Selective conversion of CO$_2$ and H$_2$ into aromatics

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Transformation of greenhouse gas CO$_2$ and renewable H$_2$ into fuels and commodity chemicals is recognized as a promising route to store fluctuating renewable energy. Although several C$_1$ chemicals, olefins, and gasoline have been successfully synthesized by CO$_2$ hydrogenation, selective conversion of CO$_2$ and H$_2$ into aromatics is still challenging due to the high unsaturation degree and complex structures of aromatics. Here we report a composite catalyst of ZnAlO$_x$ and H-ZSM-5 which yields high aromatics selectivity (73.9%) with extremely low CH$_4$ selectivity (0.4%) among the carbon products without CO. Methanol and dimethyl ether, which are synthesized by hydrogenation of formate species formed on ZnAlO$_x$ surface, are transmitted to H-ZSM-5 and subsequently converted into olefins and finally aromatics. Furthermore, 58.1% $p$-xylene in xylenes is achieved over the composite catalyst containing Si-H-ZSM-5. ZnAlO$_x$&H-ZSM-5 suggests a promising application in manufacturing aromatics from CO$_2$ and H$_2$. 

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The utilization of fossil resources such as coal, oil, and natural gas has brought us unprecedented economy and social development in the past two centuries, however, continuously increasing the emissions of greenhouse gas CO₂ is threatening our living environment. The renewable energy resources (for example, solar, tidal, wind and biomass) can generate abundant power, but low-efficiency and fluctuating nature limits their widespread applications. These problems above could be effectively overcome via CO₂ hydrogenation to fuels (e.g., gasoline) and commodity chemicals (e.g., methanol, olefins and aromatics) because hydrogen can be acquired from the clean electricity.

Considering that CO₂ (ΔG° = −396 kJ mol⁻¹) is a chemical inert molecular, CO₂ hydrogenation reactions are generally operated under high pressure and hydrogen content over reductive metal catalysts so as to improve the conversion efficiency. Nowadays, Cₓ chemical such as methanol (MeOH), dimethyl ether (DME), formic acid (HCOOH), methane (CH₄), and carbon monoxide (CO) have been selectively synthesized under above conditions. However, production of C₂+ hydrocarbons such as olefins and liquid fuels from CO₂ are not easy because of high kinetic barriers for C–C coupling. In the earlier studies, combination of reverse-water-gas-shift (RWGS, CO₂ + H₂ → CO + H₂O) and Fischer–Tropsch (FT, CO + H₂ → CₓHy) synthesis reactions was considered as a promising method to generate long-chain hydrocarbons from CO₂. Nevertheless, due to the restriction of Anderson–Schulz–Flory (ASF) distribution, the selectivity of C₂–C₄ and gasoline fraction hydrocarbons does not exceed 58% and 48%, respectively. More recently, high selective olefins or gasoline has been achieved from CO₂ hydrogenation via utilization of oxide/zeolite bifunctional catalysts which have been successfully applied in syngas-to-olefins (STO) or aromatics (STA) reactions.

Some typical results are as follows: In–Zr oxide, ZnGa₂O₄ or ZnO–ZrO₂ combined with SAPO-34 zeolites achieved more than 80% C₂–C₄ olefins, meanwhile, In₂O₃ or Na₂Fe₂O₄ coupled with H-ZSM-5 zeolites reached to approximately 80% gasoline-range hydrocarbons. Because metal catalysts or the Brønsted acid sites of the zeolites can catalyze hydrogenation reactions, it is challenging to synthesize aromatics with high unsaturation degree and complex structures under conditions of high H₂ content. Up to now, there are no reports on the highly selective conversion of CO₂ and H₂ into aromatics.

Here, we report a composite catalyst made by nano-scaled spinel structural ZnAlOₓ oxide and H-ZSM-5 zeolite (ZnAlOₓ&H-ZSM-5), which exhibits 73.9% aromatics selectivity with only 0.4% CH₄ selectivity among the carbon products without CO in CO₂ hydrogenation reaction. RWGS reaction is largely suppressed by increasing H₂/CO₂ ratio or introducing CO. 58.1% p-xylene in xylenes is achieved over the composite catalyst containing Si-H-ZSM-5. Reaction mechanism and the causes of excellent aromatization performance are also explored.

