



Accepted Article

Title: Isobutane Dehydrogenation Assisted by CO₂ over Silicalite-1-Supported ZnO Catalysts: Influence of Support Crystallite Size

Authors: Yajun Luo, Chunling Wei, Changxi Miao,* Yinghong Yue, Weiming Hua,* and Zi Gao

This manuscript has been accepted and appears as an Accepted Article online.

This work may now be cited as: *Chin. J. Chem.* **2020**, *38*, 10.1002/cjoc.202000042.

The final Version of Record (VoR) of it with formal page numbers will soon be published online in Early View: http://dx.doi.org/10.1002/cjoc.202000042.

WILEY-VCH SIOC CCS

ISSN 1001-604X • CN 31-1547/O6 mc.manuscriptcentral.com/cjoc www.cjc.wiley-vch.de

Isobutane Dehydrogenation Assisted by CO₂ over Silicalite-1-Supported ZnO Catalysts: Influence of Support Crystallite Size

Yajun Luo,^a Chunling Wei,^b Changxi Miao,^{*,b} Yinghong Yue,^a Weiming Hua,^{*,a} and Zi Gao^a

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200438, China Shanghai Research Institute of Petrochemical Technology SINOPEC, Shanghai 201208, China

ite this paper: Chin. J. Chem. 2020, 38, XXX-XXX. DOI: 10.1002/cjoc.202000XXX

ummary of main observation and conclusion The ZnO catalysts supported on Silicalite-1 zeolites with different crystallite sizes (0.08, 0.35, 1 and 1.7 µm, respectively) and 5% Zn were synthesized via an incipient wetness method. The catalysts were characterized by XRD, N₂ adsorption, SEM, TEM-EDX, "RIFT spectra and NH₃-TPD, and their catalytic performance in isobutane dehydrogenation assisted by CO₂ was investigated. The catalytic activity is strongly uependent on the crystallite size of Silicalite-1 support. The ZnO/S-1-0.35 catalyst with ca. 0.35 µm crystallite size displays the highest activity, affording an initial isobutane conversion of 51.0% and 74.5% isobutene selectivity. This can be attributed to a higher amount of acid sites present on this catalyst as well s the largest amount of nest silanols possessed by the S-1-0.35 support.

Background and Originality Content

With the depletion of fossil resources, the development of processes that specifically facilitate the conversion of hydrocarbons can be established as an improvement in the use of these resources. Two major ways to produce isobutene, i.e. naphtha steam cracking and fluidized catalytic cracking, strongly reply on petroleum reource. With the growing demand for isobutene, which is regarded as an important feedstock for the manufacture of value-added chemicals,^[1-3] a lot of attention has been paid to the process of catalytic dehydrogenation of isobutane.

In recent years, the use of CO₂ as a soft oxidant for the selective dehydrogenation of light alkanes into their corresponding alkenes has received much attention.^[4-12] Compared with employing O₂ as an oxidant, CO₂ has obvious advantages such as improving the selectivity toward targeted olefins and decreasing CO₂ emissions.^[13] everal types of catalysts such as Cr₂O₃,^[11,14] V₂O₅ ^[15–17] and V–Mg–O ^[18,19] have been explored for isobutane dehydrogenation with carbon dioxide. The catalytic activity is strongly dependent on the catalyst support. γ -Al₂O₃,^[15,19] SiO₂,^[15,19] active carbon AC),^[14,15,19] mesoporous SiO₂ molecular sieve (e.g. SBA-15) ^[11,17] are generally chosen as the supports to prepared the supported catalysts. However, the application of this technology is still chal-inged by the low activity and fast catalyst deactivation.

Silicalite-1 is an aluminum-free crystalline zeolite with MFI toplogical framework. The presence of Si atom defective sites in their attice can impose the formation of acid centers (silanol groups), which have been reported as active catalysts for the Beckmann rerrangement ^[20–22] as well as the etherification of 5-hydroxymethyl-2-furfural.^[23] More recently, we have found that the ZnO catalyst supported on Silicalite-1 zeolite exhibits a superior catalytic nerformance for CO₂ assisted dehydrogenation of isobutane, which is far more active than SBA-15-supported one with the same Zn content.^[24] Inspired by this finding, in the present work we first report the influence of Silicalite-1 crystallite size on the catalytic performance of ZnO/Silicalite-1 catalysts for isobutane dehydrogenation assisted by CO_2 . The reasons for the different activities exhibited by these catalysts were discussed in terms of both acidity and silanol groups.

