ZnO Nanoparticles Encapsulated in Nitrogen-Doped Carbon Material and Silicalite-1 Composites for Efficient Propane Dehydrogenation

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HIGHLIGHTS
Supported catalysts with stable ultrasmall ZnO nanoparticles were prepared
The N-doped carbon layer helps to protect ZnO NPs from sintering and volatilization
The catalysts exhibited excellent activity and stability in propane dehydrogenation

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ZnO Nanoparticles Encapsulated in Nitrogen-Doped Carbon Material and Silicalite-1 Composites for Efficient Propane Dehydrogenation

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SUMMARY
Non-oxidative propane dehydrogenation (PDH) is an attractive reaction from both an industrial and a scientific viewpoint because it allows direct large-scale production of propene and fundamental analysis of C-H activation respectively. The main challenges are related to achieving high activity, selectivity, and on-stream stability of environment-friendly and cost-efficient catalysts without non-noble metals. Here, we describe an approach for the preparation of supported ultrasmall ZnO nanoparticles (2–4 nm, ZnO NPs) for high-temperature applications. The approach consists of encapsulation of NPs into a nitrogen-doped carbon (NC) layer in situ grown from zeolitic imidazolate framework-8 on a Silicalite-1 support. The NC layer was established to control the size of ZnO NPs and to hinder their loss to a large extent at high temperatures. The designed catalysts exhibited high activity, selectivity, and on-stream stability in PDH. Propene selectivity of about 90% at 44.4% propane conversion was achieved at 600°C after nearly 6 h on stream.

INTRODUCTION
Propene is the second-largest building block of the chemical industry with a steadily increasing demand owing to its plentiful downstream applications. Stream cracking and fluid catalytic cracking (FCC) of various oil fractions are the most common methods for producing propene. These technologies have several drawbacks such as high-energy consumption and low selectivity to propene. In addition, metathesis of ethylene and 2-butenes (Mol and van Leeuwen, 2008) and non-oxidative propane dehydrogenation (PDH) (Caspary et al., 2008) have been developed for on-purpose propene production. The latter process is the most attractive technology because of the fast exploitation of shale gas providing an exciting opportunity for producing light olefins and aromatics (Wang and Li, 2017; Bruijninx and Weckhuysen, 2013). For this reason, the PDH technology has attracted increasing attention of researchers from industry and academia around the world (Liu et al., 2016a, Sokolov et al., 2012; Kim et al., 2017; Hu et al., 2018; Zhu et al., 2017; Sattler et al., 2014a). From a fundamental viewpoint, PDH is also of great significance because it is a good model reaction for studying the fundamentals of the activation of C-H bond.

As PDH is a strongly endothermic reaction, it requires high temperatures (>500°C) to achieve industrially attractive degrees of propane conversion. Chromium-based (Mentasty et al., 1999; Weckhuysen and Schoonheydt, 1999) and platinum-based (Jiang et al., 2015; Shi et al., 2015; Li et al., 2017; Xiong et al., 2017) materials are the commercial catalysts used for this reaction, which have, however, shortcomings related to toxicity and high cost of the active components, respectively. To overcome them, a lot of efforts have been put into developing new kinds of alternative catalysts such as gallium-based (Kim et al., 2017; Choi et al., 2017; Sattler et al., 2014b), vanadium-based (Liu et al., 2016a, Hu et al., 2018; Sokolov et al., 2012), tin-based (Wang et al., 2016, 2017), and zirconium-based (Otroshchenko et al., 2015, Otroshchenko et al., 2016, Otroshchenko et al., 2017a, 2017b) materials. Owing to the recent developments in nanoscience and synthetic technologies, ZnO nanoparticles (ZnO NPs) or ZnO quantum dots as promising semiconductor materials were elaborately synthesized and are widely used in photocatalysis (Etacheri et al., 2012; He et al., 2014), photodetectors (Tang et al., 2018; Shao et al., 2013), degradation of organic pollutants (Akkari et al., 2017), and other low-temperature applications. ZnO-based materials are promising catalysts for PDH because of their costs, environment friendliness, and high efficiency to activate C-H bond (Sun et al., 2014; Schweitzer et al., 2014; Camacho-Bunquin et al., 2017; Liu et al., 2016b; Biscardi et al., 1998). However, ZnO is often unstable under reducing reaction conditions because of the formation...
of metallic Zn, which melts at about 420°C. To improve the stability of ZnO at high temperatures, synthesis of composite oxides (Sun et al., 2014) and modification of ZnO with Pt (Liu et al., 2016b) have been proposed. To the best of our knowledge, ultrasmall ZnO NPs (<10 nm) have still not been studied in high-temperature (>420°C) reactions. The main reason is related to the difficulties in preparing catalysts possessing highly dispersed NPs with high stability against sintering and Zn/ZnO volatilization under reaction conditions (Anthrop and Searcy, 1964; Sirelkhatim et al., 2015).

