



Performance of Bifunctional ZnZr/ZSM-5 Catalysts in the Alkylation of Benzene with Syngas

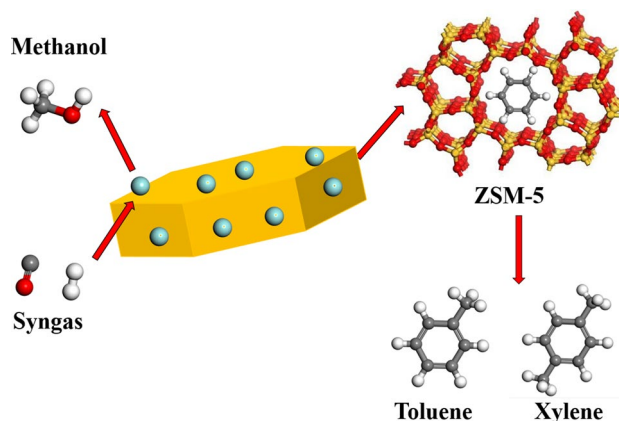
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Abstract

A novel alkylation process of benzene with syngas was successfully developed to produce toluene and xylene over a bifunctional catalyst containing zinc oxide (ZnO), zirconium oxide (ZrO₂) and ZSM-5 zeolite. Different characterizations, such as: SEM, TEM, XRD, XPS, FT-IR, NH₃-TPD and N₂ adsorption–desorption were used to measure the structure of Zn/Zr samples. ZnO was identified as the active component for the synthesis of methanol while ZrO₂ was the promoting component which helped the good dispersion of ZnO in the system. The sample with 0.75 Zn/Zr molar ratio calcined at 500 °C exhibited the best catalytic performance, resulting in benzene conversion of 34.7%, toluene and xylene selectivity of 68.8% and 18.0% at 450 °C under 3.2 MPa. Based on the experimental results, the reaction mechanism was proposed as following: methanol was firstly formed on the surface of ZnO/ZrO₂ from syngas, then it migrated onto ZSM-5 zeolite and reacted with benzene to form toluene. Furthermore, xylene was obtained through consecutive reaction.

Graphical Abstract



Keywords Benzene · Syngas · Alkylation · Zinc · Zirconium

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1 Introduction

Aromatics are very important fundamental materials in petrochemical industry, wherein para-xylene (PX) is the most valuable xylene isomer which will be ultimately converted to polyethylene terephthalate (PET) fibers, films and resins [1–3]. Although the alkylation of benzene with methanol or methane to prepare toluene and xylene have been reported a lot, which is still limited in small scale production and approximately

70% of the world's benzene, toluene and xylene is still from petroleum naphtha [4–9]. Syngas which mainly contains hydrogen and carbon monoxide can be produced from various nonpetroleum carbon resources like coal, natural gas and biomass. It has been widely used in numerous industry processes and attracted great attention recently [10–16].

Bifunctional catalysts which had both catalytic hydrogenation and alkylation function could be prepared if metals were loaded on the ZSM-5 zeolite. ZSM-5 zeolite was widely used for its high specific surface area, adjustable acidity and unique pore structure [17–19]. Only a few works by using bifunctional catalysts for the alkylation of benzene with syngas were reported previously. Imia and Ou studied the alkylation of benzene or toluene with syngas over Zn–Cr or Zn–Al loaded on different types of zeolites, unfortunately the highest conversion of benzene was only 15% [20, 21]. Xuebin reported that Cu-based catalysts showed high activity for the reaction and when the Cu content in catalysts was 11.0%, the conversion of benzene can only reach 16.8% [22]. Therefore, how to design and fabricate highly efficient catalyst for the alkylation of benzene with syngas is of great importance.

As mentioned that methanol was mainly produced from syngas with low equilibrium conversion, which means an alkylation process of benzene with methanol coupled with the synthesis of methanol would break the equilibrium and the conversion of syngas. We figured out that the $\Delta_r H_m^\theta$ was -164.22 kJ/mol and $\Delta_r G_m^\theta$ was -99.02 kJ/mol for the reaction of $C_6H_6(g) + CO(g) + 2H_2(g) \longrightarrow C_7H_8(g) + H_2O(g)$. The ideal conversion of benzene reached up to 98.83% at 450 °C with the molar ratio of H_2 , CO and C_6H_6 as 8:4:1. Herein, that process was feasible in thermodynamics by calculation.

In present work, we explored a reaction coupling process for directly converting syngas and benzene to alkylated benzenes over a bifunctional ZnZr/ZSM-5 catalyst. A mixture of zinc and zirconium oxides with different molar ratios and calcination temperatures were prepared and applied to catalyze the alkylation of benzene with syngas. Their structures, properties and corresponding catalytic performances were systematically investigated. And the reaction mechanism was proposed with methanol as the intermediate. In all, this novel and effective method could make full use of syngas without any intermediate steps and the application of syngas will be extended. Furthermore, the alkylation process of benzene with syngas would satisfy the increasing demand of xylene and solve the problems of benzene excess at the same time.

2 Experimental

2.1 Synthesis of ZnO–ZrO₂ Samples

All the chemical reagents used in experiments were in analytical grade and deionized water was used in all

experiments. The anhydrous zinc acetate, isopropanol and monoethanolamine were purchased from Shanghai Titan Scientific company. The zirconium acetyl acetonate was purchased from Shanghai Dibo Bio-technology company. Benzene was purchased from Shanghai Lingfeng chemical reagents company and syngas (mole ratio $H_2:CO:N_2=2:1:1$) was purchased from Shanghai Jiajie special gas company.

The mixture of zinc and zirconium oxides (Zn/Zr) were prepared by sol–gel method [23, 24]. Typically, anhydrous zinc acetate ($Zn(CH_3COO)_2$) was dissolved in isopropanol (400 mL). Then zirconium acetyl acetonate ($C_{20}H_{28}O_8Zr$) was added to the above solution dropwise. Subsequently, monoethanolamine (40 mL) was added to the solution used as complexing agent. The mixture was stirred at 55 °C for 1 h. The obtained clear yellow sol was aged for 48 h at 25 °C and then heated at 200 °C for 24 h. Finally, the brown powders were calcined in furnace at 500 °C for 2 h. The preparation of pure ZnO and ZrO₂ sol were similar to the said preparation with the addition of only anhydrous zinc acetate or zirconium acetyl acetonate. The calcined samples were remarked as ZnZr-ratio-temperature. For example, ZnZr-0.75-500 sample means the Zn/Zr molar ratio of the metal precursor was 0.75 and the calcination temperature was 500 °C. Zn-500 sample means only anhydrous zinc acetate was used as metal precursor and the calcination temperature was 500 °C.

