

Article

Cobalt Nanocluster Supported on ZrREnOx for the Selective Hydrogenation of Biomass Derived Aromatic Aldehydes and Ketones in Water

Yanfu Ma, Guangyue Xu, Hao Wang, Yingxiong Wang, Ying Zhang, and Yao Fu ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.7b03470 • Publication Date (Web): 09 Jan 2018 Downloaded from http://pubs.acs.org on January 10, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Catalysis is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Cobalt Nanocluster Supported on $ZrRE_nO_x$ for the Selective Hydrogenation of Biomass Derived Aromatic Aldehydes and Ketones in Water

Yanfu Ma,[†] Guangyue Xu,[†] Hao Wang,[†] Yingxiong Wang,[‡] Ying Zhang^{†,*} and Yao Fu[†]

[†]iChEM, CAS Key Laboratory of Urban Pollutant Conversion, Anhui Province Key Laboratory for Biomass Clean Energy and Department of Chemistry, University of Science and Technology of China, Hefei 230026, China.

E-mail: <u>zhzhying@ustc.edu.cn</u>; Fax: +86-551-63606689; Tel: +86-551-63603463

[‡]Shanxi Engineering Research Center of Biorefinery, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, China

E-mail: <u>wangyx@sxicc.ac.cn</u>

Abstract:

In this study, rare earth (RE) metal doped ZrO_2 was prepared by surfactant-assisted co-precipitation/hydrothermal crystallization method and used to load Co as catalyst for the hydrogenation of aromatic carbonyl compounds in water. Furfural was hydrogenated to furfural alcohol in water with up to 95 mol% yield over Co/ZrLa_{0.2}O_x at 40 °C, 2 MPa H₂ in 10 h. The doping of rare earth metal oxide has three advantages: I) promotes the ZrO₂ to reach a small-sized, stable and high-activity tetragonal phase zirconia and thus lead to a high specific surface area for metal loading; II) interacts with Co to reach an ultra-small average particle size of 1.1 nm; III) modifies the ZrO_2 surface to increase the amount of acidic sites for the adsorption of carbonyl feedstock. Adsorption experiment indicated a tight interaction between not only the carrier and C=O bond, but also the Co clusters and C=O bond, which were benefit for the hydrogenation of carbonyl groups. The surfactant addition during the carrier preparation improves the strong metal-support interactions (SMSI) to promote Co dispersion and stability. Various rare earth metals including La, Pr,Nd, and Ce could modify ZrO₂ with similar mechanism. The as-prepared Co catalyst could also catalyze the selective hydrogenation of various aromatic aldehydes and ketones (such as 5-hydroxymethyl furfural, benzaldehyde and acetophenone) in water, and 100% yield to corresponding alcohols was achieved. The catalyst kept stable and showed little deactivation during the recycling tests. This study not only presented a high-efficient, low-cost, and stable catalyst for the selective hydrogenation of various aromatic aldehydes and ketones, but also give rise to an understanding of rare earth metal oxides doped ZrO₂ supported nano Co ternary catalysts.

KEYWORDS: cobalt nanocluster, rare earth metal, doping, SMSI, biomass, hydrogenation

1. Introduction

As the chemical economy gradually shifts from fossil fuels to renewable resources, it becomes important to develop new technologies to upgrade renewable platform molecules to final industrial products.^{1,2} Comparing with traditional petrochemical supplies, platform molecules from lignocellulose biomass have more unsaturated functional groups. A representative structure is carbonyl group conjugated with aromatic rings, such as furfural and 5-hydroxylfurfural. Natural aromatic nucleus with hydroxyl groups are important structures used for the synthesis of pharmaceuticals. spices and resin.^{3,4} Therefore, it requires the selective hydrogenation of carbonyl group without the destruction of aromaticity. Many catalytic systems have been studied, and the main problem is the poor selectivity, which is caused by the easy saturation of aromatic structure and the hydrogenolysis of C-O bond at high temperature.⁵⁻⁷ Thus, the selective hydrogenation of conjugated carbonyl group under mild conditions is still a challenge. Precious metal catalyst with high hydrogenation activity at lower temperature is a good choice. Pt/Al₂O₃⁸ and Ru/UiO-66⁹ could fulfill the selective hydrogenation of furfural to fufuryl alcohol at 50 °C. Howerer, the high cost and finite reserves of precious metals limited their extensive application. Therefore, the development of none precious metal catalysts made of earth-abundant elements is meaningful.

