

Modest Strategy for Oxygen Vacancies Concentration on x/Zn-ZSM-5 Bi-functional Catalyst in the Alkylation of Benzene with Syngas

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Conflicts of Interest

There are no conflicts to declare.

ABSTRACT

Alkylation of benzene with syngas was studied over Ceria-Zirconia Solid solution and Zinc modified x/Zn-HZSM-5 catalyst. The catalyst was prepared by co-precipitation and impregnation methods. The experimental results exhibited that the insertion of Zr and Zn contents were excessive oxygen vacancies and increase in the specific surface area. The insertion of Zr and Zn content had the best catalytic performance, the sample CeZr/Zn-HZSM-5 exhibiting 26% benzene and 27% CO conversion, with the high selectivity of toluene and xylene 87%. The catalyst carefully characterized: results showed that the catalytic activity was enhanced with the doping of Zr atoms, which would increase the reducibility of Ce⁴⁺ to Ce³⁺, this event led to generate more oxygen vacancies. Besides, the modification of HZSM-5 by Zn contents, the suppressing side reaction of methanol to olefins by reduction of strong Brønsted acid and generate new Lewis acid due to the Zn (OH)⁺ species. These findings are beneficial for comprehension of the conversion of syngas to intermediate methanol and alkylation of the benzene process.

Keywords: ZIRCONIUM EFFECTS, OXYGEN VACANCIES, ALKYLATION, SYNTHESIS GAS, BENZENE

1. Introduction

In recent decades, steady economic growth and increased energy use have contributed to a dramatic reduction in the availability of fossil fuels. Therefore, the identification of other sustainable sources of energy is urgently need to end this crisis¹. Syngas (a mixture of hydrogen and carbon monoxide) is an important resource of non-petroleum carbon to replace alleviate crude oil, Syngas derived from abundant resources such as coal, biomass, natural gas or organic waste has drawn a great deal of attention from both academic and industrial perspectives as it is a significant source of carbon and hydrogen. A variety of substances such as hydrocarbons which can be fuels (gasoline, diesel, and jet fuel) or chemicals (olefins and aromatics) and oxygenates (methanol and C₂ oxygenates) can be derived from

syngas²⁻⁴.

Aromatics, individually light aromatics (benzene (B), xylene (X) and toluene (T), known as BTX, are some of the most fundamental raw materials in the, polymers, medicines, coatings, resins, perfumeries, dyestuffs, pesticides, etc^{1,5}. The production of BTX by typical routes, such as methanol to aromatics, benzene alkylation with methanol to toluene and xylene, toluene alkylation with methanol to xylene, and so on, but the amount of these in actual generation is limited and was insufficient to fulfill market demand^{2,5,6}. Accordingly, coupling catalysts with Ce/Zr mixed oxide and modified HZSM-5 could be very economical and beneficial to compare with methanol in the alkylation of benzene with syngas. Therefore, as well as, to design a type of bi-functional composite catalyst, to carry out success completing the first step of active site reaction synthesis gas into methanol intermediates on oxides such as ZrO₂ and bi-metal CeZrO₂ accompanied by rapid transition to Zn modified HZSM-5 zeolite for eventual aromatization. It is important to select an effective metal catalyst for coupling in thermodynamics. Metal catalysts such as (Na-Zn-Fe₅C₂), (Cr-Zn-Al) and (Cu-Zn-Al) are commonly used to obtain methanol from Syngas, in the temperatures range around (493-573 k), But it takes high temperatures to generate high rates of hydrocarbons. According to the Kinetics criterion, the MTA reaction temperature must be maintained around (673 K)^{3,4,7}.

However, it has been reported recently that Ceria (CeO₂) has been widely researched as a hetero-atoms catalyst, a catalyst amplifier due to its specific properties, such as excellent redox abilities, numerous oxygen storage capacity (OSC) and Specifically, a mesoporous framework with a large surface area is particularly attractive, which not only promotes the dispersion of secondary materials, however, also make capable reactant molecules to disperse readily to active sites^{8,9}. The surface oxygen vacancy of Ceria (CeO₂) oxides has been known as a C–O bond activation sites. It has been considered as a suitable catalyst for methanol extraction from Syngas. While CeO₂ has a wide range of applications, it is associated with certain disadvantages, such as thermal sintering at elevated temperatures and redox pair deactivation, resulting in a decrease in OSC and catalytic activity¹⁰. To overcome these weaknesses of CeO₂, there are a range of alternatives. In most of the applications, the catalytic performance is strongly dependent on the reduction in particle size and high densities of interfaces in nanocrystalline solids¹⁰⁻¹³. Therefore, nanostructured CeO₂ has attracted much attention due to its reduced dimensions, increased relative surface area, highly active facets, large number of active sites, changeable valence states, improved redox and oxygen transport properties, and enhanced surface to volume ratio compared to those of bulk materials. Doping with other isovalent cations changes the bulk and surface properties of CeO₂. The frequently employed isovalent dopants are Zr⁴⁺, Ti⁴⁺ and so on^{10,14,15}.

