

Study of the Conjugation of Ethyl Benzene Dehydrogenation to Styrene with Steam Conversion of Carbon Monoxide on a Magnesium-Zirconium Catalyst

Mamedova MT*

The Y.H Mamedaliev Institute of Petrochemical Processes of NAS of Azerbaijan, AZ 1025, Baku, Khojaly Avenue-30, Azerbaijan

ABSTRACT

The steam conversion of carbon monoxide, the conjugation of the conversion of ethyl benzene (EB) to styrene (St) with the steam conversion of carbon monoxide (SCCM) and the conversion of ethyl benzene to styrene in the presence of CO₂ on a low-temperature magnesium-zirconium catalyst modified with phosphoric acid and copper were studied. It has been established that by the conjugation of conversion of EB to styrene with the steam conversion of carbon monoxide, it is possible to create a highly efficient, environmentally friendly process for the production of styrene and hydrogen with a relatively low expenditure of additional capital and energy.

Keywords: Carbon monoxide; Carbon dioxide; Magnesium; Zirconium; Phosphate acid; Copper; Conjugation; Steam conversion; Ethyl benzene; Styrene

INTRODUCTION

Styrene (St) is one of the most important monomers in modern industry. It is used as a starting material in the preparation of many plastics, in particular polystyrene, as well as rubbers and resins. The most common method of producing styrene monomer is direct dehydrogenation of ethyl benzene (EB). In this method, excess superheated steam at about 800°C is combined with EB in a reactor containing a potassium-promoted iron oxide catalyst. The reaction temperature is usually about 600-650°C, and the reaction pressure is about 40 to 80 kPa. This method consumes large amounts of energy through the use of excess water vapor and the energy required for vaporization and superheating of steam. It also has the disadvantages of deactivating the catalyst. Another way to conversion of EB to ST is the Lummus/UOP Smart method [1]. In this process, the by-product of the dehydrogenation reaction, hydrogen, is selectively oxidized by oxygen to water. Removal of hydrogen shifts the equilibrium of the reaction of dehydrogenation of EB to the direction of formation of St, the selectivity for St increases and the exothermic oxidation of hydrogen with oxygen provides part of the heat required for the subsequent dehydrogenation of EB. The need to have two catalysts in the reactor (one for catalysis of the dehydrogenation reaction and the second catalyst for oxidation of hydrogen with oxygen); the formation of aromatic oxidants and CO₂, issues related to safety when introducing

oxygen into the hydrocarbon mixture, etc. are disadvantages of this method. Recently it was proposed to use CO₂ as a mild oxidizing agent for conversion of EB to St. Some effective catalytic systems have been proposed for the conversion of EB to St in the presence of CO₂. The effectiveness of CO₂ in the dehydrogenation of EB to St depends on the nature of the used catalyst. Thus, a small amount of CO₂ deactivates industrial potassium-promoted oxide-iron catalyst and, therefore, the activity of catalytic systems based on FeO_x in the dehydrogenation of EB in St in the presence of CO₂ will be very low [2]. However, iron oxides deposited on active carbon, aluminum oxide or zeolite NaZSM-5 is effective catalysts for this process [3-5]. With the use of the

catalysts of Na₂O/Al₂O₃, oxides of chromium and cerium supported on active carbon in the presence of CO₂ in comparison with the inert atmosphere, the yield of styrene increases with the same EB conversion [6]. It is noted that the high activity of the catalyst CrO_x/Al₂O₃ in the conversion of EB to C in the presence of CO₂ [7]. Depending on the method of converting, the conversion of EB to St is carried out by two reactions: (1) direct dehydrogenation of EB to St by the following reaction:



*Correspondence to: Mamedova MT, The Y.H Mamedaliev Institute of Petrochemical Processes of NAS of Azerbaijan, AZ 1025, Baku, Khojaly Avenue-30, Azerbaijan, Tel: +86-758-2716357; Email: memmedova-melahet@mail.ru

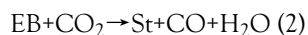
Received: October 22, 2019, Accepted: November 17, 2019, Published: December 08, 2019

Citation: Mamedova MT (2019) Study of the Conjugation of Ethyl Benzene Dehydrogenation to Styrene with Steam Conversion of Carbon Monoxide on a Magnesium-Zirconium Catalyst. J Phys Chem Biophys 9: 277. doi:10.4172/2161-0398.1000277

Copyright: © 2018 Mamedova MT. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

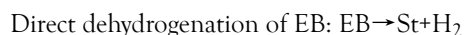
And (2) oxidative dehydrogenation of EB in the presence of carbon

dioxide by the following reaction:



The second reaction can be considered as a combination of the

Following two reactions:



Reaction 3 is the reverse reaction of steam conversion of carbon monoxide (SCCM). Using steam conversion of carbon monoxide, it is possible to generate CO_2 in the system and by this CO_2 oxidize EB in St. Thus it is possible to combine the steam conversion of CO with the conversion of EB into St. The purpose of this work is to study the pattern of conjugation of steam conversion of CO with the conversion of EB into St on a low temperature magnesium-zirconium catalyst modified with copper and phosphoric acid.