Results and Discussion

Catalyst characterization

The XRD patterns of the ZnO catalysts supported on Silicalite-1 zeolites with different crystallite sizes are depicted in Figure 1. All catalysts display MFI structure with the characteristic diffraction peaks at $2\vartheta = 8.0^{\circ}$, 8.9° , 23.1° , 23.3° and 24.0° .^[12,25] No reflections corresponding to crystalline ZnO can be observed, indicating that zinc oxide is well dispersed on the four Silicalite-1 supports. The SEM images of the Silicalite-1 supports (Figure S1) show that S-1-0.08, S-1-0.35 and S-1-1 samples display approximately sphere-like morphology with crystallite sizes of around 0.08, 0.35 and 1 µm, respectively, whereas the S-1-1.7 sample shows coffin-like morphology with ca. 1.7 µm in width. The homogeneous distribution of the Zn element on the four Silicalite-1 supports is demonstrated by HAADF STEM mapping (Figure S2), which is in accordance with the XRD result.

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/cjoc.202000042

This article is protected by copyright. All rights reserved.

(0.192–0.371 mmol/g). This implies that the acid sites present on the catalysts are mainly originated from the dispersed zinc oxide

species. Metal species can interact with the alumina or silica support by consuming the exposed support-OH groups, thus modifying

the acidic properties of the support.^[26,27]



Figure 1 XRD patterns of the catalysts. (a) ZnO/S-1-0.08, (b) nO/S-1-0.35, (c) ZnO/S-1-1, (d) ZnO/S-1-1.7.

| Sample | S _{BET} /(m ² /g) | V _{micro} ª/(cm³/g) | V _{meso} /(cm ³ /g) | V _{total} ^b /(cm ³ /g) | Acid amount/(mmol/g) | A ₃₄₉₀ /A ₃₇₃₉ ^c |
|--------------|---------------------------------------|------------------------------|---|---|----------------------|---|
| S-1-0.08 | 385 | 0.18 | 0.14 | 0.32 | 0.0445 | 8.4 |
| ZnO/S-1-0.08 | 354 | 0.17 | 0.11 | 0.28 | 0.371 | 1.0 |
| S-1-0.35 | 379 | 0.18 | 0.12 | 0.30 | 0.0387 | 16.0 |
| ZnO/S-1-0.35 | 340 | 0.16 | 0.09 | 0.25 | 0.314 | 3.9 |
| S-1-1 | 369 | 0.17 | 0.10 | 0.27 | 0.0182 | 8.1 |
| ZnO/S-1-1 | 334 | 0.16 | 0.06 | 0.22 | 0.231 | 0.3 |
| S-1-1.7 | 356 | 0.16 | 0.08 | 0.24 | 0.0108 | 5.6 |
| ZnO/S-1-1.7 | 321 | 0.16 | 0.06 | 0.22 | 0.192 | 0.2 |

^a Calculated by the *t*-plot method. ^b Total pore volume adsorbed at $P/P_0 = 0.99$. ^c A₃₄₉₀ and A₃₇₃₉ are the peak area of nest silanols (3490 cm⁻¹) and isolated silanols (3739 cm⁻¹), respectively.

The textural properties of the Silicalite-1 supports and Silicalite-1-supported zinc oxide catalysts are presented in Table 1. he BET surface areas and mesopore volumes (contribution from intercrystalline voids) of the Silicalite-1 supports increase slightly when he decrease of crystallite size, which diminish somewhat after the impregnation of zinc oxide (5% Zn). The micropore volumes the Silicalite-1 supports are almost unchanged upon the introuction of ZnO.

The amount of acid sites on the ZnO/S-1 catalysts with different crystallite sizes was measured by the NH₃-TPD method, and the result is given in Figure 2 and Table 1. Two desorption peaks on the TPD profiles of all supported zinc oxide catalysts can be found. The hw temperature peaks are located at ca. 166 °C and the high temperature shoulders are centered at around 324 °C, which correstond to the acid sites of weak and moderate strength, respectively. The total acid amount of the catalysts increases in the order of ZnO/S-1-1.7 < ZnO/S-1-1 < ZnO/S-1-0.35 < ZnO/S-1-0.08 (Table 1). It is clear in Table 1 that the Silicalite-1 supports possess a small number of acid sites (0.0108–0.0445 mmol/g), and their acidities are improved substantially after supporting zinc oxide



Figure 2 NH₃-TPD profiles of the catalysts. (a) ZnO/S-1-0.08, (b)

rticle

Report

© 2020 SIOC, CAS, Shanghai, & WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Chin. J. Chem. 2020, 38, XXX-XXX

ZnO/S-1-0.35, (c) ZnO/S-1-1, (d) ZnO/S-1-1.7.

According to the literature,^[27,28] the weight loss below 100 °C and between 100 and 200 °C was attributed to the elimination of physically and chemically adsorbed water, respectively, while the weight loss above 200 °C was assigned to the dehydroxylation by condensation of silanols. Based on the TG result, the amount of silanols on the four Silicalite-1 supports is 1.05, 1.21, 1.54 and 1.61 mmol/g for S-1-1.7, S-1-1, S-1-0.35 and S-1-0.08, respectively, which increases with decreasing the crystallite size. Higher amount of silanols on the Silicalite-1 support would favor the dispersion of upported metal oxide species,^[27] thus leading to a higher amount of acid sites on the Silicalite-1-supported ZnO catalyst, as eviclenced in Figure 3.



igure 3 Relationship between the acidity of the Silicalite-1-suprorted ZnO catalysts and the amount of silanols on the Silicalite-1 supports (■) as well as between the initial activity and acidity of the catalysts (●).

