



Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Full Length Article

Role of Ni species in ZnO supported on Silicalite-1 for efficient propane dehydrogenation

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ARTICLE INFO

Article history:

Received 31 August 2021

Received in revised form 23 February 2022

Accepted 23 February 2022

Available online 5 March 2022

Keywords:

Propane dehydrogenation

NiZn alloy

Reverse hydrogen spillover

Lewis acid

Zeolite

ABSTRACT

Propane dehydrogenation (PDH) is one of the most effective technologies to produce propene. Non-noble zinc-based catalysts have paid increasing attention because of low cost and nontoxic, compared with industrial Pt and Cr-based catalysts. However, they often suffer from limited catalytic activity and poor stability. Here, we introduced moderate Ni into ZnO supported Silicalite-1 zeolite to increase catalytic activity and stability simultaneously. Zn²⁺ was the definite active site and NiZn alloy facilitated the sluggish H recombination into H₂ via reverse spillover. Furthermore, the introduction of Ni increased Lewis acid strength caused by electron transfer from ZnO to NiZn alloy, contributing to improved stability. For resulted 0.5NiZn/S-1, propene formation rate was 0.18 mol C₃H₆·(g Zn)⁻¹·h⁻¹ at 550 °C, which was above 1.5 times higher than that over Zn/S-1 without Ni. Under stability test, the deactivation of 0.5NiZn/S-1 was 0.019 h⁻¹, which was only 1/10 of that over Zn/S-1.

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1. Introduction

Propene is one of the most important industrial raw material for the production of polypropylene, acrylonitrile, propylene oxide, acetone and other industrial products [1–4]. Clean and low-carbon utilization of fossil energy is an efficient way to achieve “carbon neutrality”. Propane dehydrogenation (PDH) technology has been paid increasing attention owing to worldwide growing demand of propene and the increasing availability of propane from shale gas [5–12]. Pt [11–14] and Cr [15–17]-based catalysts are widely applied in industrial PDH technology, but the scarcity of platinum and the environmental toxicity of chromium are still hindering their wide applications [18–20]. Therefore, it is desirable to develop alternative catalysts with low cost and environment-friendly properties.

Non-noble metal oxide applied in PDH, such as Zn [20,21], Sn [22], V [23], Co [24–28], Ga [29] oxide catalysts, were studied in recent decades. Among these catalysts, zinc oxide (ZnO) is a

promising candidate [18,21,30–32], with both low cost and low toxicity. Both Zn²⁺ and ZnO species were active sites for PDH reactions. Miller and co-workers prepared single-site Zn²⁺ on SiO₂ catalyst. Under reaction condition, 3-coordinate active center could promote the activation of C–H bond as Lewis acid [20]. ZnO supported on zeolite was a general method to improve thermal stability [18,33–34]. Pidko *et al.* reported that clustered oxygenated zinc were more active than isolated Zn²⁺ in zeolite [35]. Recently, Zhu *et al.* prepared Silicalite-1 zeolite supported ZnO through a simple impregnation method [34]. ZnO species interact with silanol nests of Silicalite-1 zeolite. Propane conversion reached 49% and propene selectivity was around 90% at 550 °C under atmospheric pressure and a space velocity of 5000 ml·h⁻¹·(g cat)⁻¹. However, Zn-based catalysts still suffer from limited activity and relative low thermal stability.

The introduction of trace platinum could effectively improve catalytic activity and stability of non-noble oxide catalysts including ZnO. Gong *et al.* [36] introduced trace Pt (0.1% (mass)) into 15% (mass) ZnO supported on Al₂O₃. Pt could promote a stronger Lewis acid and accelerate H₂ desorption. Weckhuysen and co-workers designed 0.1% (mass) Pt as a promoter in K-Ga/Al₂O₃ catalyst for PDH reaction [37]. The coordinately unsaturated Ga³⁺ species were responsible for the C–H bond activation and Pt help suppress coke

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deposition to prolong reaction time. Recently, Choi and co-workers investigated PDH detailed reaction mechanism on γ -Al₂O₃ doped Ga, Pt, and Ce [38]. Lewis acid site Ga³⁺ was responsible for the heterolytic dissociation of the C–H bond of propane, while Pt⁰ facilitates the sluggish H recombination into H₂ via reverse spillover. Atomically dispersed Ce³⁺ sites on the surface suppressed the sintering of Pt species. However, Pt is expensive and exhibits high activity in PDH, which could affect the determination of active sites. Meanwhile, non-noble metal nickel, which also widely applied in hydrogen activation, could be a better choice.