EXPERIMENTAL PART

The objects of study were samples of magnesium-zirconium catalysts (MgO , $\text{ZrO}_2/\text{Al}_2\text{O}_3$) and their forms treated by H_3PO_4 and /or CuO . Catalysts were prepared by mixing Al_2O_3 (SASOL) with calculated amounts of magnesium nitrate. For this purpose, the required quantities of were placed in separate porcelain cups and poured a given solution of magnesium nitrate. After 48 hours exposure of Al_2O_3 in these solutions, the aqueous part was evaporated, with stirring, until a homogeneous jelly-like mass was obtained. The resulting mass was formed and dried in air, and then the granulated samples were again placed in porcelain cups and continued drying at $80\text{-}120^\circ\text{C}$ (5 h) and gradually increasing the temperature to $550\text{-}570^\circ\text{C}$, calcined (3 h). The $\text{MgO}/\text{Al}_2\text{O}_3$ prepared in this way were re-placed into porcelain cups and filled with chlorine-zirconyl solution. After 24h of holding the samples in these solutions, the aqueous part was evaporated to a visually dry state and placed in an oven where the drying of these samples was continued at 80 and 120°C (3 h) and pierced at $550\text{-}570^\circ\text{C}$ (5 h). The finished samples contained 2.4 wt% MgO and 1.0 wt% ZrO_2 .

Modified catalysts were prepared on the basis of the above prepared samples. A sample of MgO , $\text{ZrO}_2/\text{Al}_2\text{O}_3$ was treated with a solution of H_3PO_4 (within 24 hours), then the water was evaporated and the resulting mass was dried at $80\text{-}120^\circ\text{C}$ and 300°C for 3 hours. The amount of phosphorus in the prepared sample corresponds to 5%

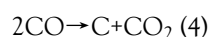
P_2O_5 . A solution of $\text{Cu}(\text{NO}_3)_2$ was added to a certain portion of this sample and the water was evaporated. Then this sample was

dried at 300°C and calcined at $500\text{-}600^\circ\text{C}$. In the composition of the finished sample, the amount of Cu corresponds to 1% by weight. The conversion of EB into St and SCCM was studied in a flow reactor at atmospheric pressure, temperature 500°C . Analysis of the reaction products was carried out chromatographically.

RESULTS AND DISCUSSION

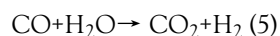
Steam conversion of carbon monoxide

The conversion of carbon monoxide on the catalyst Mg , $\text{ZrO}_2/\text{Al}_2\text{O}_3$ showed that CO is not practically converted on this catalyst. But after the reaction, the white catalyst becomes black, which is associated with the formation of coke on the surface of the sample as a result of the Voodard reaction.



This reaction takes place at the acidic center of the catalyst, and the coke formed as a result of this reaction, blocking such centers, leads to deactivation of the sample and thus the reaction does not continue. With the release of the reaction gas through a bubbler with a solution of calcium-chloride the formation of white precipitation (CaCO_3) within 3 minutes proves the progress of the Voodard reaction. After treatment of the catalyst at 600°C with air, its activity is restored.

On this sample at $400\text{-}500^\circ\text{C}$ and a molar ratio of $\text{CO} : \text{H}_2\text{O}$ components from 1 to 2.5, steam conversion of carbon monoxide reaction (5) does not occur and coke is formed on the surface of the catalyst as a result of Voodard reaction (4).



On the catalyst Mg , $\text{ZrO}_2/\text{Al}_2\text{O}_3$, reaction (5) proceeds only when the temperature rises to 600°C . In this case, the conversion of carbon monoxide reaches up to 20% with selective formation of hydrogen. Comparative studies of the conversion of $\text{CO} : \text{H}_2\text{O}$ mixtures with the participation of the catalyst MgO , $\text{ZrO}_2/\text{Al}_2\text{O}_3 + \text{CuO}$ (supported copper-modified) showed results different from Mg , $\text{ZrO}_2/\text{Al}_2\text{O}_3$. If the conversion of carbon monoxide on this catalyst does not differ from unmodified, the introduction of H_2O molecules into the process contributes to the activation of reaction (5).