DRIFT spectra were investigated to get a deep understanding of hydroxyl groups on the Silicalite-1 supports with different crysallite sizes, and the result is shown in Figure 4A. Three types of –OH groups can be found. The intense and sharp peak at 3739 cm⁻¹ assigned to isolated silanol groups located on the external surface, and the small peak at 3686 cm⁻¹ is ascribed to vicinal silanol groups located inside the micropores.^[20,29,30–32] The strong broad peak at around 3490 cm⁻¹ is generally attributed to nest silanol roups that comprise a number of silanol groups interacting through extended hydrogen bonding.^[20,32] Such nest silanol groups generally appear at crystal steps or extended defects.^[31,33] It is lear in Figure 4A that the intensity of the peak at ca. 3490 cm⁻¹



© 2020 SIOC, CAS, Shanghai, & WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

www.cjc.wiley-vch.de



Figure 4 DRIFT spectra of the Silicalite-1 supports (A) and Silicalite-1-supported ZnO catalysts (B). (a) S-1-0.08, (b) S-1-0.35, (c) S-1-1, (d) S-1-1.7, (e) ZnO/S-1-0.08, (f) ZnO/S-1-0.35, (g) ZnO/S-1-1, (f) ZnO/S-1-1.7.



Figure 5 Conversion of isobutane (A) and selectivity to isobutene (B) as a function of reaction time for the Silicalite-1-supported ZnO catalysts. (■) ZnO/S-1-0.08, (●) ZnO/S-1-0.35, (▲) ZnO/S-1-1, (▼) ZnO/S-1-1.7.

Acreases in the order of S-1-0.35 > S-1-0.08 \approx S-1-1 > S-1-1.7, suggesting that S-1-0.35 possesses the largest amount of nest silanols. The TG and IR results reveal that the total amount of silanols as ell as silanol distribution on these Silicalite-1 supports are different from each other, albeit they have the same topology and simily r texture properties. As seen from Figure 4B, after supporting ZnO on Silicalite-1 (5% Zn), there is an obvious decrease in the intensity of three bands, especially the band at 3490 cm⁻¹, which is due to the interaction of Zn species with the support–OH groups.^[29,34] This is indicative of a decrease in the number of silanol groups via consuming the exposed hydroxyl groups. As presented in Table 1, the peak area ratio of nest silanol groups (3490 cm⁻¹) to isolated silanol ones (3739 cm⁻¹) is 8.4, 16.0, 8.1 and 5.6 for S-1-0.08, S-1-0.35, S-1-1 and S-1-1.7, respectively, which declines to 1.0, 3.9, 0.3 and 0.2, respectively. The above findings imply that Zn species primarily interact with nest silanol groups. Note that after supporting ZnO, the peak intensity of the left nest silanols on the Silicalite-1 supports diminishes in the order of ZnO/S-1-0.35 > ZnO/S-1-0.08 > ZnO/S-1-1 \approx ZnO/S-1-1.7 (Figure 4B), indicating that ZnO/S-1-0.35 has the highest amount of the left nest silanols.

Catalytic performance

© 2020 SIOC, CAS, Shanghai, & WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

| rable 2 Reaction data of the Sincance-1-supported zno catalysis" | | | | | | | | | | | |
|--|----------------------------------|-----------------|---------------------------------|----------|----------|----------|----------|------------------|---------------------------------|------------|--|
| Catalyst | Conversion/% | | Selectivity/% | | | | | | i-C ₄ H ₈ | | |
| | i-C ₄ H ₁₀ | CO ₂ | i-C ₄ H ₈ | CH_4 | C_2H_4 | C_2H_6 | C_3H_6 | C₃H ₈ | $C_4H_8^b$ | yield/% | |
| ZnO/S-1-0.08 | 46.7(44.3) | 8.4(5.5) | 75.6(81.7) | 2.3(1.6) | 0.3(0.1) | 0.1(0.1) | 5.7(4.3) | 0.7(0.3) | 15.3(11.9) | 35.3(36.2) | |
| ZnO/S-1-0.35 | 51.0(49.0) | 10.1(7.2) | 74.5(79.4) | 2.5(1.8) | 0.4(0.2) | 0.1(0.1) | 6.2(4.8) | 0.8(0.5) | 15.5(13.2) | 38.0(38.9) | |
| ZnO/S-1-1 | 43.5(41.4) | 7.6(4.6) | 77.7(82.6) | 2.1(1.6) | 0.3(0.1) | 0(0) | 5.1(4.1) | 0.6(0.4) | 14.2(11.2) | 33.8(34.2) | |
| ZnO/S-1-1.7 | 37.2(36.4) | 5.1(2.7) | 78.5(83.0) | 1.9(1.4) | 0.3(0.1) | 0(0) | 4.9(4.0) | 0.6(0.3) | 13.8(11.2) | 29.2(30.2) | |

 Table 2
 Reaction data of the Silicalite-1-supported ZnO catalysts^a

^a The values outside and inside the bracket are the data obtained at 10 min and 360 min, respectively.