Results and Discussion

Catalytic results. CO₂ hydrogenation reactions were conducted over ZnAlOₓ&H-ZSM-5 under reaction conditions of H₂/CO₂/Ar = 3/1/0.2, pressure 3.0 MPa, and 593 K. The effects of space velocity on CO₂ conversion and product selectivity are shown in Fig. 1a. It is surprising to find that the selectivity of aromatics among the carbon products without CO reaches as high as 73.9% with 9.1% CO₂ conversion and 57.4% CO selectivity at space velocity = 2000 ml g⁻¹ h⁻¹. This aromatics selectivity is much higher than the about 40% obtained over Na₂Fe₂O₄/H-ZSM-5 or 14.6% acquired over In₂O₃/H-ZSM-5, respectively. Besides that, the liquid (or gasoline-range) hydrocarbons including C₃+ and aromatics (excluding CO) run up to 80.3% along with merely 0.4% CH₄. As the space velocity substantially rises to 10,000 ml g⁻¹ h⁻¹, the aromatics selectivity only slightly decreases to 56.9%. This result is quite different from STA reactions, which were often operated at the GHSV <1500 ml g⁻¹ h⁻¹ so as to peruse high aromatics selectivity. It also can be seen from Fig. 1a that MeOH, DME and C₂–C₄ olefins are progressively climbing with the space velocity growing, which suggests that these byproducts might be acted as the intermediates for aromatization.

The CO₂ hydrogenation behaviors of various catalysts are compared in Fig. 1b. ZnO exhibits 98.2% MeOH selectivity (excluding CO) with 2.6% CO₂ conversion and 63.5% CO selectivity. After mixed with H-ZSM-5, only 29.7% aromatics selectivity was achieved. Compared to ZnO, ZnAlOₓ shows a higher CO₂ conversion (5.1%) but lower CO selectivity (54.9%). The DME and MeOH selectivity is up to 42.8% and 56.2% over ZnAlOₓ, respectively. It implies that Al₂O₃ component is acted as the active site for MeOH dehydration. In contrast with the composite catalyst ZnO&H-ZSM-5, the composite catalyst ZnAlOₓ&H-ZSM-5 shows a much better aromatization performance, over which 66.2% aromatics selectivity is obtained under the same reaction conditions. As shown in Fig. 1b, although the CO₂ conversion and liquid hydrocarbons selectivity are approximate, the aromatics selectivity for ZnAlOₓ&H-ZSM-5 prepared by two components grinding in an agate mortar is 12.4% higher than ZnAlOₓ + H-ZSM-5 prepared by the granules of two components mixing. It is apparent that the proximity of oxides and zeolites for the former catalyst is better than the latter one. It means that the closer proximity favors the selective generation of aromatics. As a comparison, the dual-bed configuration catalyst ZnAlOₓ/H-ZSM-5 with H-ZSM-5 downstream from the ZnAlOₓ provided the poorest behavior with 17.9% aromatics selectivity. The effect of reaction temperature on the CO₂ hydrogenation over ZnAlOₓ&H-ZSM-5 is investigated. Although raising temperature can increase the CO₂ conversion, the ability of aromatization is considerably weakened (Supplementary Fig. 1). The optimized weight ratio of oxide/zeolite is 1:1 (Supplementary Fig. 2). We also studied the CO₂ hydrogenation over the mixture of conventional methanol synthesis catalyst CuZnAlOₓ and H-ZSM-5. As shown in Supplementary Fig. 3, the RWGS reaction is predominant, which leads to more than 95% CO selectivity. According to the conditions for CO₂ hydrogenation, CO hydrogenation over ZnAlOₓ&H-ZSM-5 was investigated at H₂/CO/Ar = 3/1/0.2, space velocity = 6000 ml g⁻¹ h⁻¹, pressure 3.0 MPa, and 593 K. As depicted in Supplementary Fig. 4, the aromatics selectivity (excluding CO₂) is only 12.8% with 4.7% CO conversion. It implies that the excellent aromatization behavior of ZnAlOₓ&H-ZSM-5 in CO₂ hydrogenation is not related to self-promotion mechanism of CO reported by Cheng et al.