Many non-precious metal catalysts have been synthesized and exhibited good hydrogenation activity in a series of aromatic aldehydes and ketones, such as Cu-Co/SBA-15¹⁰, NiMoB/ γ -Al₂O₃¹¹, and Ni-Fe-B¹². However, the poor H₂ activation ability made them require high reaction temperature and/or high H₂ pressure to achieve a comparable activity with precious metal catalysts. To enhance the specific activity of supported metal catalyst, one of the most effective method is increasing the dispersion of the active metal to enlarge the specific surface area.^{13,14} The newly hot single-atom catalysts¹⁵ is a good choice but currently hard to realize. The modification of carrier¹⁶ and new preparation technology for metal loading process¹⁷⁻²⁰ are two effective methods for the specific activity increase of supported metal catalysts.

According to the previous reports, Co particles dispersed well on TiO₂ by strong metal-support interactions (SMSI), but tended to sinter on SiO₂.²¹ Meanwhile, the SMSI could inhibit the aggregation of the catalyst.²² Thus, building SMSI has been seen as a promising approach to prepare highly dispersed non-precious catalysts. ZrO_2 also exhibited the effect of SMSI^{23,24} and gained attentions for its potential use as a matrix in the material synthesis and the carrier in the catalysis.²⁵ Moreover, doping other metals such as La^{26-29} , Ce^{30} , $Ti^{31,32}$, W^{33} , and Fe^{34} could affect the structure or electron property of ZrO_2 by forming the defect in the crystal. Especially for rare earth metal oxides, their cationic oxidation states, the degree of coordinative unsaturation, and the degree of surface hydroxylation all contribute to the catalyst modifications.^{27,35,36} The highly dispersed particles could also be stabilized by rare earth metal oxides.³⁷ Therefore, modification of ZrO_2 by rare earth oxides ($ZrRE_nO_x$) may disperse non-precious metal into small paticles with a high activity for selective hydrogenation of aromatic aldehydes and ketones.

Cobalt is a versatile catalyst for various reactions,³⁸ including hydrogenation of $C=C^{39}$, $C=N^{40}$ and $C=O^{41}$ bonds. Homogeneous Co catalyst has been reported for selective hydrogenation of C=O in the presence of C=C.⁴² Co could be a good candidate for selective hydrogenation of aromatic aldehydes and ketones. Considering that water is cheaper, more available and environment-friendly, moreover, some biomass derived molecules including furfural and 5-HMF are obtained by hydrolysis method, water should be the suitable solvent for their conversion to avoid restrict and costly water removing pretreatment. Therefore, in this work, a highly dispersed $Co/ZrRE_nO_x$ catalyst was prepared to convert aromatic aldehydes and ketones selectively to corresponding alcohols with water as solvent. The $ZrRE_nO_x$ carrier was synthesized by surfactant-assisted co-precipitation/hydrothermal crystallization method and used to load Co nanoclusters by simple impregnation method. The influence of the modification conditions, including doping ratio and the rare earth metals, on the catalyst structure and catalytic performance for aromatic aldehydes and ketones hydrogenation were studied. A series of characterizations were carried out: nitrogen adsorption-desorption, X-ray

Page 5 of 29

ACS Catalysis

diffraction (XRD), transmission electron microscope (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) with energy dispersive spectrometer (EDS) mapping, H₂ temperature programmed reduction (TPR), H₂ and NH₃ temperature programmed desorption (TPD), O₂ titration, Fourier transform infrared spectroscopy (FT-IR), *in-situ* and *ex-situ* X-ray photoelectron spectroscopy (XPS). These characterizations led to deep insights into the complex catalyst structure. The stability of catalysts was also investigated by the recycling experiments.