2.2 Preparation of Bifunctional Catalyst

The catalyst was typically prepared by physical mixing. The mass ratio of the two components (metal and ZSM-5 zeolite) was 1:1 in this work, wherein ZSM-5 zeolite (Si/Al = 12.5) was purchased from the Catalytic Plant of Nankai University. These two components were mixed in a mortar. Then the well-mixed powders were pelleted into particles of 20–40 meshes (425–850 μ m). Then the shaped catalyst was calcined in furnace at 500 °C for 6 h and this catalyst was remarked as ZnZr/ZSM-5 catalysts.

2.3 Catalytic Reaction Tests

The alkylation reaction of benzene with syngas was performed in a fixed-bed reactor with a stainless steel tube (10 mm i.d.) customized by Swagelok company. The catalyst (1 g) with quartz sands of the same volume were mixed and then loaded in the middle of reaction tube and heated to the target temperature. The catalyst was reduced under 500 °C by H_2 for 2 h. Subsequently syngas flow was introduced into the reactor by a mass flow controller (D08-1D/ZM, Beijing Sevenstar Electronics Company) in a gas hourly space velocity (GHSV) of 12,000 cm^3 (S.T.P.)/(gcat h). The

syngas with a H₂:CO:N₂ molar ratio of 2:1:1 was employed in this work and N₂ was used as an internal standard for the calculation of CO conversion. At the same time a co-feed of liquid benzene in a liquid hourly space velocity (LHSV) of 3 h⁻¹ by a high pressure constant flow pump (P100, Shanghai Wufeng Technology Company) was introduced. In this work, the syngas pressure and the reaction temperature were 3.0 MPa and 450 °C, respectively.

The effluent liquid was collected every 2 h and analyzed by off-line chromatographs till the composition was steady. The condensed liquid products were collected and analyzed by off-line gas chromatographs (GC6820), which were equipped with a DB-WAX column (30 m) produced by Agilent connecting to a FID detector. The gaseous phase products were separated by on-line gas chromatographs (GC9160) which were equipped with a TDX-01 packed column (2 m) connecting to a TCD detector and a FID detector produced by Shimadzu. The conversion of benzene (C_B) and CO conversion (C_{CO}), the selectivity of toluene (S_T) which is based on the benzene ring, the selectivity of CO₂ (S_{CO₂}) and CH₄ (S_{CH₄}), the molar quantity of carbon which is transferred to benzene ring Q1 and to gaseous products Q2 were defined as follows:

$$C_B = (A - B)/A \times 100\% = 1 - \frac{\text{Benzene peak area} \times \text{correction factor}}{\sum \text{Peak area} \times \text{correction factor}}$$

$$S_T = C/(A - B) \times 100\% = \frac{\text{Toluene peak area} \times \text{correction factor}}{\sum_{T,XY,EB,C9+} \text{Peak area} \times \text{correction factor}}$$

$$Q1 = A \times [C_B S_T + 2C_B (S_{XY} + S_{EB}) + 3C_B S_{C9+}]$$

$$C_{CO} = (G - H)/G \times 100\% = \frac{N_2 \text{ peak area} \times \text{correction factor} - CO \text{ peak area} \times \text{correction factor}}{N_2 \text{ peak area} \times \text{correction factor}}$$

$$Q2 = G \times C_{CO} - Q1$$

$$I = H \times \frac{CO_2 \text{ peak area} \times \text{correction factor}}{CO \text{ peak area} \times \text{correction factor}}$$

$$S_{CO_2} = I/Q2 \times 100\%$$

$$S_{CH_4} = \frac{CH_4 \text{ peak area} \times \text{correction factor}}{\sum_{CH_4,DME,CH_3OH,C_2-C_4} \text{Peak area} \times \text{correction factor}} \times \frac{Q_2 - I}{Q_2}$$

Wherein, A and G (G:A = 4:1) represent the molar quantity of benzene and CO in the influent. B, C, H and I represent the molar quantity of benzene, toluene, CO and

CO₂ in the effluent. The selectivity of other aromatic and gaseous products is similar.

2.4 Catalyst Characterization

Scanning electron microscopy (SEM) images were obtained from a FEI Nova Nano450 SEM microscope at 1.00 kV. Transmission electron microscopy (TEM) images were obtained from a FEI Tecnai G2 F30 transmission electron microscope operating at 300 kV.

X-ray diffraction (XRD) patterns were carried out on a RIGAKU powder diffractometer employing CuKα radiation (λ = 0.15406 nm) at 40 kV and 40 mA.

X-ray photoelectron spectrometer (XPS) were acquired on an ESCALAB 250Xi (Thermo Fish Scientific, Al Kα, hν = 1486.6 eV). The binding energy was corrected by C1s orbital, which was at 284.8 eV.

Zn and Zr contents were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Agilent 725ES ICP-AES).

Infrared (IR) spectra were recorded on a Nicolet 5DX Fourier transform infrared (FT-IR) spectrometer using KBr pellets technique in the range of 4000 cm⁻¹–400 cm⁻¹.

Temperature-programmed desorption of ammonia (NH₃-TPD) were measured by a Micromeritics Chemisorb 2720 analyzer. All samples were evacuated at 500 °C for 1 h in He flow and then they were cooled down to 35 °C and saturated with 10% NH₃-He for 30 min, after which He was introduced again and the samples were heated to

150 °C for 30 min to remove the physical adsorption of NH₃. The signal was quantified by a TCD at heating rate of 10 °C/min.

The texture properties were acquired by nitrogen adsorption–desorption equipment on a Micromeritics ASAP-2020V3.00H analyzer. All samples were outgassed at 180 °C for 12 h under vacuum to remove moisture and volatile impurities before the measurements. Corresponding isotherms were measured at –196 °C on Micromeritics ASAP-2020V3.00H analyzer.

In situ diffuse reflectance in fourier transform spectroscopy (In situ DRIFTS) were measured on a Nicolet iS50 spectrometer with a MCT detector and a high-temperature reaction chamber with ZnSe windows. The catalysts were reduced under a flow of 10% H₂ in Ar before each test. The DRIFTS spectra were collected in the range of 4000 cm⁻¹–650 cm⁻¹.