Here, we systematically studied the positive role of Ni in Zn/MFI for PDH reaction. After high temperature reduction treatment, highly dispersed NiZn alloy was formed on Zn modified Silicalite-1 zeolite. *In-situ* propane adsorbed infrared spectrum (C₃H₈-FTIR) and temperature programmed desorption of hydrogen (H₂-TPD) evidenced that propane activated on Zn²⁺ site and Ni could promote H₂ desorption by reverse hydrogen spillover. Zn²⁺ was the definite active site evidenced by catalytic test on NiZn/SiO₂ with quite low activity. Besides that, the introduction of Ni increased Lewis acid strength owing to electron transfer from ZnO to NiZn alloy. The resulted 0.5NiZn/S-1 exhibited improved catalytic activity and stability on PDH reaction.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of Silicalite-1 (S-1)

All chemicals used in this study are available in the supplementary materials. The procedure for synthesis of each zeolite is as listed below. Silicalite-1 zeolite was synthesized with the mixing gel molar composition of 10 SiO₂: 350 H₂O: 4 TPAOH (25%(mass), J&K Scientific Ltd) under conventional hydrothermal conditions at 170 °C for 96 h [39]. Firstly, put a certain amount of distilled water and 6.5 g TPAOH solution into a round-bottom flask. After stirring for 10 min, 4.16 g TEOS (Kemio Chemical Reagent Co Ltd) was added dropwise into the mixture and continue stirring for 6 hours until the solution becomes clear. Then, the sol was transferred into a 100 ml teflon-lined stainless steel autoclave and heated for 4 days in a preheated oven operating at 170 °C. The product was collected by the centrifugation and washed with water and ethanol each for several times. Dry the products for 12 hours in the preheated oven at 100 °C and then calcinate at 550 °C for 8 h in the furnace.

2.1.2. Synthesis of xNiZn/S-1 ($x = 0, 0.5, 1$)

The preparation of Ni-Zn alloy catalysts supported on Silicalite-1 zeolite was carried out by a simple incipient-wetness impregnation method. 1.0 g calcined S-1 was first impregnated by a solution of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), Zinc nitrate hydrate (Zn(NO₃)₂·6H₂O) and a certain amount of distilled water. Dry the obtained solids in the oven for 12 h at 30 °C and 90 °C under atmospheric pressure successively, followed by calcination at 550 °C for 8 h in the furnace with a ramping rate of 5 °C·min⁻¹.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) measurements were performed using 40 mA and 40 kV Cu-K α radiation beam (0.154 nm) on a Philips X'Pert MPD diffractometer. The 2 θ range was 5° to 60° with the scan rate of 5(°)·min⁻¹ or 1(°)·min⁻¹.

N₂ adsorption-desorption isotherms were conducted on a Micromeritics ASAP 2420 volumetric adsorption analyzer at -196 °C. The zeolite was preheated at 300 °C for 12 h in vacuum before measurement.

X-ray photoelectron spectra (XPS) was used to collect the electronic states of this PtZn ensembles on a Thermo ESCALAB 250XI instrument. By adjusting the binding energy of C 1s peak to 284.6 eV, the binding energy (BE) results were achieved.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 2100DV) was employed to analyze the elemental compositions.

Fourier transform infrared (FTIR) spectroscopy with propane adsorption was performed on a Bruker FT-IR spectrophotometer. Before the measurement, 15 mg sample slice was kept for 2 h at 400 °C in vacuum. The prepared samples were purged with propane and record IR results at 5 min. Then flush the instrument with argon for 5 min and record the infrared results.

Bruker FT-IR spectrophotometer was employed to analyze the adsorption of pyridine on the zeolites. As mentioned above, 15 mg sample slice was kept for 2 h at 400 °C in vacuum and gradually cooled to 50 °C. The sample was purged with pyridine steam to saturation and then flushed at 150 °C and 350 °C for 30 min. A total of 64 additional scans were used to record the spectral range of 1700–1400 cm⁻¹.

Temperature-programmed desorption of hydrogen (H₂-TPD) measurements were implemented using an AutoChem II 2920 chemisorption instrument. First, 100 mg samples were preheated at 500 °C for 30 min in a stream of helium to eliminate impurities and cooled to 50 °C in a stream of 10%(vol) H₂/Ar. Then switch the gas to flowing Ar to flush the apparatus at 50 °C for 1 h. H₂-TPD curve was recorded in the flow Ar from 50 to 700 °C at a heating rate of 10 °C·min⁻¹.

Temperature-programmed desorption of ammonia (NH₃-TPD) measurements were implemented using an AutoChem II 2920 chemisorption instrumenta downstream gas sampling mass spectrometer (MS, PfeifferBalzer Omnistar). Typically, samples (100 mg) were preheated at 500 °C in a stream of helium for half an hour and cooled to 50 °C in a stream of 10%(vol) NH₃/He. Switched the gas to flowing He to flush the apparatus at 50 °C for 1 h. NH₃-TPD curve was recorded in the flow Ar from 50 to 700 °C at a heating rate of 10 °C·min⁻¹.