Owing to their intriguing topologies and diverse functionalities, metal organic frameworks (MOFs) are widely used for gas separation (Hu et al., 2015; Cadiau et al., 2016; Rodenas et al., 2014), sensors (Campbell et al., 2015), and catalysis (Lee et al., 2009; Zhao et al., 2014; Zhao et al., 2016a, 2016b; Zhang et al., 2017). In the latter case, MOFs and metals@MOFs are applied in photocatalysis (Nasalevich et al., 2015), organic catalysis (Huang et al., 2017), and other reactions (Yang et al., 2016; Liu and Tang, 2013) as they possess highly dispersed metal sites. A recent attractive direction for MOF applications is their usage as precursors to generate highly dispersed metals or metal oxides@carbon materials (even single-site atoms@carbon material) (Chen et al., 2015, 2017; Yin et al., 2016). The formed carbon material or N-doped carbon material could isolate metal or metal oxide species, and M(metal)-N(N atom)-C(carbon material) bonds can be formed in some cases to prevent the catalytically active species from aggregation. In spite of this significant progress, reports on using non-metal heteroatoms in MOFs to synthesize stable metal and/or metal oxide-based catalysts at high temperatures are still rare. With this thought in mind, here we introduce a methodology for the preparation of composite catalysts with thermally stable ZnO NPs encapsulated into a nitrogen-doped carbon layer (NC layer) on the surface of Silicalite-1. The NC layer is formed through carbonizing zeolitic imidazolate framework-8 (ZIF-8, Zn(2-methylimidazole)2) followed by leaching with nitric acid. Scanning transmission electron microscopy and H2-temperature programmed reduction (H2-TPR) revealed that the presence of N species in the NC layer is decisive for stabilizing the NPs at temperatures up to 700°C. The potential of the so-designed catalysts was validated for the PDH reaction at 600°C. Owing to the stabilizing effect of the NC layer on ZnO NPs, the catalysts showed high on-stream stability and activity.

