oxidation treatment, air was then introduced into the reactor for 0.5 h after the flushing of N_2 at reaction temperature, and the catalyst was flushed again with N_2 for 0.5 h before the reaction.

The effluent from the reactor was condensed in a glass tube cooled with an ice water bath and analyzed by a FID gas chromatograph (Shimadzu GC-7A) using a 3 mm × 3 m OV-101 packed column. Apart from styrene and aniline, small amounts of benzene and toluene were obtained as by-products.

4. Results and discussion

4.1. Simple ethylbenzene dehydrogenation and nitrobenzene hydrogenation

Both simple ethylbenzene dehydrogenation and nitrobenzene hydrogenation were carried out on activated carbon (AC), Al_2O_3, ZSM-5 and Pt(0.02 wt%)/AC at 400 °C under atmospheric pressure as listed in table 1.

Table 1
Simple EB dehydrogenation and NB hydrogenation over different catalysts at 400 °C ($W/F = 46.9$ g-cat h/mol, $EB/NB = 3$, results were acquired after reaction lasted for 1 h)

Catalyst	Simple EB dehydrogenation		Simple NB hydrogenation	
	EB conversion (%)	ST selectivity (%)	NB conversion (%)	AN selectivity (%)
AC	1.7	86.7	3.4	2.0
Al_2O_3	0.7	81.6	4.9	29.0
ZSM-5	13.8	2.8	2.4	0.0
Pt(0.02 wt%)/AC	2.4	88.7	1.7	0.0

It can be seen that the conversions of both ethylbenzene and nitrobenzene were lower than 5% with the exception on ZSM-5. The selectivity of nitrobenzene to aniline was almost zero on AC, ZSM-5 and Pt(0.02 wt%)/AC, while the selectivity of ethylbenzene to styrene was 82–89% on AC, Al_2O_3 and Pt(0.02 wt%)/AC. The ethylbenzene conversion and selectivity to styrene on ZSM-5 were 13.8% and 2.8%, respectively, indicating that the cracking of ethylbenzene to benzene and toluene was primary on ZSM-5 due to its strong acidity.

4.2. *Coupling of ethylbenzene dehydrogenation with nitrobenzene hydrogenation*

The reaction coupling of ethylbenzene dehydrogenation with nitrobenzene hydrogenation over AC, Al_2O_3, ZSM-5 and Pt/AC catalysts at 400 °C under atmospheric pressure was investigated. The conversions of both ethylbenzene and nitrobenzene on all the catalysts excepting ZSM-5 for the coupling reactions were much higher than those for the simple dehydrogenation, and the selectivity to both styrene and aniline was close to 100% as listed in table 2. This reveals the advantage of the reaction coupling. Among the three supports investigated, the activated carbon showed the highest activity for the coupling reaction.

Effects of the pretreatment and Pt loading of the catalysts were also investigated. Pt(0.02 wt%) was pretreated by reduction (denoted as Pt/AC, R) or reduction followed by oxidation (denoted as Pt/AC, R&O). The catalysts after reduction and oxidation gave the highest activity. The investigation on the coupling reaction over the catalysts with Pt loading of 0.01 wt%, 0.02 wt% and 0.3 wt% showed that the best loading is 0.02 wt%. The best results with ethylbenzene conversion of 33.8% and styrene selectivity of 99.2% were obtained over Pt(0.02 wt%)/AC pretreated by reduction followed by oxidation.

Both styrene and aniline are manufactured on a large scale. The combination of the endothermic ethylbenzene dehydrogenation with the exothermic nitrobenzene hydrogenation is a potential process for the production of styrene and aniline in a single unit. Since the conversion of ethylbenzene realized in this work was still lower than the equilibrium conversion (98.5% at 400 °C), further works on the catalyst development and operation optimization are needed before such a process can compete with the current processes.

5. Conclusions

The chemical equilibrium for the coupling reaction of ethylbenzene dehydrogenation with nitrobenzene hydrogenation, to produce styrene and aniline simultaneously, has been calculated on the basis of the SRK equation of state. The dehydrogenation of ethylbenzene in the presence of nitrobenzene over the catalysts γ-Al_2O_3, ZSM-5, activated carbon and platinum supported on activated carbon has been carried out at 400 °C. It was revealed that the equilibrium conversion of ethylbenzene is greatly improved by the reaction coupling due to elimination of the hydrogen produced in time and the platinum supported on activated carbon was suggested as suitable catalysts.

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Table 2

Coupling of EB dehydrogenation and NB hydrogenation over different catalysts at 400 °C ($W/F = 46.9$ g-cat h/mol, EB/NB = 3, results were acquired after reaction lasted for 1 h)

Catalysts [a]	EB conversion (%)	ST selectivity (%)	NB conversion (%)	AN selectivity (%)
AC	30.9	98.0	45.2	99.9
Al_2O_3	19.1	99.2	30.0	100
ZSM-5	5.2	76.9	1.7	100
Pt(0.02 wt%)/AC	27.5	98.6	55.3	100
Pt(0.02 wt%)/AC, R	27.0	99.0	32.0	100
Pt(0.02 wt%)/AC, R&O	33.8	99.2	72.3	99.9
Pt(0.01 wt%)/AC, R&O	30.9	98.7	48.7	100
Pt(0.03 wt%)/AC, R&O	20.9	98.9	40.2	99.9

[a] R, reduced; O, oxidized.

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