In this study, a bi-functional catalyst containing Ceria-Zirconia mixed oxide and modified HZSM-5 zeolite was expanded for the alkylation of benzene with syngas. Ceria-Zirconia, Zirconia mixed oxides and HZSM-5 modified Zn have been studied to generate an optimal catalyst. Characterization techniques such as

XRD, OSC, and N₂ desorption have been employed. The structure of CeO₂ and the influence of Zr species on the structure and OSC of the Ceria-Zirconia catalyst. The catalytic activity of binary metal oxide catalyst and Zn modified HZSM-5 zeolite in the two-step reaction of benzene alkylation with syngas was systematically investigated.

2 Experimental sections

2.1 Catalyst preparation

The Ceria/Zirconia solid solutions catalysts x/Zn-ZSM-5 (x=Zr, Ce, CeZr) were synthesized with a single method of a template-assisted chemical precipitation. Typically, an aqueous solution of ammonium Hydroxide (NH₃ H₂O, 25%) was added dropwise into the mixed solution of Ce(NO₃)₃ 6H₂O, Zr(NO₃)₄ 5H₂O, PEG-4000 and H₂O₂ under rigorous stirring at 80 °C, then the combined solution was kept stirring at 80 °C for 12 h. After filtration the solid was collected and washed for 3 times with ethanol and deionize water, respectively, followed by drying at 100 °C overnight. The solid was eventually calcined for 4 h in air at 700 °C.

ZSM-5 Modification. HZSM-5 zeolite were impregnated with same amount (3.5%) of Zn(NO₃)₂.6H₂O solutions, then oscillated with ultrasonic conditions for 3 h consecutively, afterward drying for 10 h under 100 °C, and at 550 °C calcination for 5 h.

2.2 Catalytic tests and analytical methods

Alkylation process of benzene with syngas was conducted in a fixed-bed continuous-flow apparatus with a quartz tube reactor (700 mm length and 10 mm an inner diameter). In the traditional process, 5 g of the catalytic particles (20–40 mesh) is placed in the middle portion of the reaction pipeline, both ends of the catalytic converter being lined with quartz pellets (10–20 mesh) and heated to the target temperature. The catalyst was alleviated by H₂ at 400 °C for 4 h prior to the reaction. Afterward, the syngas flow (H₂/CO molar ratio of 2:1) was pumped into the reactor with a gas hourly space velocity of 3600 h⁻¹ until the inner pressure became 3.1 MPa, Simultaneously, benzene was feed by a syringe pump with a liquid hourly space velocity of 1 h⁻¹ inside the reactor. In this work, the reaction was performed at 400 °C and 3.3 MPa.

The gaseous-phase and liquid-phase products were segregated through a condenser. The gaseous-phase productions were studied off-line using a gas chromatograph (GC-920) fitted out with a 5A molecular sieve connecting to the TCD detector, a carbon molecular sieve, and a revised alumina connecting to the FID detector. Finally, the determined substance content of each column is matched with methane gas. Condensed liquid products were obtained and tested off-line by a gas chromatograph GC-950 fitted out with a capillary column DM-Wax (60 m × 0.25 mm) with an FID detector.

Indicators of the catalytic behavior include the conversion of benzene (X_B) and the conversion of CO (X_{CO}). The yield indicators of each product are classified onto two categories: one is correlated with benzene, including the selectivity of toluene (S_T), the selectivity of xylene (S_X), the selectivity of ethylbenzene (S_{EB}), the selectivity of heavy aromatic hydrocarbons (S_{HA}) and other marginal products; the other is related to CO, including the selectivity of the side chain of aromatics.

The related calculation form is as follows

$$X_B = \frac{B_{inlet} - B_{outlet}}{B_{inlet}}$$

Where B_{inlet} and B_{outlet} display mole of benzene at the inlet and outlet, respectively.

$$S_Y = \frac{Y_{outlet}}{\sum T, X, EB, HA_{outlet}}$$

Where Y_{outlet} represents the mole of individual aromatic hydrocarbons at the outlet.

$$X_{CO} = \frac{CO_{inlet} - CO_{outlet}}{CO_{inlet}}$$

Where CO_{inlet} and CO_{outlet} were means the mole of CO at inlet and outlet, respectively.

$$S_{Qi} = \frac{C_{i \text{ side chain}}}{\sum_1^4 C_{i \text{ side chain}}}$$

Where S_{Qi} represents the selectivity of the side chain of aromatics (SQ1), the selectivity of C_1 – C_4 alkanes and C_{5+} non-aromatic hydrocarbons (SQ2), the selectivity of C_2 – C_5 alkenes (SQ3) and the selectivity of CO_2 (SQ4). $C_{side \text{ chain}}$ represents the carbon mole in the side chain of the product.

2.3 Catalyst characterization

X-ray diffraction (XRD) of the catalyst was carried out using a SHIMADZU-6000 X-ray powder diffractometer (Shimadzu, Japan). The sample was scanned with monochromatic Cu- $K\alpha$ radiation at a rate of 8° min^{-1} from 5° to 85° . Oxygen storage capacity (OSC) of the samples was measured using pulse chromatographic technique on Chembet PULSAR TPR/TPD instrument (Quanta chrome Inc.). Nitrogen adsorption/desorption isotherms and pore size distribution curves of the pure CeO_2 and $CeZr$ were detected on a BELSORP-max gas adsorption analyzer.