RESULTS AND DISCUSSION

For the preparation of ZnO@NC and Silicalite-1 composite catalysts, Silicalite-1 was chosen as the support because it possesses high specific surface area and unique porosity (Figure S1), and it was synthesized according to the reference (Shen et al., 2013). Moreover, silica-based materials are typically used as supports for preparing selective PDH catalysts as they do not possess acidic sites, which are considered to negatively affect selectivity due to coke formation. To form a ZIF-8 layer on this support, Zn(NO3)2·6H2O and 2-methylimidazole were added to a suspension of Silicalite-1 in methanol. After centrifuging and drying, the obtained solid material was carbonized at 700°C in N2 atmosphere and denoted as ZnO@NC/S-1(0.0). The ZnO@NC/S-1(0.0) sample was further treated with nitric acid for partially dissolving ZnO species and thus generating more uniform ZnO NPs with smaller size. This material was abbreviated as ZnO@NC/S-1(x), where x stands for the concentration of the acid. Zn loading determined by inductively coupled plasma spectrum (ICP) in ZnO@NC/S-1(0.0) and ZnO@NC/S-1(1.0) was 2.8 wt % and 2.0 wt %, respectively. The X-ray diffraction patterns of as-synthesized ZIF-8 (Figure 1A) match well with the simulated pattern, confirming the formation of the ZIF-8 phase (Pan et al., 2011; Kuo et al., 2012). A reflex at 2θ of 7.3° characteristic for ZIF-8 is also presented in the diffractogram of Silicalite-1 coated with a ZIF-8 layer. The coated material maintained the typical MFI topological structure with good crystallinity after carbonizing the ZIF-8 layer followed by acid leaching process. No reflexes characteristic for bulk ZnO or NC material were observed. Thus the presence of large crystalline particles of ZnO and NC in the as-synthesized catalysts can be excluded. To derive an insight into the nature of carbon in the NC layer, we applied Raman spectroscopy. The obtained spectra of ZnO@NC/S-1(0.0) and ZnO@NC/S-1(1.0) are characterized by two evident bands at about 1,340 cm−1 and about 1,590 cm−1 (Figure 1B). These bands can be ascribed to the defective structure (D band) and graphitic carbon (G band), respectively (Lim et al., 2012; Zhang et al., 2014). The relatively low ratio of the D band intensity to that of the G band indicates the high degree of graphitization of the formed NC material. X-ray photoelectron spectroscopy (XPS) was applied to determine catalyst surface composition. All XPS signals were adjusted by the position of Si 1s with a binding energy of 103.3 eV. As seen in Figure 1C, two XPS signals at about 1,022 eV and about 1,045 eV are presented in the spectra of all catalysts and are characteristic for Zn 2p1/2 and Zn 2p3/2, respectively (Ma et al., 2011; Aksoy et al., 2012). However, in comparison with ZnO loaded on Silicalite-1 (ZnO/Silicalite-1, 1,022.2 eV), the Zn 2p1/2 binding energy for ZnO@NC/S-1(0.0) and ZnO@NC/S-1(1.0) is slightly shifted to lower values, i.e., 1,022.0 eV and 1,021.6 eV, accordingly. The energy shift may be caused by the electron donor property of the.
introduced NC layer. After HNO₃ leaching, the binding energy value is also shifted from 1,022.0 eV to 1,021.6 eV, which may be caused by decreasing ZnO content. Detailed N 1s spectra of ZnO@NC/S-1(0.0) and ZnO@NC/S-1(1.0) are presented in Figure S2. On their basis, three different kinds of N species were identified: pyridinic-N, pyrrolic-N, and graphitic-N. Their percentage distribution is given in Table 1. The profiles of temperature-programmed desorption of propene (C₃H₆-TPD) from these two samples are presented in Figures 1D and S3, and the temperature (T_max) of maximal desorption is given in Table 1. These data suggest that C₃H₆ adsorbs weaker on the ZnO@NC/S-1(1.0) sample than on the ZnO@NC/S-1(0.0) sample. Owing to electron-rich property of C₃H₆, it adsorbs more strongly on the ZnO@NC/S-1(0.0) sample with electron-deficient state (higher values of Zn binding energy) as confirmed by XPS results.