3 Results and Discussion

3.1 Morphology and Microstructure of Catalysts

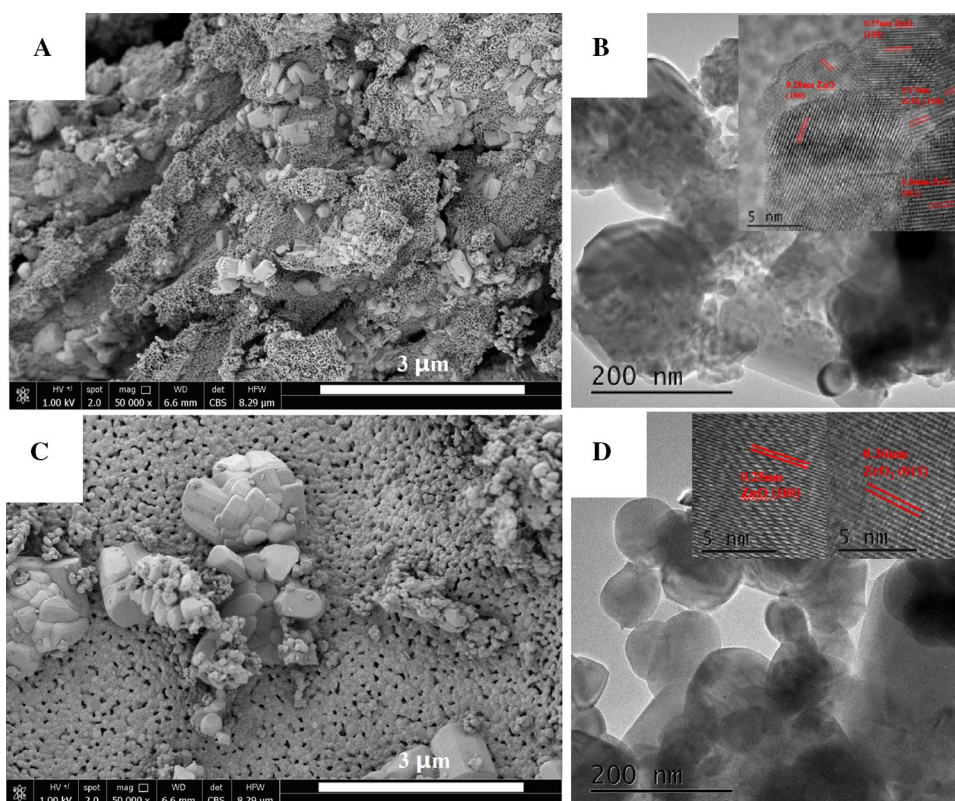
SEM and TEM images of ZnZr-0.75-500 and ZnZr-0.75-800 were shown in Fig. 1, corresponding high-resolution TEM (HRTEM) images were shown in the inset of each TEM Figure. For ZnZr-0.75-500 and ZnZr-0.75-800 samples, two obvious phases were observed in SEM images which belonged to ZnO and ZrO₂, respectively. For the samples

calcined at 500 °C, the interplanar spacing of 0.28 nm and 0.25 nm belonged to (1 0 0) and (1 0 1) plane of ZnO (JCPDS cards 36-1451) phases and the interplanar spacing of 0.37 nm and 0.36 nm belonged to (1 1 0) and (0 1 1) plane of monoclinic ZrO₂ (JCPDS cards 50-1089) phases. With the increasing temperature to 800 °C, the interplanar spacing of 0.28 nm and 0.36 nm belonged to (1 0 0) plane of ZnO (JCPDS cards 36-1451) phases and (0 1 1) plane of ZrO₂ (JCPDS cards 50-1089) phases respectively, which was consistent with XRD results that better crystallinity of ZrO₂ was formed. Also, these images revealed that grain size increased with increasing calcination temperature.

3.2 XRD Characterization of Samples

The influence of different Zn/Zr molar ratios and calcination temperatures on the structure of samples were shown in Fig. 2. There were no clear reflections of ZnO (JCPDS cards 36-1451) at 0.5 or lower Zn/Zr molar ratio but only tetragonal ZrO₂ (JCPDS cards 50-1089) of the samples calcined at 500 °C, indicating that the particle size of ZnO was small or amorphous or highly divided ZnO were formed compared with Zn-500. With the increasing of Zn/Zr molar ratio (0.75 or higher), the ZnO reflections generally appeared and became sharper and stronger, which was consistent with the lattice fringes of ZnO shown in HRTEM images. Further

Fig. 1 **a** SEM and **b** TEM images of ZnZr-0.75-500. **c** SEM and **d** TEM images of ZnZr-0.75-800



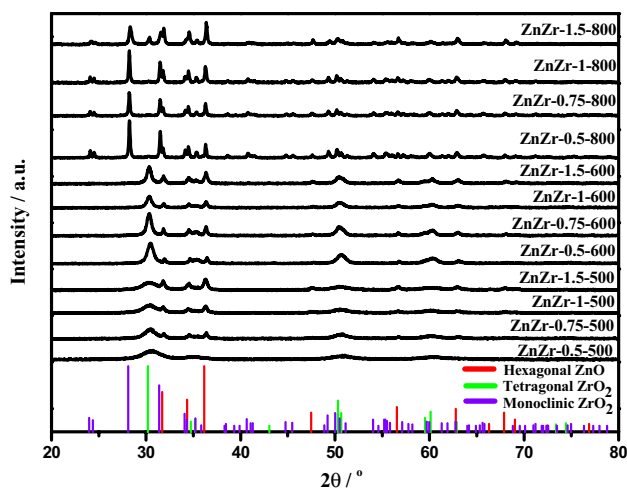


Fig. 2 XRD patterns of Zn/Zr samples with different molar ratio at different calcination temperature

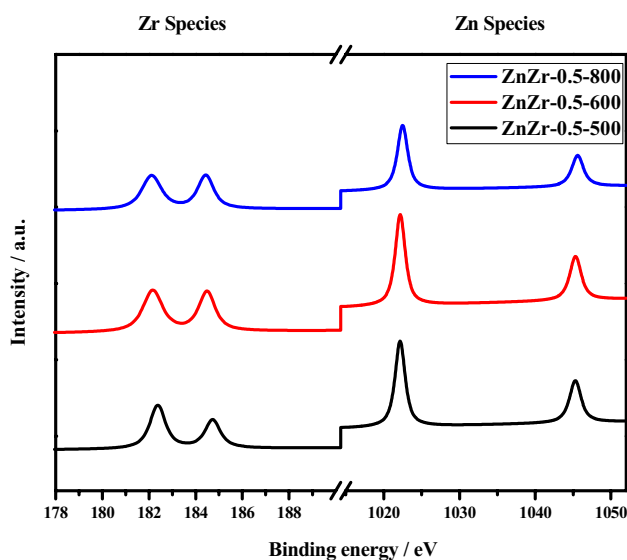


Fig. 3 XPS patterns of 0.5 Zn/Zr molar ratio at 500, 600, 800 °C for Zn and Zr species

increasing the calcination temperature, whatever the molar ratio of Zn and Zr was, the main crystal system of ZrO_2 was changed from tetragonal to monoclinic ZrO_2 (JCPDS cards 37-1484) and all of them showed better crystallinity.