3 Results and discussion

3.1 XRD

Figure 1 Shows the XRD patterns of catalyst with different Zn contents. The (ZSM-5, Zn-ZSM-5 and CeZr/Zn-ZSM-5) samples represented characteristic peaks of an MFI crystal structure between 7–10 and 22–25, and all of these three samples show the skeleton structure of ZSM-5 and have good crystallinity. Moreover, the sample (CeZr/Zn-ZSM-5) also shown two sharp peaks around the 30° and 49.8° which is corresponding to the cerium and zirconium ions respectively¹⁶. In addition, for ZnO₂ are not obvious peaks, which is indicating that the Zn species are greatly distributed in the parent ZSM-5 zeolite.

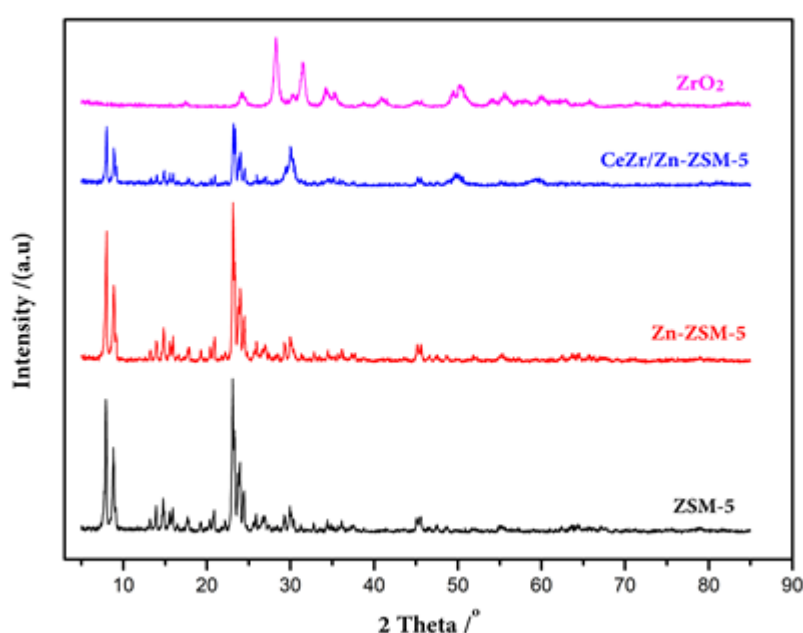


Figure 1: XRD patterns of ZSM-5, Zn-ZSM-5, CeZr/Zn-ZSM-5 and ZrO₂

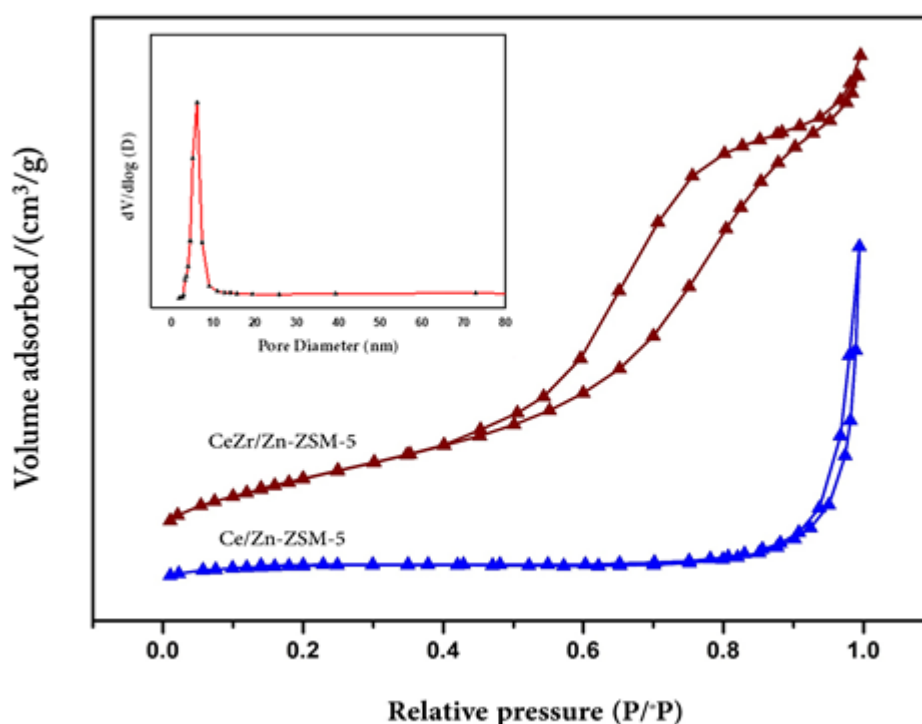
3.2 Textural properties

In general, the activity of the catalysts is a crucial factor in a catalyst that should be as high as possible in order to facilitate chemical reactions. The activity of solid solution catalysts are proportional to the region of the surface, with particles of smaller size providing a larger area of the surface and increasing the number of active sites. Hence, the surface area is a critical factor to raise the catalytic efficiency of catalysts.