Transmission Electron Microscope (TEM) images were obtained using a JEM-2800 microscope, and scanning electron microscopy (SEM) images were taken on Apreo S LoVac field emission scanning electron microscopy.

TG/DTG was performed by thermal analysis system (Beijing Henven HCT-1). The spent catalysts were put into a quartz crucible and heated with a rate of 10 °C under a flow of high purity air atmosphere (50 ml·min⁻¹).

2.3. Catalyst evaluation

Catalytic tests were performed in a quartz fixed-bed reactor at atmosphere pressure. 10–100 mg of the calcined catalyst and 1.5 g silicon carbide with a particle size of 20 to 40 meshes were mixed fully and packed inside a quartz tube (6 mm ID). Before the reactivity test, the catalyst was heated to 550 °C with a rate of 5 °C·min⁻¹ in 20%(vol) H₂/N₂ (H₂ 10·min⁻¹ and N₂ 40 ml·min⁻¹ and retained at 550 °C for 1 h. And then the gas flow was switched to pure propane (10 ml·min⁻¹) to start the reaction. The online gas chromatograph (Shimadzu GC-2010) equipped with FID detector and the Varian Micro-GC 490 equipped with TCD detector was used to analyze the obtained gas products. The propane conversion and propene selectivity were calculated from Eqs. (1) and (2), respectively.

$$\text{Con.} = ([F_{\text{C}_3\text{H}_8}]_{\text{inlet}} - [F_{\text{C}_3\text{H}_8}]_{\text{outlet}}) / [F_{\text{C}_3\text{H}_8}]_{\text{inlet}} \times 100\% \quad (1)$$

$$\text{Sel.} = [F_{\text{C}_3\text{H}_6}]_{\text{outlet}} / ([F_{\text{C}_3\text{H}_8}]_{\text{inlet}} - [F_{\text{C}_3\text{H}_8}]_{\text{outlet}}) \times 100\% \quad (2)$$

where $[F_{C_3H_8}]$ and $[F_{C_3H_6}]$ mean mole flow rate of propane and propene.

A first-order deactivation model was used to evaluate the catalyst stability:

$$k_d = \{\ln[(1 - X_{\text{final}})/X_{\text{final}}] - \ln[(1 - X_{\text{initial}})/X_{\text{initial}}]\} / t \quad (3)$$

where X_{final} and X_{initial} represent the conversion measured at the initial and final period of a catalyst test, and t represents the reaction time (h), k_d is the deactivation rate constant (h^{-1}). High k_d value means rapid deactivation, that is, low stability.

3. Results and Discussion

3.1. Structural characterization

Fig. 1 showed XRD patterns of reduced zeolites. All catalysts revealed well-crystallized samples corresponding to the typical MFI-type structure, even after high temperature calcination and reduction treatment. Besides the strong diffraction peaks of MFI topology, the broad peak at $2\theta = 43.4^\circ$ was NiZn alloy (NiZn (1 0 1) plane, JCPDS no. 65-2901) in 0.5NiZn/S-1. It indicates that the formation of high dispersion NiZn alloy after H_2 reduction at 550°C [40]. Meanwhile, for 1NiZn/S-1, the peak at $2\theta = 44.6^\circ$ corresponds to Ni (1 1 1) plane (JCPDS no. 65-2865). With the increasing amount of Ni, no sufficient Zn^{2+} was reduced to form NiZn alloy, leading to the formation of unalloyed Ni nanoparticles. For NiZn/SiO₂, the wide peak at 21.3° corresponds to conventional SiO₂ support. The weak peak between 40° and 45° could be attributed to Ni species (Fig. S1, Supplementary Material).

In Fig. S2, catalysts morphology of all zeolites was shown in scanning electron microscope (SEM). All supported Silicalite-1 zeolite exhibited typical hexagonal structure with the size of about 200 nm. Fig. 2 showed metal distribution of as-prepared catalysts by transmission electron microscope. For Zn/S-1 (Fig. 2(a), (d)), no obvious ZnO nanoparticles was observed, demonstrating highly dispersed ZnO supported on Silicalite-1 zeolite. For 0.5NiZn/S-1 (Fig. 2(b)), metal particles mainly range from 1 to 11 nm with an average size of 5.5 nm. Meanwhile, NiZn supported on SiO₂ showed high dispersed particles with an average size of 3.2 nm (Fig. 2(c)). Both catalysts exhibited certain sintering-resistance ability. Fig. 2 (e), (f) showed the lattice spacing of 0.209 nm, which well matched the interplane distance of (1 0 1) plane of NiZn alloy, corresponding to XRD results. EDS mapping of 0.5NiZn/S-1 and 1NiZn/S-1 were shown in Figs. S3–S4. For 0.5NiZn/S-1, Ni and Zn are uniformly located at nearly identical positions, demonstrating the formation of ZnNi alloy.