3.3 XPS Characterization of Samples

The X-ray photoelectron spectrums (XPS) of 0.5 Zn/Zr molar ratio samples at different calcination temperatures were shown in Fig. 3. For all samples, two main characteristic peaks of Zn and Zr were shown. The peaks at 1022.3 eV of Zn $2p_{3/2}$ and 1045.2 eV of Zn $2p_{1/2}$ in the near-surface of the samples originated from ZnO. The peaks at 182.2 eV

of $Zr_{3d5/2}$ and 184.5 eV of $Zr_{3d3/2}$ in the near-surface of the samples originated from ZrO_2 , which was consistent with the XRD results [25–27].

The atomic ratio of different catalysts in bulk (ICP-AES) and on the surface (XPS) were summarized in Table 1. The actual atomic ratios of Zn and Zr in the bulk were nearly close to the charge ratio but not close to the atomic ratio in the near-surface. Based on the XRD results, hexagonal ZnO was mainly formed in the near-surface indicated by the zinc enrichment from XPS results. Therefore, the structure that a well dispersed ZnO on the surface of ZrO_2 was formed.

3.4 FT-IR Analysis of Samples

IR spectrums of the samples were shown in Fig. 4 from 4000 cm^{-1} to 400 cm^{-1} . For all samples, the peaks at 3450 cm^{-1} were assigned to the bending vibrations of the M–O–H bonds and the peaks at 1600 cm^{-1} were assigned to the stretching vibrations of H_2O molecules which were not removed completely after sol–gel method [28]. For ZnZr-0.75-500, the most intensive reflections at 3450 cm^{-1} of O–H bonds were exhibited in Fig. 4. Zhang reported that O–H bonds were beneficial for the formation of CH_3OH which was the most important intermediate for the alkylation of benzene with syngas [29]. And that was consistent with the catalysts evaluation results that the highest benzene conversion was achieved with ZnZr-0.75-500. The peak at 1500 cm^{-1} was due to organic compounds used as metal precursor materials, and the intensity became weaker with the increasing of calcination temperature which meant the residual organics in the samples were removed [30, 31]. The peak at 1400 cm^{-1} was assigned to the bending vibrations of surface M–O–H bond. The peak at 700 cm^{-1} was attributed to Zn–O–Zr bond. The highly intense peaks at 800 cm^{-1} and 500 cm^{-1} for ZnZr-0.75-800 were attributed to symmetric and asymmetric stretching vibrations of O–Zr–O bonds and Zn–O–Zn bonds respectively, which is consistent with XRD results. Amorphous ZnO was formed at lower temperature and hexagonal ZnO with high crystallinity was formed when calcination temperature was increased to 800 °C [32, 33].

3.5 NH_3 -TPD

Catalyst acidity plays an important role in the catalytic performance in the alkylation of benzene with syngas [34]. The acid quantity of the ZSM-5 zeolite and ZnZr/ZSM-5 catalysts were summarized in Table 1. Compared to ZSM-5 zeolite, the strong acidity of ZnZr/ZSM-5 catalysts decreased a lot by the introduction of Zn and Zr, which was caused by the coverage of strong acidity. The weak acidity and strong acidity nearly remained constant with the change of Zn/Zr molar ratio and calcination temperature.

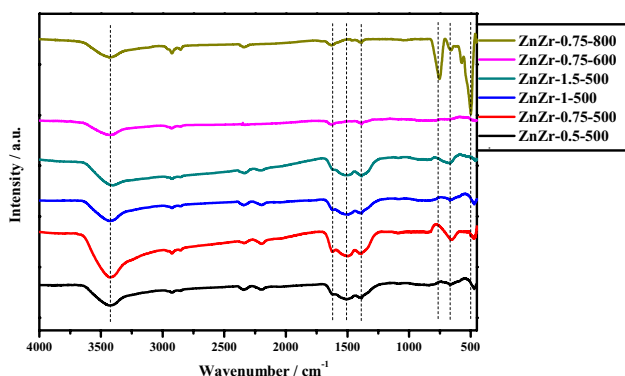
Table 1 Metal composition and texture properties as well as the acidity of catalysts with different Zn/Zr molar ratio at different calcination temperature

Catalyst	Zn:Zr		$S_{\text{BET}}^{\text{a}}$ (m^2/g)	$V_{\text{total}}^{\text{b}}$ (mL/g)	Weak acidity (mmol/g)	Strong acidity		Total acidity ^c
	Bulk	Surface						
Zn-500	/	/	6	0.04	/	/	/	
Zr-500	/	/	10	0.01	/	/	/	
ZnZr-0.5-500	0.47:1	1.17:1	35	0.04	0.26	0.10	0.36	
ZnZr-0.75-500	0.73:1	1.35:1	45	0.07	0.29	0.10	0.39	
ZnZr-1-500	1.02:1	1.52:1	30	0.05	0.31	0.11	0.42	
ZnZr-1.5-500	1.48:1	1.90:1	27	0.04	0.34	0.12	0.46	
ZnZr-0.75-600	0.74:1	1.21:1	16	0.03	0.28	0.09	0.37	
ZnZr-0.75-800	0.74:1	1.09:1	3	0.01	0.26	0.10	0.36	
ZSM-5	/	/	310	0.17	0.29	0.44	0.73	

^a S_{BET} is calculated by Brunauer-Emmett-Teller (BET) method

^b V_{total} is calculated from the adsorption branch at $P/P_0 = 0.99$

^cBy physical mixing of Zn/Zr and ZSM-5, the acidity was measured and the pure ZSM-5 (H type) acidity is higher because there are only 0.5 g zeolite in 1 g other samples

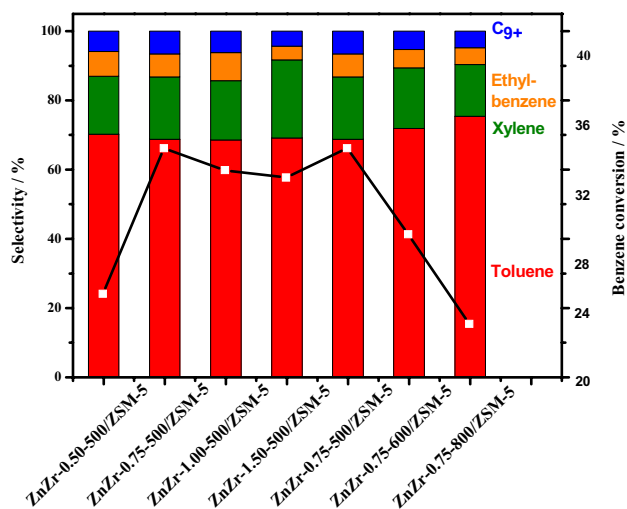
**Fig. 4** IR spectra of Zn/Zr samples with different molar ratio at different calcination temperature

3.6 Texture Properties

The texture properties were shown in Table 1. For ZnZr-0.75-500, the specific surface area and total pore volume exhibited the maximum of $45 \text{ m}^2/\text{g}$ and $0.07 \text{ mL}/\text{g}$. A further increase of the calcination temperature resulted in a decrease in specific surface area and total pore volumes because that better crystallinity and larger particle size were formed based on XRD results. It should be noted that pure ZnO or ZrO_2 samples showed a relatively smaller specific surface area than those of bi-metal. ZnO was identified as the active component for the synthesis of methanol, therefore ZrO_2 was attributed to be a promoting component which will provide a relatively higher surface area and distribution of ZnO [35, 36].