Processing a sample of MgO , $\text{ZrO}_2/\text{Al}_2\text{O}_3$ with phosphoric acid (sample MgO , $\text{ZrO}_2/\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$) also leads to an increase in steam conversion of carbon monoxide. The best catalyst in reaction (5) is a sample of MgO , $\text{ZrO}_2/\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5 + \text{CuO}$. The effect of water vapor concentration on carbon monoxide conversion was studied on this catalyst. The results of these studies are shown in Table 1.

Table 1: Effect of water vapor concentration on the conversion of carbon monoxide on the catalyst, MgO , $\text{ZrO}_2/\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5 + \text{CuO}$. $T = 500^\circ\text{C}$; $\text{WHSV} = 1 \text{ h}^{-1}$ (Time for stable operation of the catalyst).

S.No	$\text{H}_2\text{O} : \text{C O}$	C O conversion, %	$\tau^* \text{ min}$	Output of H_2 , mole fraction	Selectivity for $\text{C O}_2 + \text{H}_2$, %
------	-----------------------------------	----------------------------	----------------------	--	---

1	0	Traces	-	-	-
2	0.25	11	15	0.029	26
3	0.5	18	40	0.07	38
4	1.0	37	55	0.17	48
5	2.0	43	120	0.4	93
6	2.5	43	>120	0.41	96

As can be seen from Table 1, with an increase in the H₂O: CO ratio, the conversion of carbon monoxide increases to 43%, with the H₂O : CO ratio of 2.0. Further increases in this ratio do not affect CO conversions. In addition, the addition of synthesis gas to the mixture of CO and water vapor (at a molar ratio of H₂O : CO=2.5) shows that the reaction product-hydrogen does not affect the process, in other words, does not inhibit the conversion of CO (Figure 1).

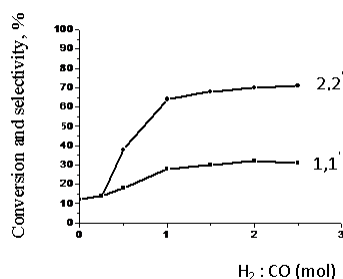
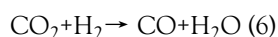


Figure 1: Effect of H₂ on steam conversion of CO on MgO, ZrO₂/Al₂O₃+P₂O₅+CuO catalyst. 1.1 and 2.2 steam conversion of CO and selectivity for H₂ before and after adding synthesis gas (CO : H₂=1:2) respectively. H₂O : CO=2.5. T=500° C and WHSV=1 h-1.

The effect of the reverse reaction (6) on the steam conversion of carbon monoxide on the MgO, ZrO₂/Al₂O₃+P₂O₅+CuO catalyst was also investigated. It was established that reaction (5) practically does not proceed in the presence of reaction (6) on this catalyst:



Conjugation of the dehydrogenation of ethyl benzene to styrene with steam conversion of carbon monoxide Conjugation of the dehydrogenation of ethyl benzene to styrene with steam conversion of carbon monoxide on MgO, ZrO₂/Al₂O₃ catalyst was carried out under the above conditions. The results of these studies are shown in Figure 2.

The results obtained show that carbon monoxide has practically no effect on EB conversion; however, the coke obtained as a result of the Voodard reaction on the catalyst surface deactivates it. In the absence of CO, the conversion of EB on this catalyst begins after 0.5 sec of catalyst operation, i.e., the induction

period of the process is 0.5 sec. Conjugation of EB conversion with water gas conversion leads to an increase in EB conversion and styrene yield.

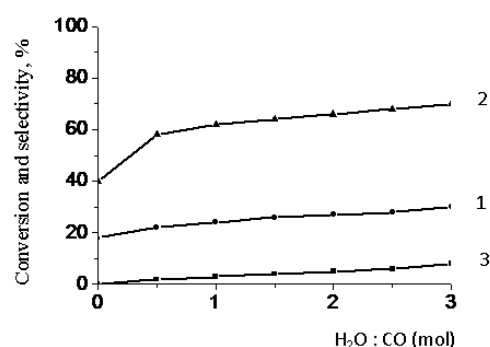


Figure 2: Effect of water gas on the conversion of ethyl benzene on MgO, ZrO₂/Al₂O₃ catalyst. T=500° C ; WHSVEB=1 h-1, WHSV water gas=500 h-1.