^b 1-Butene, cis-2-butene and trans-2-butene.

The dehyd LO₂ over the s at 570 °C. The . ydrocarbon products com ane and but strongly depe the crystallite conversion of dently from 3 ize of Silicaliti initial isobutar alyst with high ure 5B). The Zi crystallite size tane conversi hown in Tab i obutene yiel action conditiports is below pecies on the nydrogenation According ethane dehyd by Pidko and w c on over the Zi following step limination, the this reaction reaction of limination, the this reaction reaction of the sent on the Zir persed zinc oxide

The dehydrogenation of isobutane to isobutene assisted by CO2 over the Silicalite-1-supported ZnO catalysts was investigated at 570 °C. The result is shown in Figure 5 and Table 2. The major ydrocarbon product is isobutene, and the minor hydrocarbon products comprise methane, ethane, ethylene, propane, propylene and butenes (excluding isobutene). The catalytic activity strongly depends on the crystallite size of Silicalite-1 support. As the crystallite size decreases from 1.7 μm to 0.35 $\mu m,$ the initial onversion of isobutane on the ZnO/S-1 catalysts increases evidently from 37.2% to 51.0%. A further decrease in the crystallite ize of Silicalite-1 support to 0.08 µm results in a decrease in the initial isobutane conversion to 46.7%. In general, the ZnO/S-1 catalyst with higher activity displays lower isobutene selectivity (Figtre 5B). The ZnO catalyst supported on Silicalite-1 with ca. 0.35 μm crystallite size exhibits the highest activity, giving an initial isobutane conversion of 51.0% and 74.5% isobutene selectivity. As hown in Table 2, the ZnO/S-1-0.35 catalyst displays the highest obutene yield. It should be pointed out that under the same reaction conditions the isobutane conversion on the Silicalite-1 supports is below 3%, which indicates that the dispersed zinc oxide pecies on the Silicalite-1 supports are the active sites for the denydrogenation reaction.

According to the DFT calculations, the reaction pathway of ethane dehydrogenation over the Zn/ZSM-5 catalyst was proposed by Pidko and van Santen.^[35] We think that isobutane dehydrogenaon over the ZnO/Silicalite-1 catalyst could follow the same mechnism (Scheme S1).^[24] Isobutane is dissociatively adsorbed on the zinc oxide sites (i.e. acidic sites) in the initial step (Eq. (1)). In the following step, the resulting product decomposes via one-step limination, thus generating isobutene and H₂ (Eq. (2)). Based on this reaction mechanism, one would expect that the ZnO/S-1 catalyst having a higher amount of dispersed zinc oxide (i.e. more acid tes) exhibits higher catalytic activity. Note that the acid sites present on the ZnO/S-1 catalysts are mainly contributed from the dispersed zinc oxide species, as revealed by the NH₃-TPD result. This peculation is further corroborated by a good correlation between the initial activity of the ZnO/S-1 catalysts (ZnO/S-1-1.7, ZnO/S-1-1 nd ZnO/S-1-0.35) and acid amount of these catalysts (Figure 3). In our recent work we have also demonstrated the excellent correlation between the catalytic activity for CO₂-assisted isobutane dehydrogenation over the ZnO/S-1-0.35 catalysts with different Zn contents and acid amount of these catalysts.^[24] Nevertheless, the

ZnO/S-1-0.08 catalyst displays lower activity than ZnO/S-1-0.35, albeit the former catalyst has more acid sites than the latter one. This can be interpreted as follows. S-1-0.35 and ZnO/S-1-0.35 have more nest silanols than S-1-0.08 and ZnO/S-1-0.08, respectively (Figure 4). The acid strength of nest silanols is stronger than isolated ones.^[20,22] The activation energy of one-step elimination reaction (Eq. (2)) is strongly dependent on the relative position of [Zn-i-C₄H₉]⁺ and framework attached H⁺ ions. Therefore, the residual acidic -OH groups on the catalyst, especially the residual nest silanols owing to their stronger acid strength, which are close to the [Zn-i-C₄H₉]⁺ species can promote the regeneration of the active sites, thereby leading to an increase in the catalytic activity.^[24,35,36] It is thus concluded that the highest activity observed for the ZnO/S-1-0.35 catalyst can be attributed to a higher amount of acid sites present on this catalyst as well as the largest amount of nest silanols possessed by the S-1-0.35 support.