3.7 Catalysts Evaluation

All experiment was carried out under $450 \text{ }^\circ\text{C}$, 3.0 MPa . Syngas (molar ratio of $\text{H}_2:\text{CO}:\text{N}_2$ is 2:1:1)

**Fig. 5** Effect of Zn/Zr molar ratio and calcination temperature on the performance of Zn/Zr/ZSM-5 catalysts (all experiment was carried out under $450 \text{ }^\circ\text{C}$, 3.0 MPa . Syngas (molar ratio of $\text{H}_2:\text{CO}:\text{N}_2$ is 2:1:1) $\text{GHSV} = 12,000 \text{ cm}^3(\text{S.T.P.})/(\text{gcat} \cdot \text{h})$. Benzene $\text{LHSV} = 3 \text{ h}^{-1}$. Molar ratio of CO to benzene is 4:1.)

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All experiment was carried out under $450 \text{ }^\circ\text{C}$, 3.0 MPa . Syngas (molar ratio of $\text{H}_2:\text{CO}:\text{N}_2$ is 2:1:1) $\text{GHSV} = 12,000 \text{ cm}^3(\text{S.T.P.})/(\text{gcat} \cdot \text{h})$. Benzene $\text{LHSV} = 3 \text{ h}^{-1}$. Molar ratio of CO to benzene is 4:1. (Except for ZnZr-0.75-500 catalyst where there is no introduction of benzene).

Tables 2 and 3 listed the catalytic performances of various catalysts. Toluene and xylene were the primary products and ethylbenzene was the main by-product in liquid phase for all catalysts in Fig. 5. Syngas was converted to CO_2 , CH_4 , DME (dimethyl ether), CH_3OH , $\text{C}_2\text{-C}_4$ alkanes and olefins

Table 2 Product distributions of liquid phases produced under Zn/Zr/ZSM-5 catalysts

Catalysts	Aromatic ring yield ^a %	Carbon to benzene ring ^b %	Benzene conversion (%)	Selectivity (%)			
				Toluene	Xylene	Ethylbenzene	C ₉₊
Zn-500/ZSM-5	96.3	44.3	15.9	81.9	12.3	4.0	1.8
Zr-500/ZSM-5	95.5	78.1	2.7	70.4	5.5	24.1	0.0
ZnZr-0.5-500/ZSM-5	96.9	63.1	26.2	70.3	16.7	7.2	5.8
ZnZr-0.75-500/ZSM-5	96.2	47.4	34.7	68.8	18.0	6.6	6.6
ZnZr-1-500/ZSM-5	97.1	51.2	33.4	68.5	17.1	8.2	6.2
ZnZr-1.5-500/ZSM-5	95.3	59.9	33.0	69.1	22.6	3.9	4.4
ZnZr-0.75-600/ZSM-5	95.5	39.9	29.7	71.9	17.5	5.3	5.3
ZnZr-0.75-800/ZSM-5	96.7	33.9	24.5	75.4	15.0	4.9	4.7

$$^a\text{Aromatic ring yield} = \frac{\text{The mass of aromatic ring effluent}}{\text{The mass of benzene in the influent}} \times 100\%$$

$$^b\text{Carbon to benzene ring} = \frac{Q_1}{Q_1 + Q_2} \times 100\% \text{ (} Q_1 \text{ and } Q_2 \text{ are defined in Sect. 2.3)}$$

Table 3 Product distributions of gaseous phases produced under Zn/Zr/ZSM-5 catalysts

Catalysts	Carbon to gaseous products ^a %	Conversion % CO	Selectivity %				
			CO ₂	CH ₄	DME	CH ₃ OH	C ₂ -C ₄
Zn-500/ZSM-5	55.7	10.7	39.1	41.5	1.4	0.1	17.9
Zr-500/ZSM-5	21.9	0.8	6.2	92.1	0.1	0.5	1.1
ZnZr-0.5-500/ZSM-5	36.9	14.1	54.4	31.3	0.0	0.1	14.2
ZnZr-0.75-500/ZSM-5	52.6	25.2	24.5	49.8	0.2	0.8	24.7
ZnZr-1-500/ZSM-5	48.8	22.7	31.2	37.5	0.0	0.1	31.2
ZnZr-1.5-500/ZSM-5	40.1	18.6	37.2	38.9	0.0	0.1	23.8
ZnZr-0.75-600/ZSM-5	60.1	24.8	19.6	44.3	0.1	0.2	35.8
ZnZr-0.75-800/ZSM-5	66.1	23.4	11.7	41.9	0.0	0.1	46.3
ZnZr-0.75-500	100.0	1.2	12.9	59.1	1.1	10.6	16.3

$$^a\text{Carbon to gaseous products} = \frac{Q_2}{Q_1 + Q_2} \times 100\% \text{ (} Q_1 \text{ and } Q_2 \text{ are defined in Sect. 2.3)}$$

in Table 3. For Zr-500/ZSM-5, the benzene conversion was only 2.7% without the addition of Zn species, which will increase to 15.9% over Zn-500/ZSM-5. Therefore, ZnO was the active component for the synthesis of methanol. From Fig. 1, the (1 0 1) plane of ZnO phase which was only observed at 500 °C was more beneficial for the alkylation. By the introduction of Zr species, bi-metal samples showed higher catalytic activity than pure ZnO because ZrO₂ was the promoting component which helped the good dispersion of ZnO in the system and increased the specific surface area.

The benzene conversion reached the maximum 34.7% with the highest CO conversion of 25.2% at 0.75 Zn/Zr molar ratio, while the corresponding toluene selectivity and xylene selectivity was 68.8% and 18.0%, respectively. By increasing the calcination temperature from 500 °C to 800 °C, the benzene conversion was reduced from 34.7% to 24.5%. The changing trends of benzene conversion and CO conversion were consistent with the change of specific surface area. Based on XRD results, better crystallinity and larger particle size were formed at higher temperature with lower specific

area which were both unfavorable for the alkylation reaction. Moreover, much higher Zn content would be unbeneficial for the alkylation because of the decreasing of specific surface area. The main crystal phase of ZrO₂ was changed from tetragonal to monoclinic when the temperature was increased from 600 °C to 800 °C. Therefore, tetragonal ZrO₂ would provide a relatively higher surface area and better distribution of ZnO than monoclinic ZrO₂.