2. Experimental Section

Chemicals Materials

Acetone (AR, >99%), furfural (AR, >99%), furfuryl alcohol (AR, >99%), tetrahydrofurfuryl alcohol (AR, >97%), n-hexanol (AR, >99%), sodium hydroxide (AR, >99%), ethanol (AR, >99%), n-hexane (AR, >99%), ethyl acetate (AR, >99%), dichloromethane (AR, >99%), benzaldehyde (AR, >99%), benzyl alcohol (AR, >99%), phenethyl alcohol (AR, >99%), butyraldehyde (AR, >99%), acetophenone (AR, >99%), cobaltous nitrate hexahydrate (AR, >99%), sodium hydroxide (AR, >99%), lanthanum(III) nitrate hexahydrate (AR, >99%), sodium hydroxide (AR, >99%), lanthanum(III) nitrate hexahydrate (AR, >44%), praseodymium(III) nitrate hexahydrate (AR, >44%), zirconyl chloride octahydrate (AR, >99%), ceric ammonium nitrate (AR, >44%), and cetyltrimethyl ammonium bromide (AR, >99%) were obtained from Sinopharm Chemical Reagent Co., Ltd. 5-hydroxymethyl furfural (AR, >99%) and 2,5-dihydroxymethyl furan (AR, >99%) were obtained from Hefei Leaf Biotech Co., Ltd. Neodymium nitrate hexahydrate (AR, >99%) was purchased from Aladdin Chemical Reagent Co., Ltd. Purified furfural was obtained by vacuum distillation and stored at -15°C.

Catalyst preparation

The carriers with different atomic ratios of Zr to La were synthesized by surfactant-assisted co-precipitation/hydrothermal crystallization (SACPHC)³⁰ with modification. Generally, a certain amount of cetyltrimethyl ammonium bromide

(CTAB) was dissolved in deionized water at 60 °C with agitation. Zirconium oxychloride solutions and lanthanum nitrate solution were added to give a clear homogeneous solution, which including Zr, La, CTAB and H₂O at a molar ratio of 1: x: 0.5: 100 (where x equaled to 0, 0.2 and 1), respectively. After half an hour, 1 M fresh sodium hydroxide solution was added dropwise under vigorous stirring to a constant pH of 9. Then, the mixture was aged at 90 °C for 10 h followed by filtration and washing with deionized water and ethanol. Finally, the precipitate was dried at 105 °C overnight and then calcined in air at 550 °C for 4 h. The carrier was marked as ZrO₂, ZrLa_{0.2}O_x and ZrLaO_x, respectively. LaO_x was synthesized by the similar preparation method as ZrO₂ where Zr was replaced by La.

The carrier with various rare earth metals (Ce, Pr, Nd) was prepared by the same process as that of $ZrLa_{0.2}O_x$. The carrier prepared without surfactant was labeled as $ZrLa_{0.2}O_x$ -N.

The Co catalysts were prepared by impregnation method. The carrier (0.5 g) was dispersed in acetone (42 g) with stirring at 45 °C. Cobalt nitrate (0.264 g) were dissolved in 5 ml acetone and then added dropwise. After stirring for 24 hours, acetone was removed by rotary evaporation. The catalyst was dried at 110 °C overnight and calcined at 300 °C for 2 h ramping at 1 °C min⁻¹. Finally, the catalyst was calcined at 600 °C for 2 h at a rate of 1 °C min⁻¹. The calcined catalysts were reduced in H₂ atmosphere at 600 °C for 2 h with a heating rate of 1 °C min⁻¹ before reaction. The Co content was measured by ICP-AAS of PerkinElmer Corporation AA800.

Experimental procedure

The hydrogenation of furfural was performed in a 25 ml stainless steel autoclave equipped with a magnetic stirrer. Typically, the mixture of furfural (1 mmol), catalyst (50 mg) and water (10 ml) was added into the reactor and flushed with H_2 several times. The reactor was pressured with H_2 . Then it was heated to the desired temperature. After reaction, the reactor was cooled to ambient temperature. The liquid products were transferred with 20 mL of ethanol and n-hexanol was used as internal

standard for quantification. Then the sample was analyzed by a gas chromatograph (GC, Kexiao 1690) with a HP-INNOWAX capillary column ($30m \times 0.25mm \times 0.25\mu m$) and GC-MS (Agilent 7890A). The GC detecting conditions: nitrogen was the carrier gas; injection port temperature was 280 °C; detector (FID) temperature was 280 °C. Column was heated from 40 °C to 250 °C by 10 °C min⁻¹.