The catalytic performance of our catalysts (ZnO/S-1) in this work is compared with the performance of other catalysts reported in the literature. Table S1 lists the conversion, selectivity and space-time yield of isobutene, together with the reaction conditions. In fact, it is not appropriate to compare the catalytic activity because of the different reaction conditions. As far as the space-time yield of isobutene is concerned, our catalysts are obviously more active than the supported Cr-based, V-based and V-Mg-O catalysts. Furthermore, the ZnO/S-1 catalysts display higher stability.

Conclusions

The Silicalite-1-supported ZnO catalysts with 5% Zn were prepared by an incipient wetness method. The XRD and HAADF STEM mapping results reveal the homogeneous distribution of the Zn element on the Silicalite-1 supports with different crystallite sizes (0.08, 0.35, 1 and 1.7 μ m, respectively). The amount of silanols on the four Silicalite-1 supports determined by TG increases with decreasing the crystallite size, thus favoring the dispersion of supported zinc oxide species. As a result, a higher amount of acid sites are achieved on the Silicalite-1-supported ZnO catalyst. The ZnO/S-1-0.35 catalyst with ca. 0.35 μ m crystallite size exhibits the highest activity for CO₂-assisted isobutane dehydrogenation, giving an initial isobutane conversion of 51.0% and 74.5% isobutene selectivity. This can be accounted for by both a higher amount of acid sites

© 2020 SIOC, CAS, Shanghai, & WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

www.cjc.wiley-vch.de

Report

present on this catalyst and the largest amount of nest silanols possessed by the S-1-0.35 support.

Experimental

Preparation of catalyst

Submicron and micrometer Silicalite-1 zeolites were synthesized according to the literature.^[37] Typically, tetrapropylammonium hydroxide (TPAOH, 25 wt% aqueous solution), tetraethyl orthosilicate (TEOS) and distilled deionized water were mixed with Jirring at room temperature to form a clear gel with a molar composition of mTPAOH : 25SiO₂ : 480H₂O (where m = 3, 6 and 9, repectively). The gel was stirred for additional 4 h to ensure the complete hydrolysis of TEOS. Then it was transferred to an autoc ave and crystallized at 170 °C for 72 h. The as-synthesized precip-.ate was washed with deionized water, dried at 100 °C overnight, and calcined in air at 550 °C for 4 h. The resultant Silicalite-1 zeo- \dots es are labelled as S-1-x (where x = 1.7, 1 and 0.35 represent the crystallite size of ca. 1.7, 1 and 0.35 μ m corresponding to m = 3, 6Ind 9, respectively). To prepare nanosize Silicalite-1 zeolite, TPAOH, TEOS and distilled deionized water were mixed under stirring at room temperature to get a clear solution, followed by being stirred a, 80 °C for 24 h to form a gel with a molar composition of 1TPAOH : $4SiO_2$: $32H_2O$. Then the gel was transferred to an autoclave and ystallized at 170 °C for 24 h, followed by the same treatment as the above Silicalite-1 zeolites. The obtained Silicalite-1 is labelled as S-1-0.08, where 0.08 represents the crystallite size of ca. 0.08 μn

The supported ZnO catalysts were prepared by impregnating an aqueous solution of $Zn(NO_3)_2 \bullet 6H_2O$ on Silicalite-1 zeolites with fferent crystallite sizes via an incipient wetness method. The imp egnated samples were dried at 100 °C overnight and calcined at o00 °C for 6 h in air to obtain the ZnO/S-1-x catalysts. The weight content of Zn in all catalysts was 5%.

_atalyst characterization

X-ray diffraction (XRD) patterns were recorded on a MSAL XD2 X-ray diffractometer at 40 kV and 30 mA. The BET surface areas and pre volumes were measured by N₂ adsorption at -196 °C on a Micromeritics Tristar 3000 instrument. Scanning electron microscopy was collected with a FEI Nova NanoSem 450 microscope for nanosize Silicalite-1 and with a Phenom Prox microscope for subn icron and micrometer Silicalite-1. The HAADF-STEM images and plemental mapping were recorded on an FEI Tecnai G² F20 S-TWIN with an EDX instrument. Thermogravimetric (TG) analysis was perf rmed in a N₂ flow from room to 850 °C at a ramp rate of 5 °C /min on a Perkin–Elmer 7 Series Thermal Analyzer apparatus to determine the amount of silanols of the four Silicalite-1 supports.^[38]

The surface acidity was measured by NH₃ temperature-programmed desorption (NH₃-TPD) on a Micromeritics AutoChem II instrument. 0.1 g of sample (40–60 mesh) was pretreat at 550 °C r 1 h in a N₂ flow, and then cooled to 80 °C in flowing N₂. At this temperature, the flow was switched to a 10 vol.% NH₃/He mixture flowing at 30 mL/min and kept for 2 h, and then swept by He (30 mL/min) for 2 h. Finally, the sample was heated in He (30 mL/min) to 600 °C at a ramp rate of 10 °C/min. Diffuse reflectance infrared