Table 1: The textural properties and Surface Compositions of the samples

Sample	BET SA(mg ⁻¹)	Pore V(cm ³ g ⁻¹)	Pore size(nm)	Oxygen storage capacity (%)
Zn-ZSM-5	13.73	0.07	11.55	~
Ce/Zn-ZSM-5	39.87	0.11	9.59	643
Zr/Zn-ZSM-5	41.11	0.09	9.19	584
CeZr/Zn-ZSM-5	62.34	0.15	8.36	504

Figure 2 Shown the N₂ adsorption-desorption isotherms and pore size distribution curves of the pure Ce/Zn-ZSM-5 and CeZr/Zn-ZSM-5. The isotherm profile of pure Ceria and CeZr both distinctly belongs to IV type with H1-type hysteresis loop in a P/P₀ range of 0.43-0.94, which indicating the formation of mesopores of large interparticle both on the external surface and in the inner region of agglomerates. The existence of the mesoporous is an important reason for the catalyst's large specific surface area^{14,17,18}.

**Figure 2: Nitrogen adsorption/desorption isotherms of Ce/Zn-ZSM-5 and CeZr/Zn-ZSM-5**

3.3 OSC analysis

The oxygen storage capacity (OSC) profile of Ce/Zn-ZSM-5, CeZr/Zn-ZSM-5 and Zr/Zn-ZSM-5 samples were shown in **Figure 3**. It can be observed that oxygen storage capacity (OSC) affected by insertion of Zr

content because more CeO_2 provide more oxygen whenever Ce^{4+} is reduced to Ce^{3+} . Accordingly, the surface area has minor effect on the oxygen storage capacity value^{19–21}. As shown in Figure 3. After the periodical oxygen pulse titration testing, the OSC of CeO_2 at 500 °C is (643 $\mu\text{mol O}_2/\text{g}$), which is much higher than the CeZr (584 $\mu\text{mol O}_2/\text{g}$) and Zr (504 $\mu\text{mol O}_2/\text{g}$).

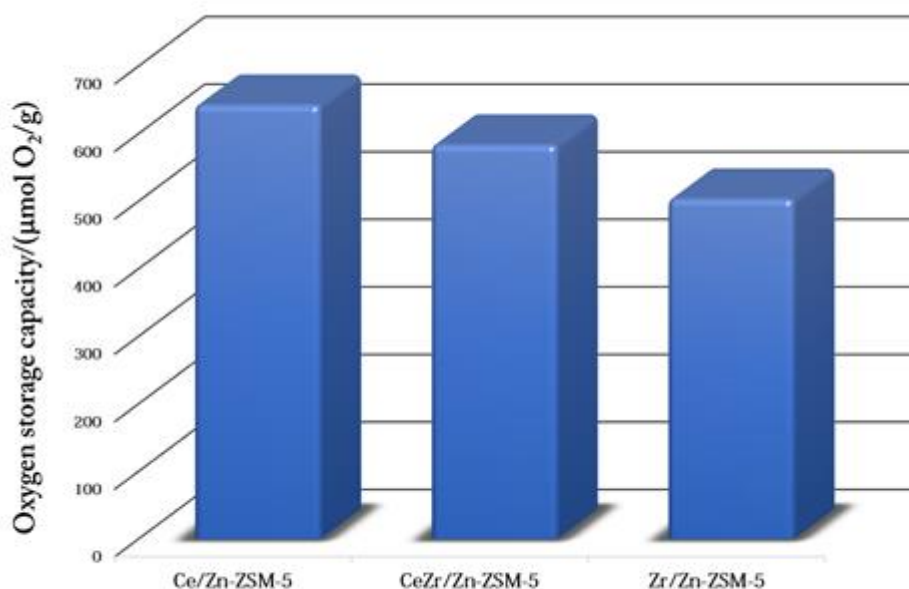


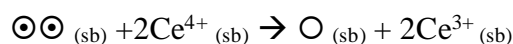
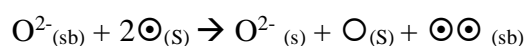
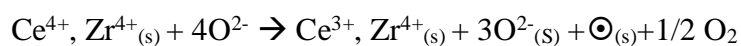
Figure 3: The oxygen storage capacity (OSC) performance of catalyst samples

3.4 Introduction effects of Zr in the x/Zn-ZSM-5 catalyst

The introduction of various metallic ions into the ceria lattice can adjust the oxygen vacancies and enlarge specific surface area, which can promote catalytic activity of ceria. Therefore, it is important to know about the influence of Zr on CeZr/Zn-HZSM-5, the above characterization indicate that the introduction of Zr species into ceria lattice, not only showed higher catalytic activity than pure CeO_2 but also incorporated as a promoting component which helped the generation more oxygen vacancies on the surface and enlarge the specific surface area of CeZr, which can be supporting the catalytic activity and also in increased the specific surface area, as listed in Table 1, which indicate that after introduction smaller Zr ions into Ceria lattice, the increase stability of oxygen defects could account for improved oxygen storage capacity and thermal stability compared to pure Ceria²⁰.