To determine the size of ZnO NPs, high-angle annular dark-field scanning transmission electron microscopy (STEM) and bright-field STEM were applied, and the corresponding representative images are shown in Figures 2A and 2B. It can be clearly seen that ZnO NPs are encapsulated into the NC layer. ZnO NPs in ZnO@NC/S-1(0.0) have a broad distribution with an average size of 4.0 nm. Treatment with 1 M HNO₃ results in a narrower distribution of ZnO NPs with an average size of 2.6 nm in ZnO@NC/S-1(1.0). This may be due to the partial dissolution of ZnO in HNO₃ as concluded from the ICP results shown in Table 1. To elucidate the factors determining the stability of ZnO NPs at high temperatures, the ZnO@NC/S-1(1.0) sample was treated in either a flow of pure N₂ (ZnO@NC/S-1(1.0)-N₂-700°C) or a mixture of 10 vol % H₂ in N₂ (ZnO@NC/S-1(1.0)-10 vol % H₂/700°C) at 700°C for 2 h. ZnO NPs are hardly visible (Figures 2A III, 2B III, and S4) in the sample treated in the H₂-containing mixture, and the ZnO loading is 0.4 wt %. The latter result suggests that most of ZnO was lost during 10 vol % H₂ treatment at 700°C. In contrast, ZnO NPs did not disappear after N₂ treatment (Figures 2A IV and 2B IV) as concluded from the fact that Zn loading decreased only slightly from 2.0 to 1.8 wt %. The size of Zn NPs also decreased from 2.6 to 2.0 nm. To derive an insight into the effect of H₂ treatment on the stability of ZnO NPs, H₂-TPR tests were additionally carried out using a fresh sample. When carefully analyzing the H₂-TPR results (Figure S5), no signal related to water could be identified, thus indicating that ZnO NPs could not be reduced upon
reductive catalyst treatment. As proven by in situ diffuse reflection infrared fourier transform spectrum (DRIFTS) analysis of the catalysts treated in different atmospheres and at different temperatures (Figure S6), no surface functional groups characteristic of aromatic C-N or C=N species could be identified after treatment at 700 °C N2. Such species were, however, present after treatment in N2. Thus we can conclude that N species could be removed in the form of NH3 upon H2 treatment at high temperatures (>650 °C). Taking the above results into account, it can be confirmed that the N species can provide protective function for ZnO NPs to a large extent at high temperatures. Consequently, the aggregation and loss of ZnO could be prevented by carbon layer and N species, respectively. Such efficient preparation of ultrasmall ZnO NPs by encapsulating in NC material via post-treatment of MOFs thus presents a platform for maintaining potential stability in PDH at 600 °C.

To check if and how the kind (ZnO@NC-based versus impregnated catalyst) of catalyst and the presence of N in NC layer affect catalytic performance in PDH, catalytic tests were performed at 600 °C and atmospheric pressure. Propane conversion and propene selectivity as a function of time on stream are summarized in Figures 3 and S7. Poor catalytic performance of bare Silicalite-1 (S-1) as well as NC and S-1 (NC/S-1) composite material (Figure S7) indicates that the support and the NC material are inactive for PDH, whereas Zn-containing materials were active. Thus ZnO NPs should be the active species. However, catalytic activity depends on how this active component was introduced on the surface of Silicalite-1. For comparison, when a similar amount of ZnO (2.5 wt %) was introduced into Silicalite-1 by incipient wetness impregnation (ZnO/S-1), propane conversion was only 13.7% and the selectivity to propene was below 70% (Figure S7). When ZnO/S-1 was treated with 1 M HNO3, the initial conversion of propane decreased from 13.7% to 6.9%, whereas the selectivity to propene slightly increased. The as-prepared ZnO@NC/S-1(x) composite catalysts performed significantly superior. This can be due to the presence of ultrasmall ZnO NPs. STEM analysis proved that the NPs were stable during the PDH. The size of ZnO NPs in spent ZnO@NC/S-1(1.0) did not change obviously (2.2 nm, Figures 2 A V and 2B V). In addition, the conversion of propane and the selectivity to propene increased with an increase in the concentration of nitric acid used for catalyst leaching. Acidic treatment is also important for catalyst stability against deactivation. The higher the acid concentration, the higher the on-stream stability was (Figure S7). For example, the conversion of propane over ZnO@NC/S-1(0.0) dropped from 52.2% to 15.3% within 315 min on propane stream, whereas the corresponding values for ZnO@NC/S-1(1.0) were 56.4% and 44.4%. For the ZnO@NC/S-1(1.0) sample, the selectivity to propene maintained at about 90% during stability test. Other undesired gas-phase products were mainly methane, ethane, and ethene (Figure S8). The selectivity to propene over ZnO@NC/S-1(1.0) was also higher than that over ZnO@NC/S-1(0.0). Such phenomenon may be caused by a decrease in particle size of ZnO after acid catalyst treatment. According to previous studies on PDH reaction (Zhang et al., 2018; Zhu et al., 2015), undesired reactions are inhibited upon decreasing the size of catalytically active species. The amount of coke formed during the PDH reaction was quantitatively determined by thermogravimetric (TG) analysis (Figure S9) and used for calculating the average rate of coke deposition (Table 1). The lowest rate was obtained for ZnO/S-1 due to its very low PDH activity and consequently low concentration of propene responsible for coke formation. Importantly, the rate of coke deposition over ZnO@NC/S-1(1.0) is 10 times lower than that over the ZnO@NC/S-1(0.0) catalysts, although the samples operated with a similarly high initial activity. Taking into account the results of C3H6-TPD (Figure 1D) and TG tests, it can be concluded