As shown in Table 1, all catalysts showed similar Zn loading amount of 2.11%–2.36%(mass), as measured by inductively coupled plasma-atomic emission spectroscopy (ICP-OES). The Ni amounts of all samples were close to theoretical loading amount (0.5% (mass) and 1.0% (mass)). According to the N_2 adsorption-desorption results, all zeolite catalysts showed typical Langmuir Type-I adsorption [41], corresponding to microporous material (Fig. S5). They possessed high area of about $400 \text{ m}^2 \cdot \text{g}^{-1}$. With the increase of Ni loading, some decrease of $\sim 10 \text{ m}^2 \cdot \text{g}^{-1}$ could be observed, but these catalysts still showed sufficient surface area [42]. For NiZn/SiO₂, the surface area was $159 \text{ m}^2 \cdot \text{g}^{-1}$ and almost no micropores.

3.2. Characterization of active sites

The chemical state of Zn and Ni species supported on Silicalite-1 was evaluated by X-ray photoelectron spectrum (XPS) analysis. For Zn LMM spectra over 0.5NiZn/S-1 (Fig. 3(a)), the peak at about 985 eV could be assigned to that Zn species interact with lattice O atoms in zeolite framework, because the lattice O^{2-} ligand of the zeolite exhibits higher electronegativity than in bulk ZnO [32,43–45] (Fig. 3(b), (c)). In Fig. S6, almost all Zn species was bonded with lattice O in Zn/S-1. For Zn/S-1, the peak was at 985.9 eV, which was higher than 0.5NiZn/S-1 (985.5 eV). It indicated that NiZn alloy could increase the bonding strength between Zn^{2+} and lattice O. Six bands of Ni 2p were assigned to Ni^0 , Ni^{2+} and the satellite peak from NiO [46–47]. For 0.5NiZn/S-1, after reduction treatment, Ni was mainly zero valent in NiZn alloy and part of Ni bonding with framework O with strong interaction (Fig. 3 (d)). NiZn/SiO₂ with same NiZn loading showed similar nickel valence composition with 0.5NiZn/S-1. When Ni amount increased to 1.0%(mass), most Ni species were divalent Ni^{2+} , Zn species were not enough to be reduced to form alloy with Ni, corresponding to XRD results.

In Fig. 4(a), acid amount was measured by temperature-programmed desorption of ammonia (NH_3 -TPD-mass). For Zn/S-1, the main peak at 232°C was weak acid and the strong acid at about 370°C was with low ratio. Meanwhile, the desorption peak was at 242°C for 0.5NiZn/S-1, indicating a stronger acid strength with the introduction of Ni species. It may be caused by electron transfer from ZnO to NiZn alloy and help increase the stability of Zn^{2+} on zeolites. Based on the Py-FTIR results (Fig. 4(b)), nearly no Bronsted acid was detected in 0.5NiZn/S-1 and Zn/S-1. Side reactions, such as catalytic cracking of propane and propene, are easily occurred on Bronsted acid sites [22,48]. Only Lewis acid exist on NiZn catalysts favor high propene selectivity and low carbon

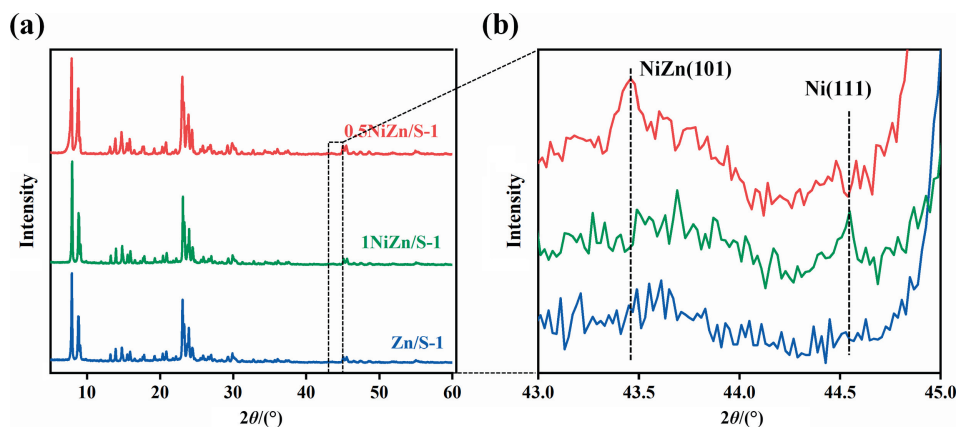


Fig. 1. (a) XRD patterns of as-prepared samples after reduction treatment and (b) partially enlarged image.