Based on the above analysis, we found that I- the introduction of Zr species to CeO_2 lattice could directly affect the oxidation state of Ce. II- as expected, due to the reduction of Ce^{4+} to Ce^{3+} , there is an increase in Ce^{3+} ions, and hence, the increase of Ce^{3+} ions on the surface is closely associated with the formation of Oxygen vacancies. III- Zr caused the accumulation from deep in ceria to the bottom of the metal region of subsurface oxygen vacancies. Representation of the surface reduction hypostasis process and

surface deficiency in the following:



The symbol (O) represents surface oxygen vacancy with no electron's, one electron (\odot) or two electrons ($\odot\odot$) production of surface defects, (s) shows surface and (sb) species of near subsurface.

3.5 Catalysts evaluation

Evaluation of x/Zn-HZSM-5 catalysts in the alkylation of benzene and syngas. Error! Reference source not found.. Listed the catalytic performance of all as-prepared catalysts in the alkylation of benzene with syngas, it displays the catalytic reactivity of Ceria/Zirconia solid solution and Zn-modified HZSM-5 catalysts in the alkylation of benzene with syngas. The benzene conversion was reached the maximum 26% with the highest CO conversion of 27%, while maintaining a higher TX selectivity. This result indicated that, the modification of HZSM-5 with Zn and the introduction of Zr species to the Ceria lattice to form bi-metal samples, which showed higher catalytic activity than pure Ceria and Zirconia because ZrO_2 was enhanced the formation of oxygen vacancies and increased the specific surface area. Furthermore, the Zr species activate CO to the formation of methoxide in the presence of H_2 . Furthermore, the H_2 dissociation explored on the stoichiometric ceria surface, the $-\text{Ce}-\text{O}-$ pairs on CeO_2 surface from the heterolytic products as (H^+ , H^-), these species will work for CO hydrogenation reactions, therefore generating more methanol^{22,23}.

Table 2 Reactant conversion and product distribution catalyzed by bi-functional catalysts

Catalysts	$X_B\%$	$X_{CO}\%$	Selectivity%							
			S_T	S_X	S_{EB}	S_{HA}	Q_1	Q_2	Q_3	Q_4
Zn-ZSM-5	7.5	9.4	65.7	10	15.2	7.2	11	83	3	6
Ce/Zn-ZSM-5	16.1	17.7	66.9	14	9.6	7.5	15	71	7	9
Zr/Zn-ZSM-5	24.3	25.8	65.2	21	7.4	6.1	18	64	7	13
CeZr/Zn-ZSM-5	26.1	26.8	63.8	23	6.3	6.3	21	51	8	17

While for Zn modified HZSM-5 and x/Zn-ZSM-5 metal catalysts under the same condition, the conversion of benzene and CO, and selectivity's to related products, were both increased as compared to those of unmodified catalysts.

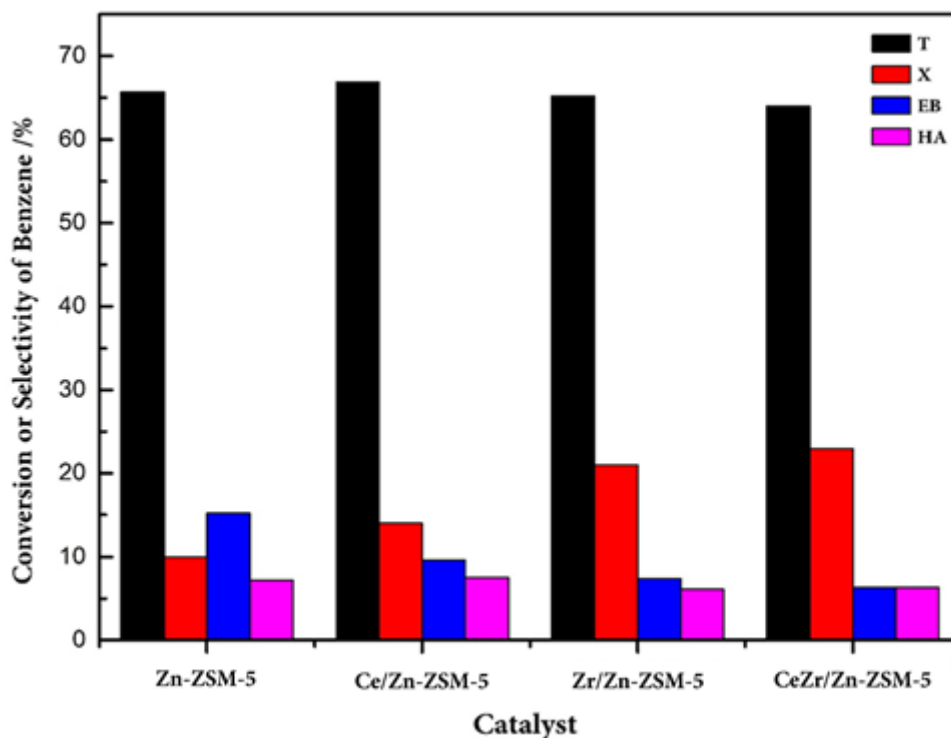


Figure 4: Conversion and selectivity of benzene over Zn-ZSM-5, Ce/Zn-ZSM-5, Zr/Zn-ZSM-5 and CeZr/Zn-ZSM-5 catalysts.