| Samples           | S BET (m²/g) | Zn Loading (wt %) | T coke (g kg⁻¹ cat⁻¹ h⁻¹) | Tmax (°C) | N Species |
|-------------------|--------------|-------------------|---------------------------|-----------|-----------|
|                   |              |                   |                           |           | Pyridinic | Pyrrolic | Graphitic |
| ZnO/S-1           | 426          | 2.5               | 0.004                     | –         | –         | –        | –         |
| ZnO@NC/S-1(0.0)   | 351          | 2.8               | 0.10                      | 324       | 32%       | 40%      | 28%       |
| ZnO@NC/S-1(1.0)   | 370          | 2.0               | 0.01                      | 316       | 48%       | 25%      | 27%       |

Table 1. Specific Surface Area (S BET), Zn Loading, Rate of Coke Formation (T coke), Temperature (Tmax) of Maximal Propene Desorption, and Surface Distribution of Different N Species
See also Figures S1 and S9.

a Zn loading was determined by ICP.
b T coke was calculated on the basis of thermogravimetric analysis (TGA) according to Equation 1. (See it in Supplemental Information)
c Determined from temperature-programmed profiles of propene desorption.
d Obtained through deconvolution of detailed N 1s peak in the XPS.
Figure 2. Electron microscopic characterization of as-prepared catalysts

(A) HAADF STEM images and (B) BF-STEM images of as-synthesized catalysts. (I) ZnO@NC/S-1(0.0), (II) ZnO@NC/S-1(1.0), (III) ZnO@NC/S-1(1.0)-10 vol % H₂–700°C, (IV) ZnO@NC/S-1(1.0)-N₂–700°C, (V) spent ZnO@NC/S-1(1.0) (Scale bars, 50 nm in A [I–IV] and 20 nm in A [V] and B [I–V]).

See also Figures S4–S6.
that C\textsubscript{3}H\textsubscript{6} interacts weaker with ZnO@NC/S-1(1.0) than with ZnO@NC/S-1(0.0). As a consequence, appropriate adsorption/desorption properties of C\textsubscript{3}H\textsubscript{6} species would effectively hinder their transformation into coke precursors (Jiang et al., 2015; Shi et al., 2015). On the basis of the results of carbon and ICP analysis of catalysts before and after reaction (Table 1 and Figure S9), reaction-induced carbon deposition should be the main reason for catalyst deactivation, which is slow over ZnO@NC/S-1(1.0). In addition, although the loss of ZnO has been hindered in the present case, it will also result in a drop in the activity to some extent. Unfortunately, when carrying out oxidative catalyst regeneration, not only carbon deposits but also NC layer will be oxidized, thus resulting in the loss of their protection function. The problem may be solved by selective coke removal by controlling combustion parameters. The related work is ongoing in our group.

In summary, a facile strategy was developed to prepare catalysts with ultrasmall ZnO NPs being stable up to 700°C. An NC layer in situ formed through carbonization of MOFs is used for encapsulation of such NPs and thus protects ZnO NPs from sintering and volatilization at high-temperature. The so-designed catalysts demonstrate high activity, selectivity, and on-stream stability in PDH. Such efficient utilization of MOFs via simple post-treatment for the construction of stable ZnO NPs may provide new insights into the design of highly effective metal oxide NPs and promote their catalytic applications.

**Limitations of the Study**
Additional characterization of the ZnO nanoparticles would be warranted, and regeneration of the catalyst would be also valuable.

**METHODS**
All methods can be found in the accompanying Transparent Methods supplemental file.

**SUPPLEMENTAL INFORMATION**
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.02.018.

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AUTHOR CONTRIBUTIONS

G.J., B.G., and E.V.K. designed and conceived this work; D.Z. and Y.L. contributed equally to this work and carried out the synthesis, characterization, and catalytic test. D.Z. wrote the manuscript, and Y.L., G.J., and E.V.K. revised the manuscript. S.H. and Y.Z. analyzed the catalytic results. R.L. and C.Y. performed the H2-TPR measurements. B.G. carried out the STEM characterization. K.G. performed the in situ DRIFTs and part of ICP analysis. All the authors participated in the discussion of the results and the preparation of the paper.