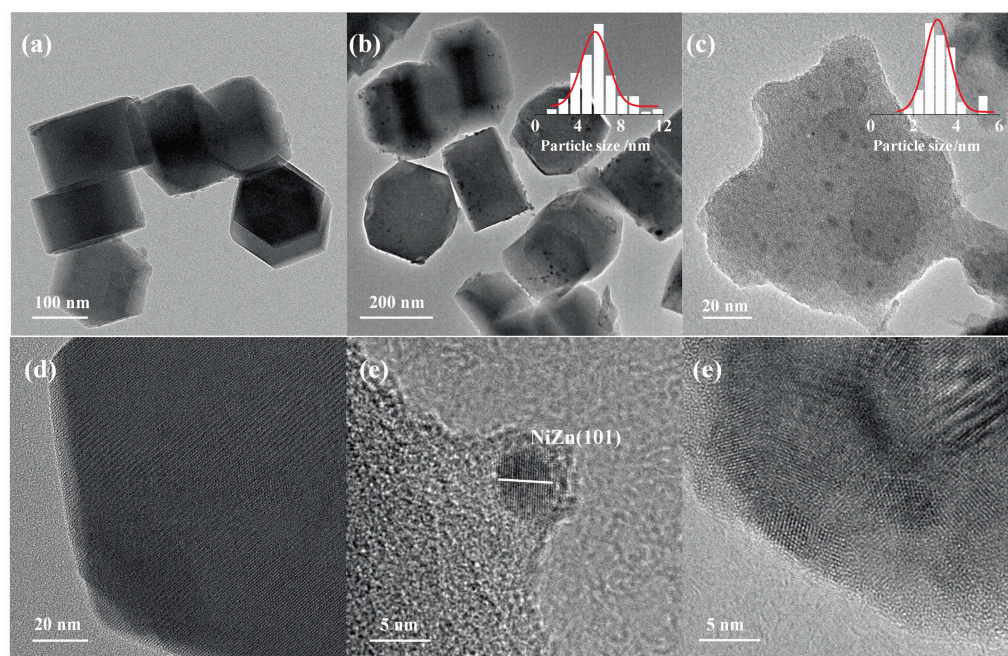


Fig. 2. HR-TEM images of (a, d) Zn/S-1, (b, e) 0.5NiZn/S-1 and (c, f) 0.5NiZn/SiO₂.

Table 1

Metal loading and pore properties of prepared samples

Sample	Ni loading ^① /%(mass)	Zn loading ^① /%(mass)	$S_{\text{BET}}^{\text{②}}/\text{m}^2\cdot\text{g}^{-1}$	$S_{\text{micro}}^{\text{③}}/\text{m}^2\cdot\text{g}^{-1}$	$S_{\text{external}}^{\text{③}}/\text{m}^2\cdot\text{g}^{-1}$	V_{total}
Zn/S-1	–	2.35	402	367	35	0.220
0.5NiZn/S-1	0.46	2.36	398	366	32	0.215
1NiZn/S-1	0.94	2.24	392	362	30	0.207
NiZn/SiO ₂	0.42	2.11	159	–	159	–

① Pt and Zn content are determined by ICP-OES.

② S_{BET} (total surface area) calculated by the BET equation using the linear part ($0.05 < P/P_0 < 0.30$) of the adsorption isotherm.

③ S_{micro} (micropore area) and S_{ext} (external surface area) calculated using the t -plot method.