Fourier transform (DRIFT) spectra were obtained on a Nicolet 6700 spectrometer equipped with an MCT detector cooled by liquid N₂. The DRIFT cell was fitted with CaF₂ windows and a heating cartridge. The samples were pretreated in a He flow (30 mL/min) at 450 °C for 1 h, and cooled to 300 °C under flowing He. DRIFT spectra were collected at 300 °C under flowing He with a resolution of 4 cm⁻¹ and accumulation of 128 scans.

Activity measurement

Catalytic tests for isobutane dehydrogenation to isobutene assisted by CO₂ were performed at 570 °C in a fixed-bed flow microreactor at atmospheric pressure.^[39] The catalyst load was 0.1 g (40–60 mesh), and it was pretreated at 570 °C for 1 h in a N₂ flow prior to the reaction. The gas reactant contained 50 vol.% CO₂ and 50 vol.% isobutane. The flow rate of isobutane was 2.9 mL/min, corresponding to the weight hourly space velocity (WHSV) of 4.1 h⁻¹. The hydrocarbon products were analyzed using an on-line gas chromatograph (GC) equipped with a FID and a HP-AL/S capillary column (50 m × 0.53 mm × 15 µm). CO and CO₂ were analyzed on-line by another GC equipped with a TCD and a 2-m packed column of carbon molecular sieve 601.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2020xxxxx.

Acknowledgement

This work was supported by the National Key R&D Program of China (2017YFB0602200), the National Natural Science Foundation of China (91645201), the Science and Technology Commission of Shanghai Municipality (19DZ2270100) and the Shanghai Research Institute of Petrochemical Technology SINOPEC (19ZC06070005).

References

- Iannazzo, V.; Neri, G.; Galvagno, S.; Serio, M. Di; Tesser, R.; Santacesaria, E. Oxidative dehydrogenation of isobutane over V₂O₅-based catalysts prepared by grafting vanadyl alkoxides on TiO₂-SiO₂ supports. *Appl. Catal. A* 2003, 246, 49–68.
- [2] Pozan, G. S.; Tavman, A.; Boz, I. Dehydroisomerization of n-butane over Cr/SiO₂. Chem. Eng. J. 2008, 143, 180-185.
- [3] Wang, G. W.; Li, C. Y.; Shan, H. H. Highly efficient metal sulfide catalysts for selective dehydrogenation of isobutane to isobutene. ACS Catal. 2014, 4, 1139–1143.
- [4] Ding, J. F.; Qin, Z. F.; Li, X. K.; Wang, G. F.; Wang, J. G. Catalytic dehydrogenation of isobutane in the presence of carbon dioxide over nickel supported on active carbon. J. Mol. Catal. A 2010, 315, 221– 225.
- [5] Chen, M.; Wu, J. L.; Liu, Y. M.; Cao, Y.; Guo, L.; He, H. Y.; Fan, K. N. Study in support effect of In₂O₃/MO_x (M = Al, Si, Zr) catalysts for dehydrogenation of propane in the presence of CO₂. *Appl. Catal. A* **2011**, 407, 20–28.
- [6] Michorczyk, P.; Ogonowski, J.; Zenczak, K. Activity of chromium oxide

© 2020 SIOC, CAS, Shanghai, & WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Chin. J. Chem. 2020, 38, XXX-XXX

deposited on different silica supports in the dehydrogenation of propane with CO_2 - A comparative study. *J. Mol. Catal. A* **2011**, *349*, 1–12.