DECLARATION OF INTERESTS

Y.L. has filed a patent application based on the work in this manuscript. All other authors declare no competing financial interests.

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Supplemental Information

ZnO Nanoparticles Encapsulated in Nitrogen-Doped Carbon Material and Silicalite-1 Composites for Efficient Propane Dehydrogenation

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Supporting Information

1 Transparent Methods

1.1 Experimental

1.1.1 Chemicals

Tetraethyl orthosilicate (Sinopharm Chemical Reagent Co., Ltd), Zn(NO$_3$)$_2$$\cdot$6H$_2$O (Sinopharm Chemical Reagent Co., Ltd), 2-Methylimidazole (Energy Chemical), tetrapropylammonium hydroxide (Shanghai Cairui Chemical Engineering Technology Co., Ltd) and nitric acid (Beijing Chemical Industry Group Co. Ltd) were used as received without any further purification.

1.1.2 Synthesis of Silicalite-1 zeolite

Silicalite-1 was synthesized according to the reference (Shen et al. 2013) but with some modifications. In a typical process, measured amount of tetrapropylammonium hydroxide (25wt%, 48.8 g) was blended in deionized water (25.92 g), after 10 minutes agitating, 50 g of tetraethyl orthosilicate was added to the above mixture with continuous stirring and the solution was aged for additional 6 h. The solution was then placed in 200 mL Teflon stainless-steel autoclaves under static conditions at 100°C for 2 days. The solid product was obtained by centrifugation, washed several times with deionized water, dried overnight at 110°C, and calcined in air at 550°C for 6 h to remove structure-directing agent, and the as-prepared Silicalite-1 was abbreviated as S-1.

1.1.3 Synthesis of Silicalite-1 with ZIF-8

1 g of Silicalite-1 was dispersed in 25 ml methanol with agitating and ultrasound condition to form a milk white suspension. Then 0.3 g of Zn(NO$_3$)$_2$$\cdot$6H$_2$O was added into the slurry under agitating condition for 1 h, and 1.75 g of 2-methylimidazole was added into the mixture, after that, the mixture was stirred at room temperature for 6 h. The Silicalite-1 with ZIF-8 coating catalyst was obtained by centrifugation and dried overnight at 60°C. Single ZIF-8 sample was synthesized as similar as above processes without Silicalite-1.

1.1.4 Carbonization of Silicalite-1 with ZIF-8

Carbonization process of Silicalite-1 with ZIF-8 layer was carried out in N$_2$ atmosphere at 700°C for 2 h with a heating rate of 5°C/min, and the sample were denoted as ZnO@NC/S-1(0.0). For ZnO@NC/S-1(0.0) sample, the amount of Zn is 2.8 wt % which was measured by ICP-OES (Inductively Coupled Plasm-Optical Emission Spectrum).

1.1.5 Leaching process

1 g of ZnO@NC/S-1(0.0) sample was dispersed in HNO$_3$ solution with different concentrations (0.3 M/0.5 M/1 M) under agitating condition at room temperature for 30 min. Then the products were collected by filtration, and washed with copious amount of water until the pH value was ~7. And then dried at 100°C overnight, and the samples were denoted as ZnO@NC/S-1(x), where x means the concentration of HNO$_3$. For ZnO@NC/S-1(1.0) sample, the content of Zn is 2.0 wt% measured by ICP-OES. All the samples were pressed and sieved to particles in the range of 40-60 mesh.
1.1.6 Synthesis of ZnO/Silicalite-1

The ZnO/Silicalite-1 sample with desirable Zn content was synthesized by incipient wetness impregnation, and the as-synthesized catalyst was dried at 100°C for overnight, then it was calcined at 700°C for 2 h, and the obtained sample was denoted as ZnO/S-1. The amount of Zn is 2.5 wt % which was measured by ICP-OES. The obtained ZnO/S-1 sample was leached by 1M HNO₃ at room temperature for 30 min, denoted as ZnO/S-1(1.0).