Catalytic stability. The catalytic stability of ZnAlOₓ&H-ZSM-5 in CO₂ hydrogenation reaction was studied. It is apparent from Fig. 2 that the composite catalyst delivers a good stability in a 100 h test. The CO₂ conversion, liquid hydrocarbons, and CH₄ selectivity among the carbon products without CO levels off at around 5.4, 74.0, and 0.5% after 50 h on stream. Although the aromatics selectivity is slightly decreased from 72.0% in the initial state to 66.0% after 100 h on stream, the formation rate of aromatics can keep about 15 mg g⁻¹ h⁻¹ because the CO selectivity progressively declines.

Selectivity optimization. In order to improve the efficiency for CO₂ hydrogenation to valuable hydrocarbons such as aromatics, light olefins and gasoline, the RWGS reaction should be suppressed as much as possible. It is very interesting to find from Fig. 3a that as the H₂/CO₂ ratio rises from 3/1 to 9/1, the CO₂
Reaction conditions: Space velocity and ZnAlO

Catalytic performance for CO2 hydrogenation. a The effect of space velocity over ZnAlO&H-ZSM-5. Reaction conditions: 593 K, 3.0 MPa, H2/CO2/Ar = 3/1/0.2. b Comparisons of the CO2 conversion and product selectivity over various catalysts. Reaction conditions: Space velocity = 12,000 (for ZnO and ZnAlOx) or 6000 (for composite catalysts) ml g−1 h−1, 3.0 MPa, 593 K, H2/CO2/Ar = 3/1/0.2. Note that the CxHy excludes aromatics. C2–4+ and C2–C4 refer to C2–C4 olefins and paraffins, respectively; ZnAlO&H-ZSM-5 prepared by grinding; ZnAlOx + H-ZSM-5 prepared by granules mixing; ZnAlOx/H-ZSM-5 denoted as dual-bed catalysts.

**Fig. 1** Catalytic performance for CO2 hydrogenation. a The effect of space velocity over ZnAlO&H-ZSM-5. Reaction conditions: 593 K, 3.0 MPa, H2/CO2/Ar = 3/1/0.2. b Comparisons of the CO2 conversion and product selectivity over various catalysts. Reaction conditions: Space velocity = 12,000 (for ZnO and ZnAlOx) or 6000 (for composite catalysts) ml g−1 h−1, 3.0 MPa, 593 K, H2/CO2/Ar = 3/1/0.2. Note that the CxHy excludes aromatics. C2–4+ and C2–C4 refer to C2–C4 olefins and paraffins, respectively; ZnAlO&H-ZSM-5 prepared by grinding; ZnAlOx + H-ZSM-5 prepared by granules mixing; ZnAlOx/H-ZSM-5 denoted as dual-bed catalysts.

**Fig. 2** The stability test for CO2 hydrogenation over ZnAlO&H-ZSM-5. Reaction conditions: Space velocity = 6000 ml g−1 h−1, 3.0 MPa, 593 K, H2/CO2/Ar = 3/1/0.2. Note that the liquid hydrocarbons include aromatics. Conversion is dramatically increased from 5.8% to 15.7% with the CO selectivity sharply decreasing from 56.9% to 28.7%. It means that the generated CO can be further converted by hydrogenation in the high H2/CO2 ratio. Although raising H2/CO2 ratio can slightly decrease aromatics selectivity, its formation rate keeps growing. Further increasing H2/CO2 ratio to 15/1 leads to a decline in aromatization rate. Moreover, the liquid hydrocarbons are not sensitive to H2/CO2 ratio. As shown in Fig. 3b, another effective method to weaken RWGS reaction is adding CO into the mixture gas of CO2 and H2. The CO selectivity is nearly monotonically decreasing with CO/CO2 ratio increasing and as low as 12.6% at CO/CO2 ratio = 1.8/1, nevertheless, the aromatics or liquid hydrocarbons selectivity is slightly influenced after CO introduction. As known, RWGS is a typical equilibrium reaction. Therefore, introduction product CO does not benefit the formation of itself. These results above are vital to applications. On the one hand, the source of feed gas is more extensive because its composition can be adjusted in a wide range; on the other hand, the product CO can be recycled and accumulated so as to practically depress the RWGS reaction. As presented in Fig. 3c, aromatics with 9 to 10 carbons are predominant over ZnAlO&H-ZSM-5. We tried to optimize the distributions of aromatics by using Si-H-ZSM-5 made by tetraethoxysilane (TEOS) modification. Compared to ZnAlO&H-ZSM-5, ZnAlO&Si-H-ZSM-5 obviously produces more toluene (2.7%) and xylenes (16.8%) (Fig. 3c). Moreover, 58.1% p-xylene in xylenes, 25.3% ethylene and 11.9% propylene (excluding CO) along with little C1–3 alkane are obtained over ZnAlO&Si-H-ZSM-5 (Fig. 3c and Supplementary Fig. 5). The catalytic behavior for ZnAlO&Si-H-ZSM-5 would be interesting to industry, because ethylene, propylene and p-xylene are the most important commodity hydrocarbon chemicals.