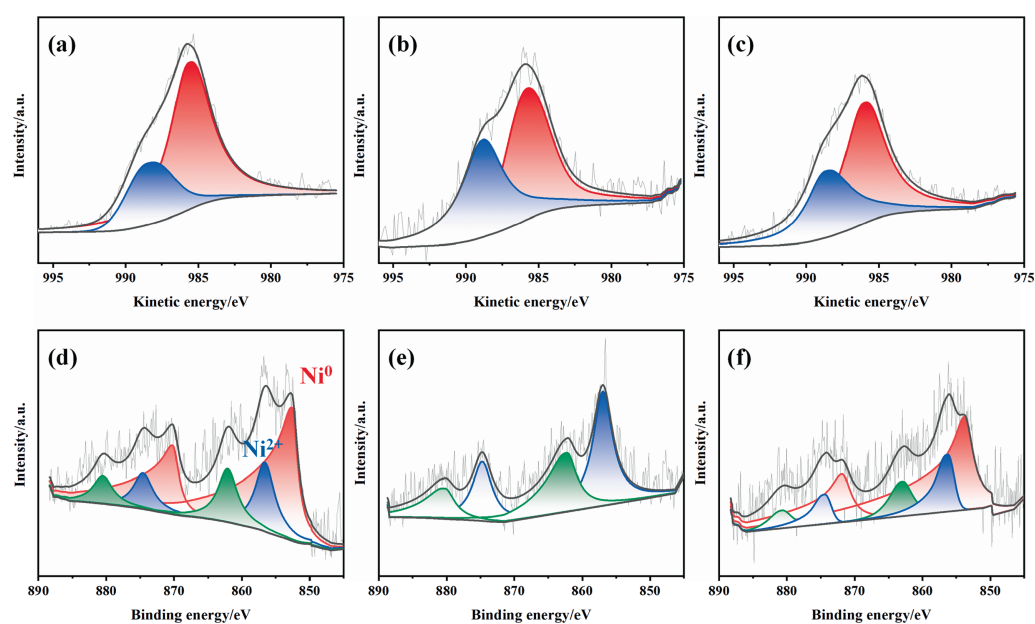


Fig. 3. Zn LMM Auger and Ni 2p XPS spectra of 0.5NiZn/S-1 (a, d), 1NiZn/S-1 (b, e) and NiZn/SiO₂ (c, f).

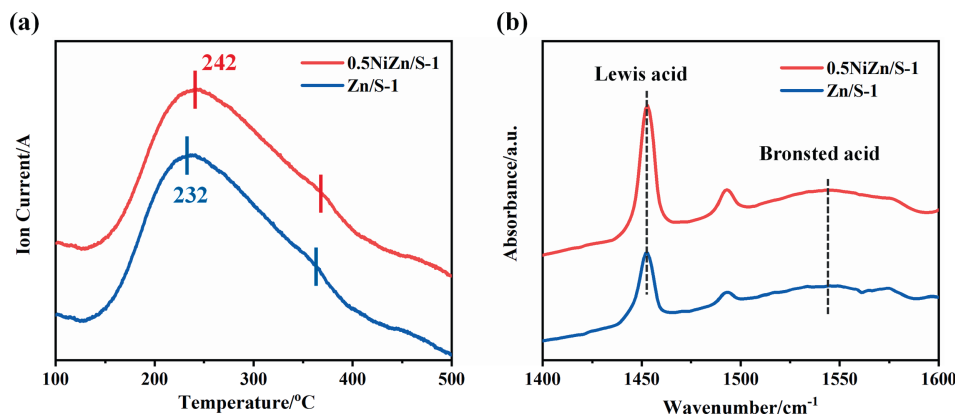


Fig. 4. (a) NH_3 -TPD-mass and (b) FTIR spectra of pyridine adsorption (Py-FTIR) on 0.5NiZn/S-1 and Zn/S-1.

deposition. The Lewis acid amount of 0.5NiZn/S-1 was $112.3 \mu\text{mol} \cdot \text{g}^{-1}$, above 1.8 times higher than that of Zn/S-1 ($61.0 \mu\text{mol} \cdot \text{g}^{-1}$).

3.3. Catalytic performance

PDH reaction was tested under atmospheric pressure at 550°C . In Fig. 5(a), the initial propane conversion of Zn/S-1 was 8.7%, and rapidly decreased below 3% in 10 h. After the introduction of Ni, the resulted 0.5NiZn/S-1 exhibited a propane conversion of 13.4% and maintain above 10% after 16 h test, with a high propene selectivity above 97%. NiZn/SiO₂ was prepared by impregnation method with same metal loading and exhibited a low catalytic ability with the propane conversion of 3.5%. Ni/S-1 also showed low activity and propene selectivity (Fig. S7). It demonstrated that Zn^{2+} species was active site and NiZn alloy played as promoter. However, with the increase of Ni, catalytic activity and stability were both decrease. For 1NiZn/S-1, the initial propane conversion was only 6.9% and rapid inactivation. Unalloyed Ni particles may cause side reactions such as cracking and deep dehydrogenation, and further lead to coke deposition. In summary, the introduction of appropriate amount of Ni could improve the catalytic ability and stability at the same time. In Fig. 5(b) and Fig. S8, 0.5NiZn/S-1 exhibited a high specific activity of $0.18 \text{ mol C}_3\text{H}_6 \cdot (\text{g Zn})^{-1} \cdot \text{h}^{-1}$, which was 1.5 times higher than that of Zn/S-1. Besides that, a first-order deactivation model was used to estimate the catalyst stability [49–50] (Eq. (3)). The deactivation constant of 0.5NiZn/S-1 was only 0.019 h^{-1} , which was only 1/10 of that over Zn/S-1. NiZn alloy could increase the bonding strength between Zn^{2+} and lattice O, which was evidenced by Zn LMM Auger XPS and NH_3 -TPD results.