The reaction that benzene reacted with syngas to form toluene, as well as toluene reacted with syngas to form xylene were a consecutive reaction. Since ZnO was supposed to be responsible for methanol formation while ZSM-5 was responsible for the alkylation of benzene with methanol related species. The selectivity to aromatic products related to benzene was irrelevant to Zn/Zr molar ratio and calcination temperature. However, the selectivity to gaseous products related to CO was greatly dependent on the Zn/Zr molar ratio and calcination temperature. More methanol was formed with the increasing of CO conversion, resulting in the increasing of benzene conversion.

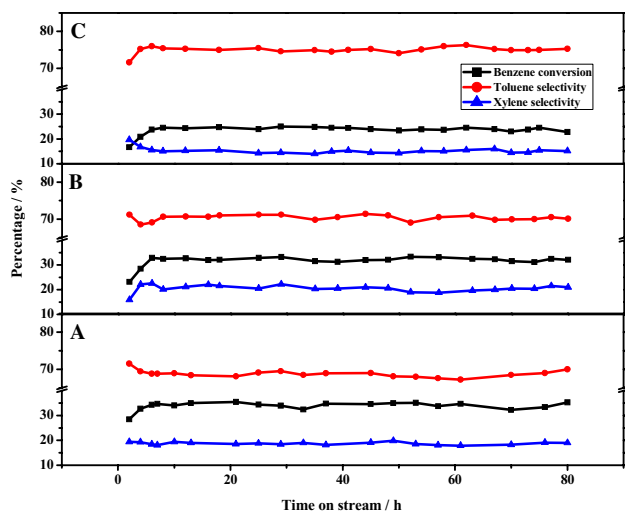


Fig. 6 Time on stream of **a** ZnZr-0.75-500/ZSM-5 catalyst. **b** ZnZr-1.5-500/ZSM-5 catalyst. **c** ZnZr-0.75-800/ZSM-5 catalyst (all experiment was carried out under 450 °C, 3.0 MPa). Syngas (molar ratio of H₂:CO:N₂ is 2:1:1) GHSV = 12,000 cm³(S.T.P.)/(gcat h). Benzene LHSV = 3 h⁻¹. Molar ratio of CO to benzene is 4:1.)

As shown in Fig. 4, the higher benzene conversion was also attributed to the most intensive peak of O–H bonds which were beneficial for the formation of methanol with the same conclusion reported by Zhang [29]. In some previous works, density functional theory (DFT) has been used to calculate the energy barriers and investigate the reaction mechanism. For syngas conversion to methanol, the energy barrier was 255.06 kJ/mol over Mo₆P₃–Si₃O₉ cluster, 284.3 kJ/mol over Rh/γ–Al₂O₃ catalyst on D(RH4)

surface and 177.66 kJ/mol over Ni catalyst, wherein the rate-limiting step was the formation of CHO* from CO hydrogenation [29, 37, 38]. For alkylation of benzene with methanol, the achieved energy barriers for the formation of methoxy group and the methylation of benzene with methoxy group over ZSM-5 zeolite were 149 kJ/mol and 97 kJ/mol, respectively [39]. In all, it is reasonable to believe that the rate-limiting step was 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 for the alkylation of benzene with syngas because there are more active sites on a larger Zn/Zr surface. The time on stream behavior over the catalysts was shown in Fig. 6. There hasn't significant change of the catalytic performance with varied Zn/Zr molar ratio and calcination temperature in 80 h, which suggested that the catalysts were highly stable.

Above all, the best catalytic performance was achieved by 0.75 Zn/Zr molar ratio and the calcination temperature was 500 °C due to its highest specific surface area, most intensive O–H bonds and the structure of highly divided ZnO on the surface of ZrO₂. Other catalysts showed worse catalytic performance due to their lower specific surface area, lower active sites on metals and higher crystallinity.

3.8 Mechanism

In order to gain insights into the mechanism and detect the intermediate, the ZnZr-0.75-500 catalysts were prepared without the addition of ZSM-5 zeolite and only the syngas was introduced to the system without benzene. In Table 3,

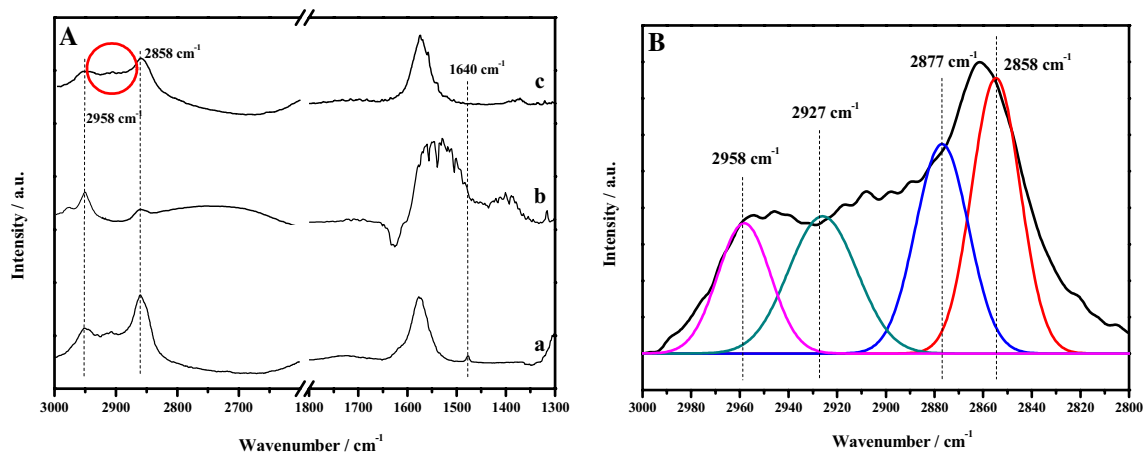


Fig. 7 **A** In-situ DRIFTS spectra of ZnZr-0.75-500/ZSM-5. **B** In-situ DRIFTS spectra of ZnZr-0.75-500/ZSM-5 between 3000 cm⁻¹ and 2800 cm⁻¹ of Fig. 7(A)c. (a) Syngas (15 ml/min, H₂:CO:N₂ = 2:1:1, mole ratio) was introduced to an in-situ cell (200 °C and 1 atm) for 15 min. Then the cell was swept by argon for 5 min and measured for IR spectra. (b) Saturated methanol vapor carried by argon was intro-

duced to and in-situ cell (200 °C and 1 atm) for 15 min. Then the cell was swept by argon for 5 min and measured for IR spectra. (c) Saturated benzene vapor carried by syngas (15 ml/min, H₂:CO:N₂ = 2:1:1, mole ratio) was introduced to an in-situ cell (200 °C and 1 atm) for 15 min. The cell was swept by argon for 5 min, and measured for IR spectra