**Structural characterization.** Figure 4a shows the X-ray diffraction (XRD) patterns of ZnAlOx oxide. The reflection peaks of ZnAlOx can be approximately assigned to cubic ZnAl2O4.28 (JCPDS 05-0669, Supplementary Fig. 6). The reflection peaks of ZnO (Supplementary Fig. 7) are hardly detectable for ZnAlOx. The Field-emission scanning electron microscopy (SEM) image (Supplementary Fig. 8) shows that the morphology of ZnAlOx is porous and made by small particles. The BET surface area of ZnAlOx (Supplementary Table 1) is up to 151.0 m2 g−1, which is much higher than ZnO (11.9 m2 g−1). High-resolution transmission electron microscopy (TEM) image in Fig. 4b gives us the fact that the ZnAlOx sample consists of a lot of tiny nanoparticles with the sizes of <10 nm. Moreover, the lattice spaces of 0.28 and 0.45 nm which respectively correspond to the (220) and (111) planes of cubic ZnAl2O4.33. The element distribution analysis (Supplementary Fig. 9) shows that the Zn, Al, and O are uniformly dispersed. As presented in Supplementary Fig. 10, the ZnO sample in this study is consisted of about 100 nm nanoparticles with a clear lattice space. The H-ZSM-5 zeolite embraces a typical nano-sized MFI structure (Supplementary Fig. 11). The acidcontent of H-ZSM-5 is 1.3 times as high as Si-H-ZSM-5 (Supplementary Table 2). The temperature-programmed reduction (TPR) results in Fig. 4c and Supplementary Table 3 show that both of ZnAlOx and ZnO can be hardly reduced by H2 below 700 K and <7% zinc oxides might be reduced to their metal phase above 1000 K. As known, Zn2+ cannot be reduced by H2 due to the positive free Gibbs energy. However, the reduction may proceed if H2 is split into hydrogen atoms or alloy phase with other metals like Cu is formed. Furthermore, the spinel structure of ZnAlOx has been proved to be more durable under H2 reduction. As a result, we consider that it is not zinc metal but Zn2+ in ZnAlOx.

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activates CO₂ hydrogenation reactions in this study. For a long time, the debate about the role of zinc species in industrial Cu/ZnO/Al₂O₃ catalysts for methanol synthesis has always existed. ZnO in Cu/ZnO/Al₂O₃ was not reckoned as catalytic centers but structural promoter or others. However, our results prove that in the absence of Cu species, ZnAlOₓ can also convert CO₂ into MeOH and derived DME. The FT-IR spectra of catalysts after 2,6-di-tert-butyl-pyridine absorption (DTBPy-FTIR) are exhibited in Fig. 4d. DTBPy-FTIR was usually utilized to investigate the external surface Bronsted acid sites because the kinetic diameter (10.5 Å) of DTBPy is larger than the pore opening (5.5 Å) of H-ZSM-5. The characteristic bands at 3365, 1614 and 1531 cm⁻¹ were assigned to the decrease of bridging hydroxyls on the external surface. Surprisingly, these typical bands almost disappeared for the composite catalyst ZnAlOₓ&H-ZSM-5. It indicates that external Brønsted acid site of H-ZSM-5 can be shielded by ZnAlOₓ after mixing, grinding and pressing under high pressure. The external Brønsted acid has no ability to aromatization but can promote the hydrogenation of unsaturated hydrocarbons to paraffins, which is detrimental to the aromatics selectivity. The aromatics or C₂-₄ olefins selectivity follows the order ZnAlOₓ&H-ZSM-5 > ZnAlOₓ + H-ZSM-5 > ZnAlOₓ/H-ZSM-5 (Fig. 1b), whereas the order of C₂-₄ paraffins selectivity completely reverses, which verifies this point of view.