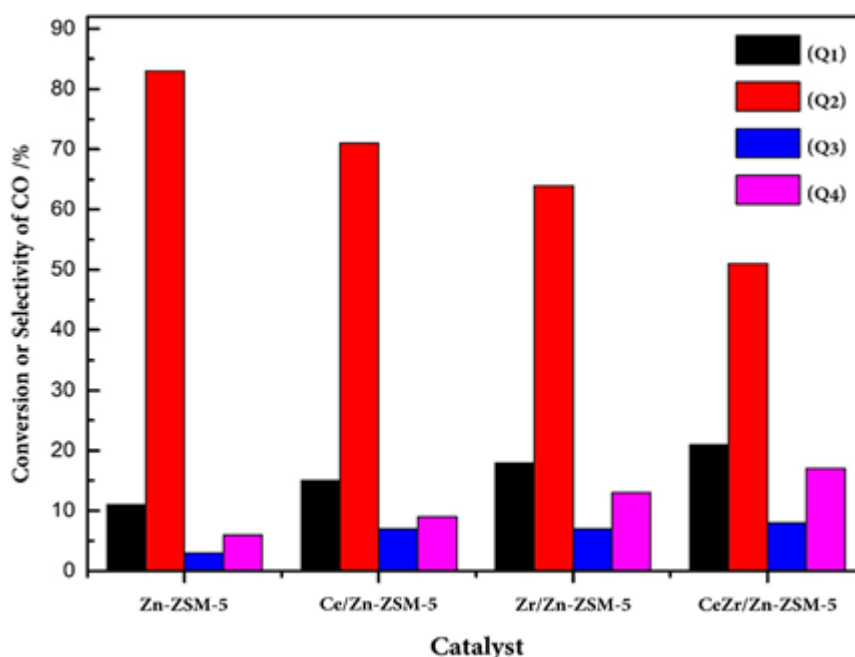


Figure 5: Conversion and selectivity of CO over Zn-ZSM-5, Ce/Zn-ZSM-5, Zr/Zn-ZSM-5 and CeZr/Zn-ZSM-5 catalysts.

Figure 4 and **Figure 5** demonstrate the composition of the substances in the products relevant to benzene and CO. It can be seen that modified catalysts could suppress the formation of ethylbenzene and alkanes. Based on these results obtained and the literature, we deduced that modification of CeZr/Zn-

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HZSM-5 with Zn species could decrease the selectivity of ethylbenzene from 15.2 to 6.3% and the selectivity of alkanes from 83 to 51%, which suggests that methanol's side reaction to olefins was suppressed because it is well known that the fundamental materials for the formation of ethylbenzene are ethylene, the main component of alkenes. Simultaneously, all of the selectivity of C₁-C₄ alkanes and C₅+ non-aromatic hydrocarbons slightly decreased, while the selectivity to toluene and xylene gradually increased. These phenomena imply that the insertion of Zn not only prevents the transfer reaction of hydrogen but also enhanced dehydrogenation reaction²⁴.

The evolution trends of benzene and CO conversion were consistent with the evolutions of oxygen storage capacity and specific surface area. Based on catalysts textural properties results, the promising characteristics of CeZr due to the insertion of Zr especially the increments of oxygen vacancies on the higher specific surface area and pore size distribution, leads to the enhancement of catalytic activity in the alkylation reaction. Similarly, Parag M et al²⁵. Believe that the insertion of Zr species to the Ceria led to a relative increase in surface oxygen defect species compared to pure ceria.

A two-step reaction was performed by the bi-functional catalyst at two active sites, resulting in the reaction of syngas on the x/Zn-ZSM-5 catalyst to form intermediate methanol whereas Zn-ZSM-5 was responsible for the alkylation of benzene with methanol relevant species. Huang et al, proposed methanol and/or dimethyl ether are the main products on CZ. Density functional theory (DFT) has been used in some previous works to calculate the energy barriers and investigate the mechanism of reaction, for syngas conversion to methanol, the barrier energy was 284.3 kJ/mol over Rh/ γ -Al₂O₃ catalyst on D (RH₄) surface, 255.06 kJ/mol over Mo₆P₃-Si₃O₉ cluster and 177.66 kJ/mol over Ni catalyst, Wherein the rate-limiting step was the formation of CHO* from CO hydrogenation^{26,27}. For benzene alkylation with methanol, the energy barriers obtained for methoxy group formation and methoxy group methylation of benzene over ZSM-5 zeolite were 149 kJ / mol and 97 kJ / mol, respectively, for the alkylation of benzene with methanol, the obtained energy barriers to the formation methoxy group and the methylation of benzene with methoxy group over ZSM-5 zeolite were 149kJ/mol and 97KJ/mol respectively²⁸.

In all, it is reasonable to believe that the rate-limiting step is syngas conversion to methanol with a higher energy barrier than alkylation of benzene with methanol. And that may explain why surface area plays a key role in the alkylation of benzene with syngas because there are more active sites and more oxygen on a larger CeZr surface area.