Characterization methods

X-ray diffraction (XRD) was conducted on an X-ray diffractometer (TTR-III, Rigaku Corp, Japan) using Cu K α radiation (λ = 1.54056 Å). The data were recorded over 20 ranges of 10-70°.

Transmission electron microscopy (TEM) image of the samples were obtained with a JEOL JEM-2010 high-resolution transmission electron microscope operated at 200 kV. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the energy dispersive spectrometer (EDS) mapping image of the samples were obtained with a JEOL JEM-2010F at 200 kV.

The nitrogen adsorption/desorption isotherms were measured by a Micromeritics TriStar II system (TriStar II 3020 V1.03). The specific surface area was determined by Brunauer–Emmett–Teller (BET) equation. The pore sizes were calculated by the thermodynamic based Barrett–Joyner–Halenda (BJH) method.

In situ XPS measurements were carried out on a Kratos AXIS Ultra DLD spectrometer using a monochromatic Al K_{α} (1486.6 eV) irradiation source operated at 150 W. The spectra were recorded using an aperture slot of 300 × 700 μ m². The survey spectra were recorded with pass energy of 160 eV and high-resolution spectra were recorded with pass energy of 40 eV. The pressure in the analyser chamber was 10⁻⁸ Pa. Binding energies were calibrated using the C 1s peak at 285.0 eV.

All the temperature-programmed desorption and/or reduction were carried out in a home-built reactor system coupled with a gas chromatograph. All the gas flow was 40 ml min⁻¹. Temperature-programmed reduction with hydrogen (H₂-TPR) was performed to determine the reducibility of the catalysts. 75 mg catalyst was treated in

Ar at 500 °C for 1 h and then cooled to 80 °C. Afterwards, the sample was heated to 800 °C at a rate of 10 °C min⁻¹ in a mixture of H₂ (5.08%v/v)/Ar flow. The outlet gas was analyzed with an on-line gas chromatograph.

The O₂ titration^{43,44} was carried out to characterize the Co dispersion. In a typical run, 70 mg catalyst was activated at 450 °C for 10 h using a flow of hydrogen and cooled to 100 °C in hydrogen stream. The sample was held at 100 °C under flowing Ar for 1.5 h to remove physisorbed and/or weakly bound species before increasing temperature to the reduction temperature. At this temperature, the catalyst was heated to 800 °C in Ar to desorb the remaining chemisorbed hydrogen (H₂-TPD process). When the temperature cooled to 450 °C, the calibrated pulses of O₂ were added until no further consumption of O₂ could be detected by a thermal conductivity detector. The mole number of O₂ consumed was recorded and the percentage of reduction was calculated, assuming that Co⁰ was re-oxidized to Co₃O₄.

Temperature-programmed desorption of ammonia (NH₃-TPD) was employed to determine the total acidity of the catalysts. Prior to absorption of ammonia, 60 mg of catalyst sample was heated at 500 °C for 1 h under Ar flow and then cooled to 80 °C followed by saturating with pure NH₃ for 1 h. After flushing with Ar for 1h, the NH₃-TPD was performed from 80 °C to 650 °C with a heating rate of 10 °C min⁻¹. The desorbed ammonia was monitored by an on-line gas chromatograph equipped with a thermal conductivity detector (TCD).

FT-IR was performed by Nicolet 8700. The catalyst was mixed with substrates solution for 10 h at room temperature and then dried in N_2 flow overnight.