Analysis of the composition of the initial reagents and reaction products shows that the maximum conversion of carbon monoxide is achieved by 8% (Figure 2). This fact indicates that the studied reactions, i.e., conversion of EB to styrene and steam conversion of carbon monoxide depend to some extent on each other.

The increase in activity and selectivity of the conversion of EB to styrene in the presence of water gas is undoubtedly associated with a shift in the reaction towards the products, and this implies the efficient removal of the resulting hydrogen from the reaction zone.

Considering the low oxidative properties of CO, it can be assumed that the conjugation is based on either the product of the disproportionation of carbon monoxide-CO₂ or its intensive hydrogenation to methane. Thus, the above was noted the absence of the effect of hydrogen on the steam conversion of carbon monoxide. Therefore, the contribution of such a process to the conversion of EB to styrene is very insignificant.

Treatment of the catalyst MgO, ZrO₂/Al₂O₃ with phosphoric acid and modifying it with CuO promotes the growth of activity

and selectivity of the conversion of EB to styrene in the presence of water gas (Table 2).

Table 2: Conversion of EB to styrene in the presence of water gas on MgO, ZrO₂/Al₂O₃; MgO, ZrO₂/Al₂O₃+P₂O₅ and MgO, ZrO₂/Al₂O₃+P₂O₅+CuO catalysts; T=500° C; WHSVEB=1 h⁻¹, WHSV water gas=500 h⁻¹.

S No	Catalysts	Conversion of EB, %	Conversion of CO, %	Selectivity for St, %
1	MgO, ZrO ₂ /Al ₂ O ₃	37	8	72
2	Mgo, ZrO ₂ /Al ₂ O ₃ +P ₂ O ₅	42	12	83
3	MgO, ZrO ₂ /Al ₂ O ₃ +P ₂ O ₅ +CuO	53	45	89

Note that the treatment of MgO, ZrO₂/Al₂O₃ with phosphoric acid leads to a noticeable reduction in the induction period of the reactions on this catalyst [11]. Bearing in mind that the formation of compaction products (CP) on the surface of dehydrogenating catalysts proceeds with the participation of acid centers [8,9] and, therefore, the treatment with phosphoric acid accelerates the formation of CP on the catalyst surface.

But the increase in the activity of the MgO, ZrO₂/Al₂O₃+P₂O₅+CuO catalyst in the target reaction can be explained not only by the accumulation of CP, which is facilitated by the modification of the catalyst with the P₂O₅, but also by the more likely activation of the steam conversion of carbon monoxide with CuO, which increases the accumulation of CO₂, which is reverse reaction of steam conversion of carbon monoxide.

Experiments carried out with the replacement of CO by CO₂ in the conversion of EB to styrene confirm this assumption (Scheme 1).

As can be seen from Figure 3, the conversion of EB to St depends substantially on the molar ratio of CO₂: EB. With an increase in the molar ratio of CO₂: EB to 4-5, the conversion of EB is increased 5 times (up to 53-54%), and the selectivity for St reaches 84%.

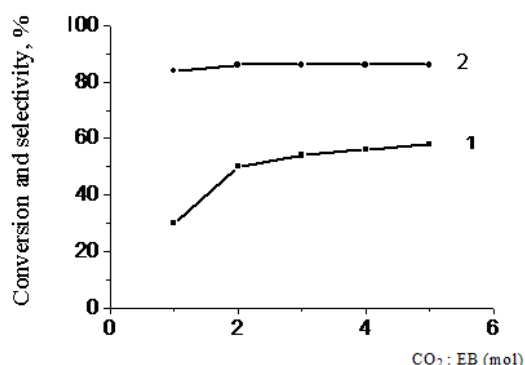
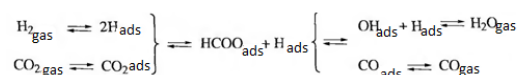


Figure 3: The conversion of EB to St in the presence of CO₂ on the catalyst MgO, ZrO₂/Al₂O₃+P₂O₅. T=500° C; WHSVEB=1 h⁻¹; WHSVC₂=500 h⁻¹; τ=2 h-1-conversion of EB; 2-styrene selectivity

At the same time in the conversion of EB, no hydrogen is formed and finally CO₂ serves as an oxidizing agent. From the

realization of this process it has been established that it proceeds through a mechanism similar to the mechanism of steam conversion of carbon monoxide [10].



Scheme 1: Conversion of EB to St in the presence of CO₂.