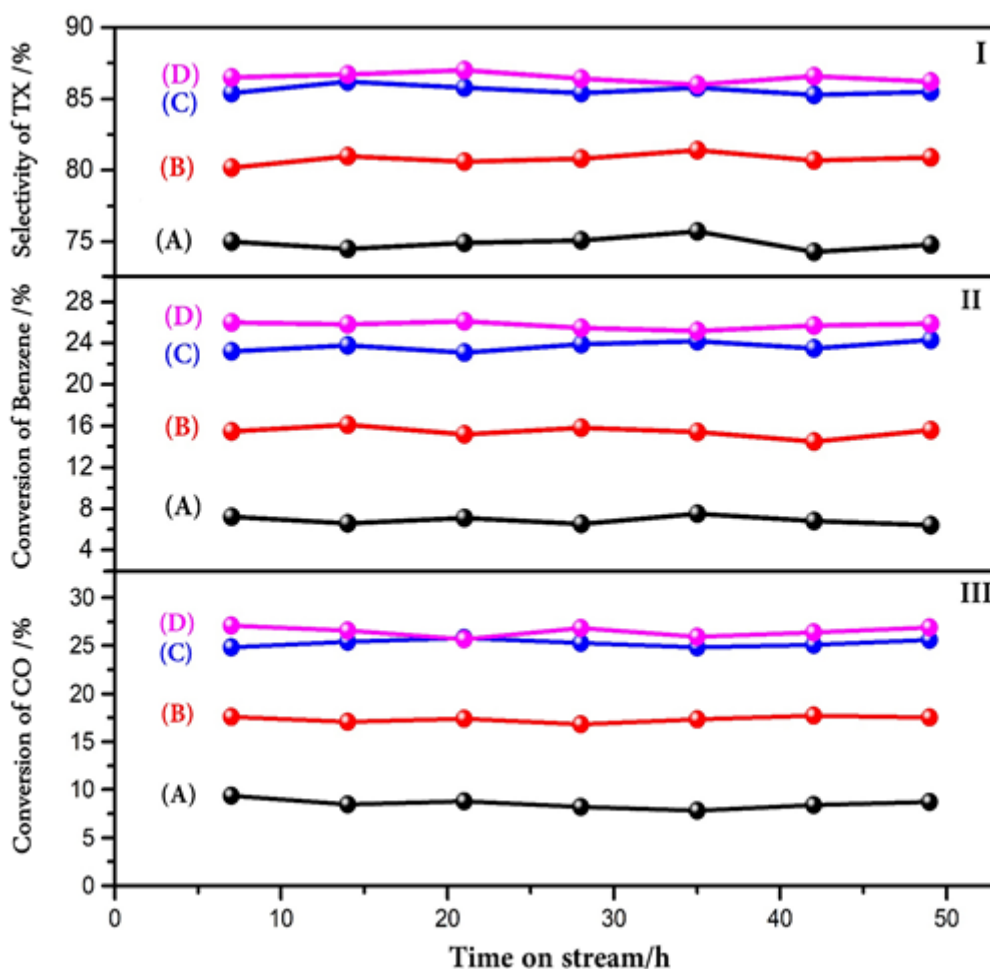


Fig.6. Time on stream of conversions of CO and benzene catalyzed by bi-functional catalysts: Zn-ZSM-5, Ce/Zn-ZSM-5, Zr/Zn-ZSM-5 and CeZr/Zn-ZSM-5

The time on stream and catalytic performance of different x/Zn-HZSM-5 catalysts was shown in **Figure 6**. There has no significant change in the catalytic performance during 52 h, which suggested that the catalysts were highly stable. Consequently, the best catalytic performance was achieved by CeZr/Zn-ZSM-5 bi-functional catalyst due to it is high reducibility, high specific surface area, and high oxygen storage capacity.

3.6 Reaction mechanism

To obtain insights about the process, as we mentioned in the above section, we have hypothesized that the reaction mechanism of the alkylation of benzene and syngas in the bi-functional catalyst as shown in **Figure 7**. A two-step reaction from two active sites was performed by the bi-functional catalyst, so the reaction consists of two stages: the first is the reaction of syngas on metal oxide (Ce, Zr, CeZr) catalysts to formed intermediate methanol. And the second has been further divided into two stages one of which is the methanol and raw benzene alkylation reaction (stage 1) while the other is methanol's direct aromatization to produce aromatic compounds (stage 2).as shown in scheme1, on the first stage, to form dimethyl ether, the

methanol was dehydrated, and the generated dimethyl ether and undehydrated methanol to form methanol carbonate combined with the Bronsted acid sites, thus the generated carbonate was attacked on benzene molecule to form protonated toluene. Afterward, when the proton returned to the zeolite from the protonated toluene, toluene was formed. Similarly, xylene and trimethyl benzene are obtained in this route. On the second stage, under the catalysis of the bronsted acid sites of zeolite, methanol was directly converted to aromatic hydrocarbons. First, through dehydration, methanol is transformed to dimethyl ether as well as further reacts to form ethylene with bronsted acid sites, which would then be polymerized into form high alkenes. Afterward, C_{6+} olefins undergo cyclization, transfer hydrogen, and dehydrogenation to form polymethylbenzene and alkanes intermediate. Then, by alkylation and dealkylation, polymethylbenzene proceeds to form C_6 - C_{9+} aromatic hydrocarbons, and alkanes are dehydrogenated to form light olefins through isomerization. Meanwhile, to form light olefins, C_{9+} aromatics have been further cracked and then the olefins undergo hydrogen transfer reaction to form light alkanes. An Olefin-aromatic double-cycle mechanism has been formed by the above process.