- [7] Baek, J.; Yun, H. J.; Yun, D.; Choi, Y.; Yi, J. Preparation of highly dispersed chromium oxide catalysts supported on mesoporous silica for the oxidative dehydrogenation of propane using CO₂: Insight into the nature of catalytically active chromium sites. ACS Catal. **2012**, *2*, 1893 – 1903.
- [8] Wu, J. L.; Chen, M.; Liu, Y. M.; Cao, Y.; He, H. Y.; Fan, K. N. Sucrosetemplated mesoporous beta-Ga₂O₃ as a novel efficient catalyst for dehydrogenation of propane in the presence of CO₂. *Catal. Commun.* **2013**, *30*, 61–65.
- [9] Koirala, R.; Buechel, R.; Krumeich, F.; Pratsinis, S. E. Oxidative dehydrogenation of ethane with CO₂ over flame-made Ga-loaded TiO₂. ACS Catal. 2015, 5, 690-702.
- [0] Rahmani, F.; Haghighi, M.; Amini, M. The beneficial utilization of natural zeolite in preparation of Cr/clinoptilolite nanocatalyst used in CO₂-oxidative dehydrogenation of ethane to ethylene. J. Ind. Eng. Chem. 2015, 31, 142–155.
- [11] Wei, C. L.; Xue, F. Q.; Miao, C. X.; Yue, Y. H.; Yang, W. M.; Hua, W. M.; Gao, Z. Dehydrogenation of isobutane to isobutene with carbon dioxide over SBA-15-supported chromia-Ccria ctalysts. *Chin. J. Chem.* 2017, 35, 1619–1626.
- [12] Cheng, Y. H.; Lei, T. Q.; Miao, C. X.; Hua, W. M.; Yue, Y. H.; Gao, Z. Ga₂O₃/NaZSM-5 for C₂H₆ dehydrogenation in the presence of CO₂: Conjugated effect of silanol. *Micropor. Mesopor. Mater.* 2018, 268, 235-242.
- [13] Wang, S. B.; Zhu, Z. H. Catalytic conversion of alkanes to olefins by carbon dioxide oxidative dehydrogenation - A review. *Energy Fuels* 2004, 18, 1126-1139.
- [14] Ding, J. F.; Qin, Z. F.; Li, X. K.; Wang, G. F.; Wang, J. G. Coupling dehydrogenation of isobutane in the presence of carbon dioxide over chromium oxide supported on active carbon. *Chin. Chem. Lett.* **2008**, *19*, 1059–1062.
- [15] Ogonowski, J.; Skrzyńska, E. Dehydrogenation of isobutane in the presence of carbon dioxide over supported vanadium oxide catalysts. *React. Kinet. Catal. Lett.* **2006**, *88*, 293-300.
- [16] Yuan, R. X.; Li, Y.; Yan, H. B.; Wang, H.; Song, J.; Zhang, Z. S.; Fan, W. B.; Chen, J. G.; Liu, Z. W.; Liu, Z. T.; Hao, Z. P. Insights into the vanadia catalyzed oxidative dehydrogenation of isobutane with CO₂. *Chin. J. Catal.* **2014**, *35*, 1329–1336.
 - Vei, C. L.; Xue, F. Q.; Miao, C. X.; Yue, Y. H.; Yang, W. M.; Hua, W. M.; Gao, Z. Dehydrogenation of isobutane with carbon dioxide over SBA-15-supported vanadium oxide catalysts. *Catalysts* **2016**, *6*, 171.
- [18] Ogonowski, J.; Skrzyńska, E. Catalytic dehydrogenation of isobutane in the presence of carbon dioxide. *React. Kinet. Catal. Lett.* **2005**, *86*, 195 -201.
- [19] Ogonowski, J.; Skrzyńska, E. Activity of vanadium magnesium oxide supported catalysts in the dehydrogenation of isobutane. *Catal. Lett.* 2006, 111, 79-85.
- [20] Heitmann, G. P.; Dahlhoff, G.; Hölderich, W. F. Catalytically active sites for the Beckmann rearrangement of cyclohexanone oxime to epsiloncaprolactam. *J. Catal.* **1999**, *186*, 12–19.
- [21] Ichihashi, H.; Sato, H. The development of new heterogeneous catalytic processes for the production of epsilon-caprolactam. *Appl. Catal.* A 2001, 221, 359–366.
- [22] Ichihashi, H.; Ishida, M.; Shiga, A.; Kitamura, M.; Suzuki, T.; Suenobu,

K.; Sugita, K. The catalysis of vapor-phase Beckmann rearrangement for the production of epsilon-caprolactam. *Catal. Surv. Asia* **2003**, *7*, 261–270.