1.1.7 Preparation of NC/S-1 sample

The NC/S-1 sample was synthesized by calcining the ZnO@NC/S-1(0.0) sample at 900°C for 2 h in N₂ flow with a heating rate of 5°C/min.

1.1.8 Treatment of ZnO@NC/S-1(1.0) sample under different gas flow

The 40-60 mesh of ZnO@NC/S-1(1.0) sample was treated under 10 vol%H₂-N₂ and N₂ in a 6 mm quartz tube, then the process lasted for 2 h at 700°C with a heating rate of 5°C/min and cooled down to room temperature, and the sample was denoted as ZnO@NC/S-1(1.0)-gas flow-temperature. The ZnO loadings are determined by ICP, which are 1.8 wt% and 0.4 wt% after N₂ and 10 vol%H₂-N₂ treatment, respectively.

1.2 Characterization

The catalysts were characterized by various techniques. X-ray diffraction (XRD) patterns were obtained from an X-ray diffractometer (Bruker, D8 Advance) with Cu Kα radiation at a voltage of 40 kV, a current of 40 mA and the 2θ was at the range of 5-90°.

Textural properties of catalysts were measured by N₂ adsorption at 77 K on an automatic adsorption instrument (Micromeritics Instrument, Tristar II 3020). The samples were outgassed at 350°C for 4 h before measurement.

Temperature programmed desorption of propene (C₃H₆-TPD) was carried out on Xianquan TP-5076 equipment with TCD detector. Typically, 100 mg catalyst was pre-treated on N₂ flow (20 ml/min) at 600°C for 1 h. Subsequently, the catalyst was cooled down to room temperature (about 30°C) to adsorb propene for 30 min. Then, the C₃H₆-TPD profile was obtained at a heating rate of 10°C/min from 100°C to 450°C.

H₂-temperature programmed reduction was carried out in an in-house developed setup (equipped mass spectrum detector). 0.3 g of samples was pretreated under Ar flow (40 ml/min) at 420°C or 620°C. After cooling down to room temperature, the profile was obtained when the Ar flow was switched to 10%H₂-Ar (20 ml/min) with a heating rate of 15°C/min to 750°C and stayed 30 min.

X-ray photoelectron spectroscopy was carried out on Thermo Fisher K-Alpha. And all the peaks were adjusted by the position of Si 1s with a binding energy of 103.3 eV.

The HAADF-STEM and BF-STEM images were obtained by 200KeV JEOL ARM 200.

TG analysis was carried out on Mettler-Toledo TGA/DSC-1. The profile was obtained at O₂ flow with a heating rate of 10°C/min. And the coke deposition rate was calculated by below equation:

\[
\text{Coke deposition rate} = \frac{[m_{\text{after reaction}}]-m_{\text{before reaction}}]}{[m_{\text{catalyst}}]*\text{reaction time}} \quad \text{eq1}
\]

Here, \(m_{\text{after reaction}}\) and \(m_{\text{before reaction}}\) is the mass of coke and carbon material, respectively, \(m_{\text{catalyst}}\) is the mass of catalyst, time is the reaction time.
1.3 Catalytic test

The catalytic performances of as-synthesized catalysts for propane dehydrogenation were carried out in quartz tube with fixed bed. Before evaluation, the catalysts were pretreated on N$_2$ flow at reaction temperature 600°C for 30 min. Then switched the C$_3$H$_8$, H$_2$ and N$_2$ with ratio of 1:1:5, and N$_2$ flow rate is 7.5 ml/min. A gas chromatograph equipped aluminum capillary column and flame ionization detector (FID) was employed to analyze all products. Propane conversion, propene selectivity and yield were calculated according to the following equations:

$$X_{(C_3H_8)} = \frac{m_{(C_3H_8, \text{inlet})} - m_{(C_3H_8, \text{outlet})}}{m_{(C_3H_8, \text{inlet})}} \times 100\%$$

$$S_{(C_3H_8)} = \frac{m_{(C_3H_8, \text{outlet})}}{\sum m_{(C_3H_j, \text{products})}} \times 100\%$$

$$Y_{(C_3H_8)} = S_{(C_3H_8)} \times X_{(C_3H_8)}$$

$m_{(C_3H_8, \text{inlet})}$ and $m_{(C_3H_8, \text{outlet})}$ stand for the mass fraction of the C$_3$H$_8$ before and after reaction. $m_{(C_iH_j)}$ means the mass fraction of products.
2 Additional characterization of the catalysts