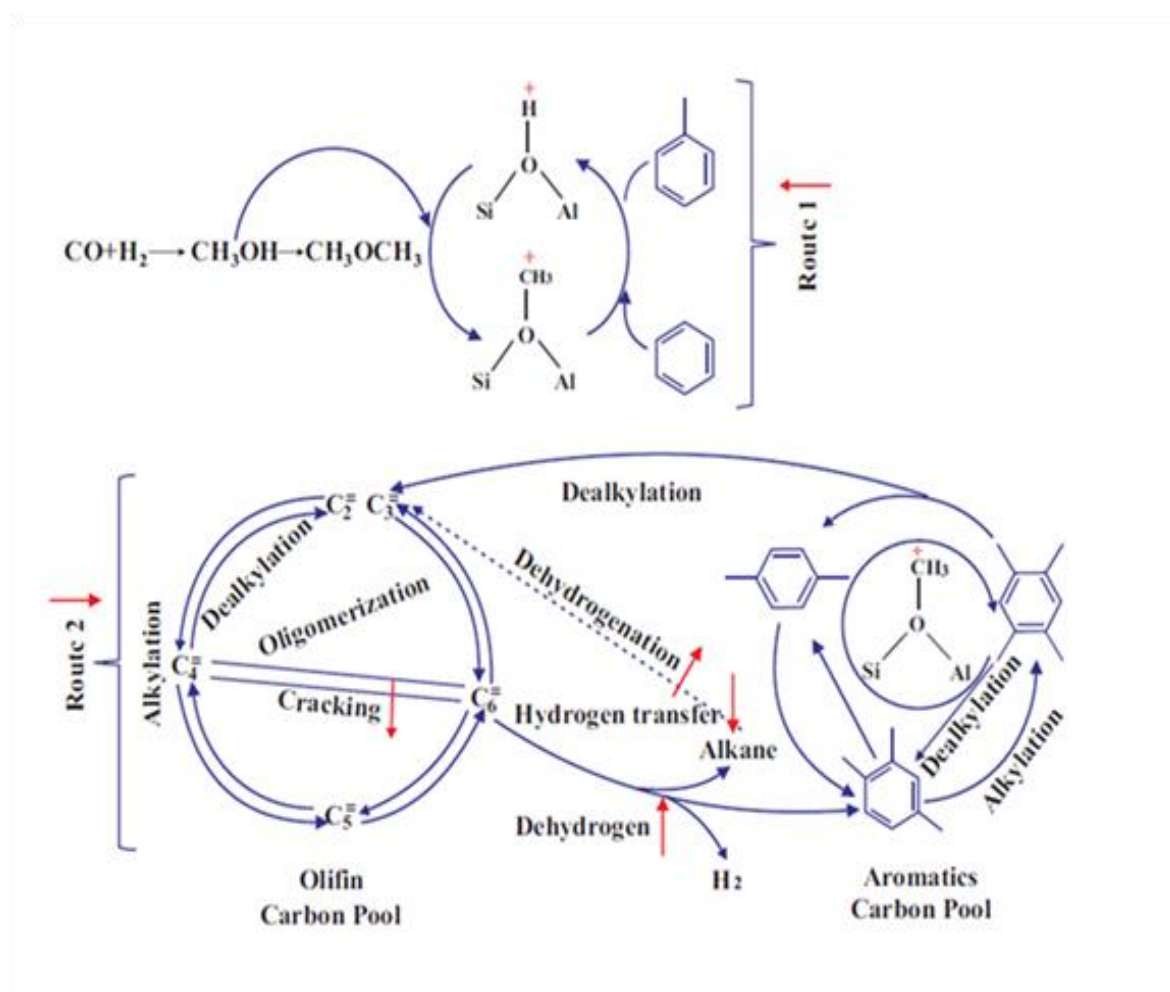


Figure 7. The hypostasis reaction mechanism of alkylation of benzene with syngas

4 Conclusions

In summary, a bi-functional x/Zn-HZSM-5 Zn-modified catalyst for alkylation of benzene and syngas is designed in the present work, it was demonstrate that the insertion appropriate amount of Zr could improve the surface oxygen vacancies and increase specific surface area, thus generating more methanol, as well as the conversion of benzene and conversion of CO simultaneously improved. In liquid phase products, the selectivity of TX increase with the introduction of Zr, the catalytic reactivity of CeZr/Zn-HZSM-5 was closely related to the Zr species.

Modification of x/Zn-HZSM-5 bi-functional catalyst by Zn species has a certain impact, which is suppressing side reaction of methanol to olefins, by the reduction of strong Bronsted acid and generates new Lewis acid sites.

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