- [23] Lanzafame, P.; Barbera, K.; Perathoner, S.; Centi, G.; Aloise, A.; Migliori, M.; Macario, A.; Nagy, J. B.; Giordano, G. The role of acid sites induced by defects in the etherification of HMF on Silicalite-1 catalysts. *J. Catal.* 2015, *330*, 558–568.
- [24] Luo, Y. J.; Miao, C. X.; Yue, Y. H.; Hua, W. M.; Gao, Z. ZnO supported on Silicalite-1 as an efficient catalyst for isobutane dehydrogenation to isobutene assisted by CO₂. *Micropor. Mesopor. Mater.* doi: 10.1016/j.micromeso.2019.109864.
- [25] Sang, S.; Chang, F.; Liu, Z.; He, C.; He, Y.; Xu, L. Difference of ZSM-5 zeolites synthesized with various templates. *Catal. Today* 2004, 93–95, 729–734.
- [26] Zhao, H. H.; Song, H. L.; Chou, L. J.; Zhao, J.; Yang, J.; Yan, L. Insight into the structure and molybdenum species in mesoporous molybdenaalumina catalysts for isobutane dehydrogenation. *Catal. Sci. Technol.* 2017, 7, 3258–3267.
- [27] Cheng, Y. H.; Zhou, L. B.; Xu, J. X.; Miao, C. X.; Hua, W. M.; Yue, Y. H.; Gao, Z. Chromium-based catalysts for ethane dehydrogenation: Effect of SBA-15 support*Micropor. Mesopor. Mater.* 2016, 234, 370-376.
- [28] Hartmeyer, G.; Marichal, C.; Lebeau, B.; Rigolet, S.; Caullet, P.; Hernandez, J. Speciation of silanol groups in precipitated silica nanoparticles by H-1 MAS NMR spectroscopy. J. Phys. Chem. C 2007, 111, 9066-9071.
- [29] Liu, G. D.; Liu, J. X.; He, N.; Miao, C. L.; Wang, J. L.; Xin, Q.; Guo, H. C. Silicalite-1 zeolite acidification by zinc modification and its catalytic properties for isobutane conversion. *RSCAdv.* **2018**, *8*, 18663–18671.
- [30] Zecchina, A.; Bordiga, S.; Spoto, G.; Scarano, D. Low-temperature Fourier-tansform infrared Investigation of the interaction of CO with nanosized ZSM5 and Silicalite. J. Chem. Soc. Faraday Trans. 1992, 88, 2959-2969.
- [31] Bolis, V.; Busco, C.; Bordiga, S.; Ugliengo, P.; Lamberti, C.; Zecchina, A. Calorimetric and IR spectroscopic study of the interaction of NH₃ with variously prepared defective silicalites - Comparison with ab initio computational data. *Appl. Surf. Sci.* 2002, 196, 56–70.
- [32] Barbera, K.; Bonino, F.; Bordiga, S.; Janssens, T. V. W.; Beato, P. Structure-deactivation relationship for ZSM-5 catalysts governed by framework defects. J. Catal. 2011, 280, 196-205.
- [33] Bordiga, S.; Ugliengo, P.; Damin, A.; Lamberti, C.; Spoto, G.; Zecchina, A.; Spanò, G.; Buzzoni, R.; Dalloro, L.; Rivetti, F. Hydroxyls nests in defective silicalites and strained structures derived upon dehydroxylation: vibrational properties and theoretical modelling. *Top. Catal.* 2001, 15, 43-52.
- [34] Shi, L. H.; Liu, G. D.; Guo, H. C. Efficient Pt/Silicalite-1 catalyst for isomerization of n-heptane. *Catal. Commun.* 2017, 101, 111–115.
- [35] Pidko, E. A.; van Santen, R. A. Activation of light alkanes over zinc species stabilized in ZSM-5 zeolite: A comprehensive DFT study. J. Phys. Chem. C 2007, 111, 2643-2655.
- [36] Ren, Y. J.; Zhang, F.; Hua, W. M.; Yue, Y. H.; Gao, Z. ZnO supported on high silica HZSM-5 as new catalysts for dehydrogenation of propane to propene in the presence of CO₂. *Catal. Today* **2009**, *148*, 316–322.
- [37] Butt, T.; Tosheva, L. Synthesis of colloidal silicalite-1 at high temperatures. *Micropor. Mesopor. Mater.* 2014, 187, 71–76.
- [38] Wang, L. F.; Yang, R. T. Increasing selective CO₂ adsorption on aminegrafted SBA-15 by increasing silanol density. J. Phys. Chem. C 2011, 115, 21264-21272.

© 2020 SIOC, CAS, Shanghai, & WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

www.cjc.wiley-vch.de

Report

[39] Luo, Y. J.; Miao, C. X.; Yue, Y. H.; Yang, W. M.; Hua, W. M.; Gao, Z. Chromium oxide supported on Silicalite-1 zeolite as a novel efficient catalyst for dehydrogenation of isobutane assisted by CO₂. *Catalysts* 2019, *9*, 1040.

(The following will be filled in by the editorial staff)

Manuscript received: XXXX, 2019 Manuscript revised: XXXX, 2019 Manuscript accepted: XXXX, 2019 Accepted manuscript online: XXXX, 2019 Version of record online: XXXX, 2019

Entry for the Table of Contents

Page No.

Isobutane Dehydrogenation Assisted by CO₂ over Silicalite-1-Supported ZnO Catalysts: Influence of Support Crystallite Size



The ZnO catalyst supported on Silicalite-1 with ca. 0.35 μ m crystallite size exhibits the highest activity for CO2-assisted isobutane dehydrogenation, which can be attributed to both a higher amount of acid sites present on this catalyst and the largest amount of nest silanols possessed by the Silicalite-1 support.

Yajun Luo, Chunling Wei, Changxi Miao,* Ying-

WILEY Chin. J. Chem. 2018, template© 2018 SIOC, CAS, Shanghai, & WILEY-VCH Verlag GmbH & Co. KGaA, Wein-ONLINE LIBRARY heim This article is protected by copyright. All rights reserved.