3.4. Hydrogen spillover mechanism

Reverse hydrogen spillover mechanism was evidenced by propane-FTIR [38] and H_2 -TPD. In Fig. 6(a), after propane flow for 5 min at 400°C , Zn/S-1 exhibited the peak at about 3750 cm^{-1} . It could be ascribed to the $-\text{OH}$ group generated by C–H bond scission on ZnO sites. After Argon flow treatment for 5 min, certain amount hydroxyl group remain on catalyst. Meanwhile, for 0.5NiZn/S-1, more hydroxyl group generated by C–H bond activation on ZnO after propane flow for 5 min, indicating a higher activity. It also proved that ZnO was the definite active site. After Argon flow for 5 min, a large proportion of hydroxyl disappeared. It demonstrates that NiZn alloy promoted H_2 formation and desorption by reverse hydrogen spillover. In Fig. 6(c), the H_2 desorption peak of 0.5NiZn/S-1 was at 123°C , which was lower than of Zn/S-1 (129°C). It indicated that the introduction of Ni increased the capacity of H_2 desorption, caused by reverse hydrogen spillover [51]. In summary, reaction mechanism was shown in Fig. 6(d), C–H in propane was activated on Zn^{2+} as Lewis acid sites, and H could transfer to NiZn alloy. NiZn could facilitated the sluggish H recombination into H_2 via reverse spillover. And NiZn alloy with quite low activation activity could not cause side reactions. It acted as promoter to enhance the dehydrogenation activity of Zn/S-1.

3.5. Spent catalysts

Thermogravimetric analysis (TGA) characterization of spent catalysts were carried out to determine the amount of carbon deposition quantitatively. As the mass loss profiles in Fig. 7(a),

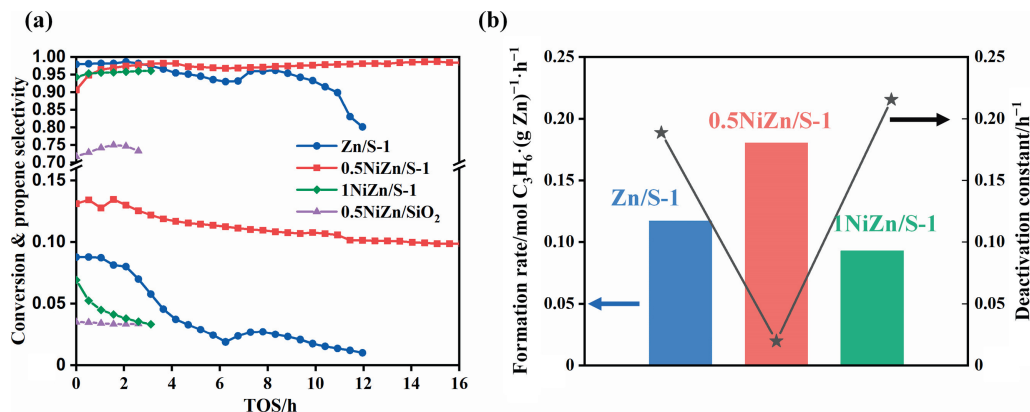


Fig. 5. (a) Propane dehydrogenation and propene selectivity with time on stream over prepared samples. Reaction condition: $T = 550^\circ\text{C}$, $\text{WHSV} = 1.2 \text{ h}^{-1}$, $P = 0.1 \text{ MPa}$, C_3H_8 : $\text{N}_2 = 1:9$. (b) Formation rate and deactivation constant of NiZn catalyst with different Ni loading.