**Operando DRIFT study.** The operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CO₂ hydrogenation over ZnAlOₓ at 593 K and 0.1 MPa are explored. It is obvious from Supplementary Fig. 12 that absorbed surface formate species were first formed, then, absorbed surface methoxy species were generated by hydrogenation of formate species. As presented in Fig. 5, compared to DRIFTS of CO₂ hydrogenation over ZnAlOₓ, the bands for surface formate (1620, 1375 and 2910 cm⁻¹) and methoxy (2940 and 2840 cm⁻¹) species over ZnAlOₓ&H-ZSM-5 are sharply weakened, which suggests that these active surface species over ZnAlOₓ were converted by H-ZSM-5. Combined the catalytic results in Fig. 1a with DRIFTS results discussed above, we propose a mechanism for CO₂ hydrogenation to aromatics over ZnAlOₓ&H-ZSM-5. First, surface formate species on ZnAlOₓ hydrogenation generates much less surface formate species. Then, absorbed surface methoxy species were spread to H-ZSM-5 to synthesize olefins. Finally, transformation of olefins to aromatics consecutively take place in the micropores of H-ZSM-5. Furthermore, compared to CO₂ hydrogenation over ZnAlOₓ, CO hydrogenation generates much less surface formate species. That is to say, more active metal species sites of ZnAlOₓ are utilized to activate H₂ during CO hydrogenation, so that higher C₂-₄ paraffins but lower aromatics are obtained in Supplementary Figure 5 because hydrogenation reactions of intermediates like olefins are enhanced. From Supplementary Fig. 13,
we believe that CO₂ hydrogenation cannot proceed over H-ZSM-5. Some evidences were put forward by Jiao et al.\textsuperscript{14,17,20} to support the ketene intermediate mechanism for STO or STA reactions over oxides/zeolites composite catalysts, however, we consider that this mechanism does not work in CO₂ hydrogenation over ZnAlOₓ&H-ZSM-5 due to very low concentration of CO in the reaction process.

In summary, composite catalyst of ZnAlOₓ with a nano-scaled spinel structure and H-ZSM-5 exhibits an excellent performance for CO₂ hydrogenation to aromatics. The selectivity of aromatics (excluding CO) reaches as high as 73.9\% with 9.1\% CO₂ conversion and 0.4\% CH₄ selectivity. Increasing H₂/CO₂ ratio or introducing CO can effectively suppress RWGS reaction without obviously weakening aromatization. The composite catalyst containing Si-H-ZSM-5 presents higher p-xylene, ethylene and propylene selectivity. It is not zinc metal but Zn²⁺ in ZnAlOₓ activates CO₂ hydrogenation. The shield of the external Brønsted acid of H-ZSM-5 by ZnAlOₓ is beneficial to aromatization. MeOH, DME and olefins are acted as reaction intermediates. CO₂ hydrogenation over ZnAlOₓ&H-ZSM-5 shows much higher aromatics selectivity than CO hydrogenation because the former reaction generates more formate species on ZnAlOₓ surface so that less metal species sites are left for hydrogenation of unsaturated intermediates like olefins. ZnAlOₓ&H-ZSM-5 suggests a promising application in manufacturing aromatics from CO₂ and H₂.

Fig. 4 Structural characterization of various catalysts. a X-ray diffraction patterns (XRD) of ZnAlOₓ. b High-resolution transmission electron microscopy (TEM) image of ZnAlOₓ. Scale bar: 10 nm. c H₂-TPR profiles. The relative intensity was normalized by weight. The relative intensity of the standard sample Ag₂O was divided by 50. d FTIR subtraction spectra relative to adsorption of DTBPy

Fig. 5 Operando DRIFT spectra over various catalysts. Conditions: 593 K, 0.1 MPa. CO₂&H₂ refers to the mixed gas of H₂/CO₂/Ar = 3/1/0.2; CO&H₂ refers to the mixed gas of H₂/CO/Ar = 3/1/0.2