As noted above, the modification of the catalyst MgO, ZrO₂/Al₂O₃ with CuO and the treatment with phosphoric acid increases the conjugation of steam reforming of CO with oxidative dehydrogenation of EB in St (Table 2). An increase in the activity of the catalyst in such treatment is also observed in the conversion of EB to St in the presence of CO₂. However, instead of this, the reverse reaction is enhanced. As can be seen from Figure 4, with a molar ratio of CO₂: EB=4, the conversion of EB to St and selectivity for St (62 and 90.6% respectively) passes through a maximum. The formation of these maxima is associated with the formation of hydrogen (the product of reaction CO+H₂O → CO₂+H₂). So, as the presence of hydrogen in the reaction medium increases the probability of hydrogenolysis of an alkyl substituent.

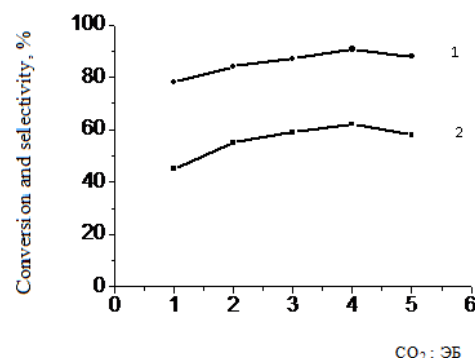


Figure 4: Conversion of EB to St in the presence of CO₂ on the MgO, ZrO₂/Al₂O₃+P₂O₅+CuO catalyst. T=500° C; WHSVEB=1 h⁻¹; WHSVC₂= 00 h⁻¹; τ=2 h-1-styrene selectivity; 2-conversion of EB.

Thus, the results of the conducted studies show the possibility of conjugation of dehydrogenation of EB in St with the steam conversion of carbon monoxide. Such a conjugation of the two

noted above reaction can create a highly efficient, environmentally friendly process for the production of styrene and hydrogen with a relatively low cost of additional capital and energy.

CONCLUSION

The synthesized MgO , $\text{ZrO}_2/\text{Al}_2\text{O}_3+\text{P}_2\text{O}_5+\text{CuO}$ catalyst allows the conversion of EB to St in the presence of CO_2 at atmospheric pressure and at a temperature of 500°C . In this case, the conversion of EB is reached 62%, and the selectivity for styrene is 90.6%. Conjugation of steam conversion of carbon monoxide with the dehydrogenation of EB in St creates effective conditions for the preparation of industrially important styrene monomer and hydrogen.

REFERENCES

1. Schwint KJ, Wilcox RJ. Method for producing of styrene monomer by oxidative dehydrogenation of ethyl benzene using CO_2 as a mild oxidant. USA. 2012.
2. Do-Young H, Vislovskiy VP, Sang-Eon P, Min-Seok P, Yoo JS, et al. Dehydrogenation of ethyl benzene with carbon dioxide as soft oxidant over supported vanadium-antimony oxide catalyst. Bull Korean Chem Soc. 2005;26: 1743-1748.
3. Mimura N, Saito M. Dehydrogenation of ethylbenzene to styrene over $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts in the presence of carbon dioxide. Catal Letters. 1999;55:173 -178.
4. Badstube T, Papp H, Dziembaj R, Kustrowski P. Screening of catalysts in the oxidative dehydrogenation of ethyl benzene with carbon dioxide. Appl Catal A. 2000;204:153-165.
5. Chang JS, Park SE, Park MS. Beneficial Effect of Carbon Dioxide in Dehydrogenation of Ethyl benzene to Styrene over Zeolite-Supported Iron Oxide Catalyst. Chem Lett. 1997;26:1123-1124.
6. Ikenaga NO, Tsuruda T, Senma K, Yamaguchi T, Sakurai Y, et al. Dehydrogenation of ethyl benzene with carbon dioxide using activated carbon-supported catalysts. Ind Eng Chem Res. 2000;39:1228-1234.
7. Xingnan YE, Weiming H, Yinghong Y, Weilin D, Changxi M, et al. Ethyl benzene dehydrogenation to styrene in the presence of carbondioxide over chromia-based catalysts. New J Chem. 2004;28:373-378.
8. Alkhazov TG, Lisovskiy AE. Oxidative dehydrogenation of hydrocarbons. M Chem. 1980;p: 240.
9. Lisovskii AE, Aharoni C, Catal Rev Sci Eng. 1994;36:25-31.
10. Krylov OV. Heterogeneous catalysis M. Academkniga. 2004;p: 679.