2.1 BET

Figure S1 (A) N\textsubscript{2} adsorption-desorption isotherms, (B) pore size distribution (BJH adsorbed branch). Related to Table 1.
2.2 XPS

Figure S2. (A) Zn 2p core level spectra of post-treated sample over ZnO@NC/S-1(1.0); (B), (C), (D) and (E) N 1s core level spectra of ZnO@NC/S-1(0.0), ZnO@NC/S-1(1.0), ZnO@NC/S-1(1.0)-N$_2$-700°C and ZnO@NC/S-1(1.0)-10 vol%H$_2$-700°C, respectively. For ZnO@NC/S-1(1.0)-10 vol%H$_2$-700°C sample (Figure S2A), the peaks of Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$ are contributed to ZnO, and the peaks are ambiguous, speculating that the content of ZnO is very low on the catalyst surface after 10% H$_2$ treatment at 700°C (0.4 wt% of ZnO loading). Related to Figure 1.
2.3 C\textsubscript{3}H\textsubscript{6}-TPD

![C\textsubscript{3}H\textsubscript{6}-TPD profile](image)

**Figure S3** The C\textsubscript{3}H\textsubscript{6}-TPD profiles of ZnO@NC/S-1(x) samples. For ZnO@NC/S-1(x), the peak position was shifted to a lower temperature after acid leaching with increasing concentration of nitric acid, indicating that the interaction between the C\textsubscript{3}H\textsubscript{6} and catalysts was weakened. Related to Figure 1

2.4 STEM

![STEM images](image)

**Figure S4** STEM images of (A) ZnO@NC/S-1(1.0) with lattice fringe of ZnO NPs and (B–E) ZnO@NC/S-1(1.0)-10%H\textsubscript{2}-700°C sample. Related to Figure 2
2.5 H₂-TPR

Figure S5 H₂-TPR profiles of as-synthesized catalysts. (A) ZnO/S-1 (B) ZnO@NC/S-1(0.0), (C) ZnO@NC/S-1(1.0). (A), (B) and (C) samples were pretreated at 420°C. (D) ZnO@NC/S-1(1.0) sample was pretreated at 620°C. For ZnO/S-1 and ZnO@NC/S-1(1.0) sample, a slight amount of H₂O was detected by mass spectrum detector (MS). In order to identify the source of H₂O during the reducing reaction, the ZnO@NC/S-1(1.0) sample was pretreated at 620°C (Figure S5D), and it was found that no water was detected by MS, indicating that the water was produced by dehydration of Si-OH on the Silicalite-1. For the ZnO@NC/S-1(0.0) and ZnO@NC/S-1(1.0) samples (Figure S5B and C), NH₃ could be formed during the H₂ reducing process at high temperature (>650°C). Related to Figure 2.
2.6 *In-situ* DRIFTS

![In-situ DRIFTS spectra of ZnO@NC/S-1(1.0) under different treatment conditions.](image)

*Figure S6* *In-situ* DRIFTS spectra of ZnO@NC/S-1(1.0) under different treatment conditions. Related to Figure 2

2.7 Catalytic performances

![Catalytic performances](image)

*Figure S7* (A) propane conversion, (B) propene selectivity, (C) propene yield. Reaction conditions: 0.2 g of catalyst, 600°C, V(H₂):V(C₃H₈):V(N₂)=1:1:5, N₂ flow rate: 7.5 ml/min. Related to Figure 3
2.8 The original gas chromatogram

![Gas Chromatogram](image)

**Figure S8** The original gas chromatogram. Related to Figure 3

2.9 TG

![Thermogravimetric Analysis](image)

**Figure S9** The TG profiles of fresh catalyst and spent catalyst. Related to Table 1