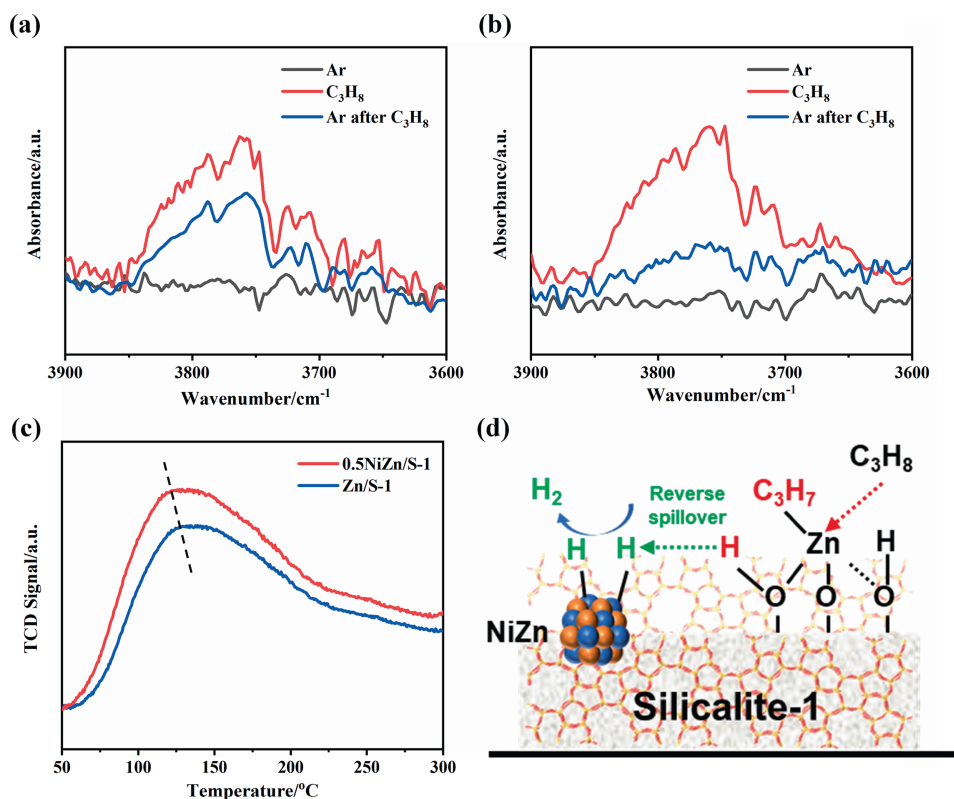


Fig. 6. In situ FTIR spectra of Zn/S-1 (a) and 0.5NiZn/S-1 (b) under the sequential flows of Ar (grey), C₃H₈ (red), and Ar (blue) at 400 °C. Each gas flow was held for 5 min. (c) H₂-TPD profile of Zn/S-1 and 0.5NiZn/S-1, (d) Proposed reaction mechanism for PDH on 0.5NiZn/S-1.

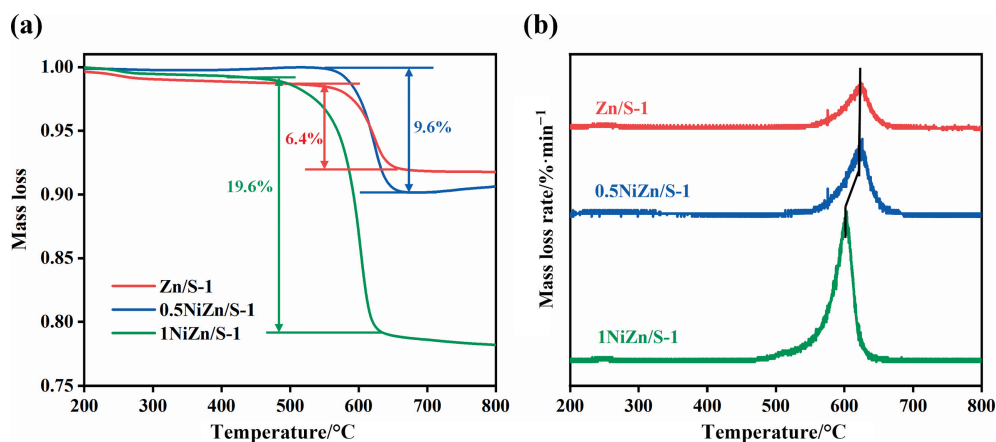


Fig. 7. (a) TG and (b) DTG profiles of spent catalysts.

the peaks from 500 to 650 °C could be derived from the combustion of filamentous and graphitic carbon. Except for the loss of adsorbed H₂O, the weight loss of 0.5NiZn/S-1 was 9.6%, slightly higher than that of Zn/S-1 (6.4%). It may be ascribed to NiZn catalyst exhibited higher activity. But for 1NiZn/S-1, the mass loss was high as 19.6%. Side reactions such as deep dehydrogenation occurred on unalloyed Ni sites caused coke deposition formation. In Fig. 7(b), the peak of Zn/S-1 and 0.5NiZn/S-1 was similar at about 620 °C, which represented similar carbon deposition composition. For 1NiZn/S-1, the peak was at about 600 °C, lower than that of Zn/S-1 and 0.5NiZn/S-1. It demonstrated more defective carbonaceous formed on unalloyed Ni by side reactions.

4. Conclusions

The role of Ni in ZnO supported on Silicalite-1 for propane dehydrogenation was detailed studied in this work. Zn²⁺ was the identified active sites due to the quite low dehydrogenation activity over NiZn/SiO₂. For NiZn/S-1, after high temperature reduction treatment, NiZn alloy was formed and facilitated the sluggish H recombination into H₂. Reverse hydrogen spillover effect was evidenced by propane-FTIR and H₂-TPD. Meanwhile, the introduction of Ni increased Lewis acid strength caused by electron transfer from ZnO to NiZn alloy. Thus, NiZn/S-1 exhibited a high specific activity of 0.18 mol C₃H₆/(g Zn)⁻¹·h⁻¹ at 550 °C, which was 1.5

times higher than that of Zn/S-1 without nickel. The deactivation constant of 0.5NiZn/S-1 was only 0.019 h^{-1} , which was only 1/10 of that over Zn/S-1.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Financial supports by the National Natural Science Foundation of China (22025802) and the Haihe Laboratory of Sustainable Chemical Transformations (CYZC202101) is gratefully acknowledged.

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