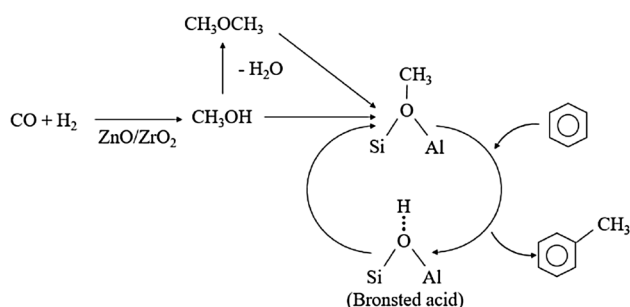


Fig. 8 Proposed mechanism of alkylation of benzene with syngas

methanol had been proposed as the intermediate for the alkylation of benzene with syngas which was detected in our experiments [40, 41]. By the introduction of ZSM-5 zeolite, the CO conversion increased from 1.2% to 25.2% while the selectivity of methanol decreased a lot from 10.6% to 0.8% at the same time, which indicated that the intermediate methanol was formed mainly on the surface of ZnO/ZrO₂.

In-situ DRIFTS spectra of ZnZr-0.75-500/ZSM-5 was shown in Fig. 7 to study the reaction pathway. Under the syngas ambience (Fig. 7A(a)) the peaks at 2958 cm⁻¹ and 2858 cm⁻¹ were assigned to the stretching vibration of C–H bonds while 1640 cm⁻¹ were assigned to the bending vibration of C–H bonds of the methoxy groups on zeolite. They all became weaker after the introduction of benzene (Fig. 7A(c)) [42, 43]. And the new peaks at 2927 cm⁻¹ and 2877 cm⁻¹ (Fig. 7B) were assigned to the symmetrical stretching vibration of C–H bonds of toluene or methyl, which is further confirmed by the liquid phase products. Under the methanol ambience (Fig. 7A(b)), the spectrum was nearly the same as syngas, further illustrated that methanol was the key intermediate in the alkylation of benzene with syngas. Above all, methoxy groups on the zeolite were of great importance for the reaction.

Based on the experimental results, the reaction mechanism was proposed as following in Fig. 8: First, CH₃OH was formed on the surface of ZnO/ZrO₂ from syngas. Second, CH₃OH migrated onto the ZSM-5 zeolite reacting with the acid sites on ZSM-5 zeolite, forming methoxy group which participated in the reaction cycle. Finally, toluene was formed by the alkylation of benzene with methoxy group.

4 Conclusions

In summary, the present work designed a bifunctional ZnZr/ZSM-5 catalyst for a coupling process of directly converting syngas and benzene to alkylated benzenes. The highly efficient catalyst containing zinc oxide (ZnO), zirconium oxide (ZrO₂) and ZSM-5 zeolite for the alkylation of benzene with syngas was prepared through the simple method as sol–gel and physical mixing. The influence of

different molar ratio of zinc (Zn) to zirconium (Zr), and calcination temperatures on the structure and catalytic performance of the samples were systematically investigated. ZnZr-0.75-500/ZSM-5 was found to be the optimal catalyst for the alkylation with the benzene conversion of 34.7%, toluene and xylene selectivity of 68.8% and 18.0% at 450 °C under 3.0 MPa at GHSV of 12,000 cm³(S.T.P.)/(gcat·h) and LHSV of 3 h⁻¹. The reaction mechanism was proposed, in which methanol was the intermediate and it was firstly formed on ZnO/ZrO₂ and then migrated onto ZSM-5 zeolite to react with benzene. This work not only provided a feasible route to produce toluene and xylene from the alkylation of benzene with syngas, but also opened a new way for syngas chemistry.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Lee SM, Choi WJ, Hwang K, Kim JH, Lee JY (2014) Effect of catalyst concentration and reaction time on one-step synthesized hypercrosslinked polyxylene. *Macromol Res* 22(5):481–486
- Niziolek AM, Onel O, Floudas CA (2016) Production of benzene, toluene, and xylenes from natural gas via methanol: process synthesis and global optimization. *AIChE J* 62(5):1531–1556
- Kim TW, Kim SY, Kim JC, Kim Y, Ryoo R, Kim CU (2016) Selective p-xylene production from biomass-derived dimethylfuran and ethylene over zeolite beta nanosponge catalysts. *Appl Catal B* 185:100–109
- Wang X, Xu J, Qi G, Li B, Wang C, Deng F (2013) Alkylation of benzene with methane over ZnZSM-5 zeolites studied with solid-state NMR spectroscopy. *J Phys Chem C* 117(8):4018–4023
- Yunsheng L, Zhenhao W, Zhenhao W, Fan Y, Xuedong Z (2017) Study on catalytic alkylation of benzene with methanol over ZSM-22 and ZSM-35. *China Pet Process Petrochem Technol* 19(4):38–46
- Rakoczy J, Romotowski T (1993) Alkylation of benzene with methanol on zeolites: Infrared spectroscopy studies. *Zeolites* 13(4):256–260
- King ST, Garces JM (1987) In situ infrared study of alkylation of toluene with methanol on alkali cation-exchanged zeolites. *J Catal* 104(1):59–70
- Adebajo MO, Long MA, Frost RL (2004) Further evidence for the oxidative methylation of benzene with methane over zeolite catalysts. *Catal Commun* 5(3):125–130
- Hu H, Lyu J, Wang Q, Zhang Q, Cen J, Li X (2015) Alkylation of benzene with methanol over hierarchical porous ZSM-5: synergy effects of hydrogen atmosphere and zinc modification. *RSC Adv* 5(41):32679–32684
- Jiao F, Li J, Pan X, Xiao J, Li H, Ma H, Wei M, Pan Y, Zhou Z, Li M, Miao S, Li J, Zhu Y, Xiao D, He T, Yang J, Qi F, Fu Q, Bao