Methods

Catalyst preparation. ZnAlOₓ oxide was prepared by a conventional co-precipitation method. Typically, solution A was made by 59.5 g Zn(NO₃)₂ 6H₂O, 75.0 g Al(NO₃)₃ 9H₂O and 40.0 g H₂O dissolved in 150 ml deionized water and solution B was prepared by 23.5 g (NH₄)₂CO₃ dissolved in 150 ml deionized water. Solutions A and B were dividedly added into one beaker by two peristaltic pumps with constant pH of 7.1–7.3 at 343 K under continuous stirring for 0.5 h, then followed by aging for 3 h at the same temperature. After filtered and washed by 200 ml deionized water for three times, the obtained mixture was dried at 373 K overnight and then calcined at 773 K for 4 h.

Commercial Na-ZSM-5 zeolite was supplied from Zhongke New Catalytic Technology Company, China. Na-ZSM-5 zeolites were transformed into NH₄-ZSM-5 by exchanging 50 g Na-ZSM-5 with 0.51 NH₄NO₃ (1 mol l⁻¹) aqueous solution at 353 K for 2 h, followed by filtration and washing with deionized water.
After repeating the exchanging process for three times, the resultant samples were dried overnight at 373 K, followed by calcination at 823 K for another 4 h in air to obtain the H-ZSM-5 zeolite.

Si-H-ZSM-5 zeolite was prepared by tetraethoxysilane (TEOS) modification. In brief, an organic solution was firstly made by 11.5 g TEOS mixed with 5 ml cyclohexane; then 10.9 g H-ZSM-5 was added into this solution, impregnated for 24 h at room temperature; after that, organic solvent was removed by evaporation at 353 K and the resultant powder was dried overnight at 373 K, followed by calcination at 823 K for another 4 h in air. After repeating the procedure above for twice, the Si-H-ZSM-5 was obtained.

The composite catalysts were typically prepared by physical mixing. Unless specially stated, the weight ratio of oxides and zeolites was 1:1. For preparation of the composite catalyst ZnAlO₄/H-ZSM-5, ZnAlO₄ oxide and H-ZSM-5 zeolite were grinded in an agate mortar for 4 min, pressed under 40 MPa and granulated into the required size in the range of 0.4–0.8 mm.

**Catalytic tests.** Catalytic reaction experiments in Fig.1 and Supplementary Figure 2 and 3 were performed in a 16-channel continuous flow fixed-bed stainless steel reactor (from Yashentech Corporation, Shanghai, China) with an 8.3 mm inner diameter for each channel. The inlet gas flow and composition along with the reaction temperature and pressure for each channel were identical. All the reaction products were kept in the gas phase and analyzed online by two gas chromatographs (Agilent 7890A equipped with a HP-PLOT/Q capillary column connected to a flame ionization detector (FID) and a TDX-1 column (produced from DCIP) connected to a thermal conductivity detector (TCD). CH₄ was taken as a reference gas for carbon balance. CO₂in: moles of CO₂ at the inlet; CO₂out: moles of CO₂ at the outlet; COout: moles of CO at the inlet; COselectivity: \(\frac{CO_{out}}{CO_{in} - CO_{selectivity}} \times 100\%\)

Other catalytic reaction experiments were performed in a typical fixed-bed stainless steel reactor with 8 mm inner diameter. All products were analyzed online by two tandem gas chromatographs. One is Agilent 7890A equipped with a HP-PLOT/Q capillary column connected to FID and a TDX-1 column connected to TCD. The other one is Agilent 6890N equipped with a HP-FFAP capillary column connected to FID and a Porapak Q column connected to TCD. The detailed analysis for aromatics such as ethylbenzene, m-xylene, and o-xylene is dependent on HP-FFAP capillary column.

**Data availability.** The data supporting the findings of this study are available within the article and its Supplementary Information files. All other relevant source data are available from the corresponding author upon reasonable request.

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Author contributions

Y.N., who made the initial discovery, designed and conducted the experiments and wrote the manuscript. Z.C. and Y.F. conducted the experiments. Y.L. discussed the results. W.Z. and Z.L. supervised the experiments and discussed the results.