- X (2016) Selective conversion of syngas to light olefins. *Science* 351(6277):1065–1068
- Zhang P, Tan L, Yang G, Tsubaki N (2017) One-pass selective conversion of syngas to para-xylene. *Chem Sci* 8(12):7941–7946
 - Al-Rahbi AS, Williams PT (2017) Hydrogen-rich syngas production and tar removal from biomass gasification using sacrificial tyre pyrolysis char. *Appl Energy* 190:501–509
 - Forman C, Gootz M, Wolfersdorf C, Meyer B (2017) Coupling power generation with syngas-based chemical synthesis. *Appl Energy* 198:180–191
 - Mujeebu MA (2016) Hydrogen and syngas production by superadiabatic combustion—a review. *Appl Energy* 173:210–224
 - Ding D, Yu J, Guo Q, Guo X, Mao H, Mao D (2018) Highly efficient synthesis of $C_2 +$ oxygenates from CO hydrogenation over Rh–Mn–Li/SiO₂ catalyst: the effect of TiO₂ promoter. *Catal Lett* 148(8):2619–2626
 - Heinrich D, Raberg M, Steinbuchel A (2018) Studies on the aerobic utilization of synthesis gas (syngas) by wild type and recombinant strains of *Ralstonia eutropha* H16. *Microb Biotechnol* 11(4):647–656
 - Todorova S, Su BL (2004) Effects of acidity and combination of Ga and Pt on catalytic behavior of Ga–Pt modified ZSM-5 catalysts in benzene alkylation with pure propane. *Catal Today* 93(1):417–424
 - Llopis FJ, Sastre G, Corma A (2004) Xylene isomerization and aromatic alkylation in zeolites NU-87, SSZ-33, β , and ZSM-5: molecular dynamics and catalytic studies. *J Catal* 227(1):227–241
 - Cheng K, Zhou W, Kang J, He S, Shi SL, Zhang QH, Pan Y, Wen W, Wang Y (2017) Bifunctional catalysts for one-step conversion of syngas into aromatics with excellent selectivity and stability. *Chem* 3(2):334–347
 - Imai T, Prospect M (1984) Synthesis of alkylaromatic compounds. US Patent 4487984A
 - Ou JDY, Waddick TJ (2002) Selective methylation to para-xylene using fuel syngas. US Patent 6459006B1
 - Xuebin Z, Feng Z, Bin Z, Haohui G (2015) Alkylation activity of benzene with syngas over Cu-based catalysts. *China Pet Process Petrochem Technol* 17(1):31–38
 - Habibi MH, Askari E (2013) Spectrophotometric studies of photo-induced degradation of tertrodirect light blue (TLB) using a nanostructure zinc zirconate composite. *J Ind Eng Chem* 19(4):1400–1405
 - Habibi MH, Askari E, Habibi M, Zendehtdel M (2013) Novel nanostructure zinc zirconate, zinc oxide or zirconium oxide pastes coated on fluorine doped tin oxide thin film as photoelectrochemical working electrodes for dye-sensitized solar cell. *Spectrochim Acta A* 104:197–202
 - Tian S, Wang S, Wu Y, Gao J, Bai Y, Wang P, Xie H, Han Y, Tan Y (2015) Cation distribution in Zn–Cr spinel structure and its effects on synthesis of isobutanol from syngas: structure–activity relationship. *J Mol Catal A* 404–405:139–147
 - Shu Z, Jiao X, Chen D (2013) Hydrothermal synthesis and selective photocatalytic properties of tetragonal star-like ZrO₂ nanostructures. *CrystEngComm* 15(21):4288
 - Ramarao SD, Murthy VRK (2015) Structural, Raman spectroscopic and microwave dielectric studies on Ni_{1-x}(Zn_{1/2}Zr_{1/2})_xW_{1-x}Nb_xO₄ ceramic compounds with wolframite structure. *Dalton Trans* 44(5):2311–2324
 - Zhang Z, Liao Z, Zhang G (2015) Degradation performance of a Keggin type Zn–Mo–Zr catalyst for acidic green B with ultrasonic waves. *RSC Adv* 5(77):63104–63110
 - Zhang R, Duan T, Wang B, Ling L (2016) Unraveling the role of support surface hydroxyls and its effect on the selectivity of C₂ species over Rh/ γ -Al₂O₃ catalyst in syngas conversion: a theoretical study. *Appl Surf Sci* 379:384–394
 - Khan I, Khan S, Nongjai R, Ahmed H, Khan W (2013) Structural and optical properties of gel-combustion synthesized Zr doped ZnO nanoparticles. *Opt Mater* 35(6):1189–1193
 - Khalaf MM, Abdelhamid AA (2015) Sol–gel derived mixed oxide zirconia: titania green heterogeneous catalysts and their performance in acridine derivatives synthesis. *Catal Lett* 146(3):645–655
 - Aghabeygi S, Khademi-Shamami M (2018) ZnO/ZrO₂ nanocomposite: sonosynthesis, characterization and its application for wastewater treatment. *Ultrason Sonochem* 41:458–465
 - Kant A, He Y, Jawad A, Li X, Rezaei F, Smith JD, Rownaghi AA (2017) Hydrogenolysis of glycerol over Ni, Cu, Zn, and Zr supported on H-beta. *Chem Eng J* 317:1–8
 - Žilková N, Bejblova M, Gil B, Zones SI, Burton AW, Chen CY, Musilova-Pavackova Z, Kosova G, Cejka J (2009) The role of the zeolite channel architecture and acidity on the activity and selectivity in aromatic transformations: the effect of zeolite cages in SSZ-35 zeolite. *J Catal* 266(1):79–91
 - Song H, Laudenschleger D, Carey JJ, Ruland H, Nolan M, Muhler M (2017) Spinel-structured ZnCr₂O₄ with excess Zn is the active ZnO/Cr₂O₃ catalyst for high-temperature methanol synthesis. *ACS Catal* 7(11):7610–7622
 - Chafik T, Bianchi D, Teichner SJ (1995) On the mechanism of the methanol synthesis involving a catalyst based on zirconia support. *Top Catal* 2(1–4):103–116
 - Zaman SF, Smith KJ (2010) A DFT study of the effect of K and SiO₂ on syngas conversion to methane and methanol over an Mo₆P₃ cluster. *Mol Simul* 36(2):118–126
 - Zhu YA, Chen D, Zhou XG, Yuan WK (2009) DFT studies of dry reforming of methane on Ni catalyst. *Catal Today* 148(3–4):260–267
 - Wen Z, Yang D, He X, Li Y, Zhu X (2016) Methylation of benzene with methanol over HZSM-11 and HZSM-5: a density functional theory study. *J Mol Catal A* 424:351–357
 - Sun Y, Sermon PA (1994) Cu-doped ZrO₂ aerogel: a novel catalyst for CO hydrogenation to CH₃OH. *Top Catal* 1(1–2):145–151
 - Lee S, Kim D, Lee J, Choi Y, Suh Y, Lee C, Kim TJ, Lee SJ, Lee JK (2013) An in situ methylation of toluene using syngas over bifunctional mixture of Cr₂O₃/ZnO and HZSM-5. *Appl Catal A* 466:90–97
 - Forester TR, Howe RF (1987) In situ FTIR studies of methanol and dimethyl ether in ZSM-5. *Cheminform* 109:5076–5082
 - Saepurahman, Visur M, Olsbye U, Bjorgen M, Svelle S (2011) In situ FT-IR mechanistic investigations of the zeolite catalyzed methylation of benzene with methanol: H-ZSM-5 versus H-beta. *Top Catal* 54(16–18):1293–1301