3. Results and discussion

3.1 Catalyst Characterization

A series of Co catalysts were prepared on ZrO_2 , La_2O_3 and various ZrLaOx oxides. X-ray diffraction (XRD) was carried out on various carriers (Figure 1A) and catalysts (Figure 1B). As shown in Figure 1A, the diffraction peaks of ZrO_2 can be indexed to two types of unit cells: the peaks at 2 θ positions 30.3°, 35.2°, 50.6°, 60.0° and 62.23° were assigned to tetragonal zirconia (t-ZrO₂) while 24.3°, 28.1°, 31.3°, 34.6°, 35.2°,

ACS Catalysis

49.2° and 50.1° stood for monoclinic zirconia (m-ZrO₂).⁴⁵ Both the two phases were detected in as-prepared ZrO₂. After La addition, only the diffraction peaks of t-ZrO₂ were found, and no signal corresponding to m-ZrO₂ or any La species was detected in ZrLa_{0.2}O_x. The main peaks of t-ZrO₂ in ZrLa_{0.2}O_x slightly shifted to lower diffraction angle when the larger metal ions La³⁺ (106.1 pm) was doped in Zr⁴⁺ (80 pm), suggesting that La had been doped into ZrO₂ lattice and increased the interplanar spacing.⁴⁶ When the molar ratio of La/Zr increased from 0.2 to 1, the amorphous species were formed, while the diffraction peaks of t-ZrO₂ crystal structure were not found. As exposed to air during calcination, it was La₂O₂CO₃ phase in as-prepared LaO_x due to La₂O₃ was sensitive to carbon dioxide.⁴⁷

The XRD patterns of Co loaded catalysts were showed in Figure 1B. If detected, the diffraction peaks of Co₃O₄ should be at 36.9 and 65.2°. The diffraction peak of CoO and metallic Co can be observed at 42.4° and 44.4°, respectively.⁴⁸ After Co precipitation, calcination, and reduction treatment, a significant change of phase occurred in Co/ZrO₂ from t-ZrO₂ to m-ZrO₂ compared with unloaded carrier while it almost kept unchanged in Co/ZrLa_{0.2}O_x. As studied in previous literatures, impurities and structural defects could stimulate the formation of meta-stable t-ZrO₂ at temperature lower than its crystal transition temperature.^{49,50} Herein, a stable t-ZrO₂ phase can be obtained easily by La doping. There was La(OH)₃ in Co/LaO_x which could come from the reaction of La₂O₃ with H₂O produced from the decomposition of Co(NO₃)₂·6H₂O during the calcination.⁵¹ Except for Co/ZrLaO_x, no signal of Co species was observed in the rest catalysts, suggesting that Co was highly dispersed. The diffraction peak in Co/ZrLaO_x was assigned to metallic Co.



Figure 1. (A): XRD patterns of ZrO₂, ZrLa_{0.2}O_x, ZrLaO_x and LaO_x. (B): XRD patterns of Co/ZrO₂, Co/ZrLa_{0.2}O_x, Co/ZrLaO_x and Co/LaO_x.

Entry	Catalysts	Co content (wt%)	S _{BET} (m ² g ⁻¹) Carrier	S _{BET} (m ² g ⁻¹) Catalysts	Dispersion (%) ^a	Average particle size (nm) ^a
1	Co/ZrO ₂	8.90	54.7	49.1	50.67	1.9
2	Co/ZrLa _{0.2} O _x	8.81	125.3	53.3	89.72	1.1
3	Co/ZrLaO _x	8.40	52.5	24.9	24.54	3.9
4	Co/LaO _x	8.30	7.3	9.5	37.11	2.6
5	Co/ZrLa _{0.2} O _x -N ^b	8.53	107.9	15.5	16.19	5.9

ACS Catalysis

(a) The dispersion and average particle size were measured by O_2 titration, (b) No surfacant was used for the catalyst preparation.

The surface area was measured and shown in Table 1. The ZrLa_{0.2}O_x revealed the highest BET surface area. Compared with lower specific surface area of ZrO₂, the doping of small amount of La could lead to a significant increase in specific surface area from 54.7 to 125.3 m^2g^{-1} . Further increasing La content led to an amorphous state so that the specific surface area decreased. After Co loading, the BET surface area of Co/ZrLa_{0.2}O_x decreased (Entry 2), but was still the highest among all Co catalysts. The nitrogen adsorption-desorption isotherm and BJH adsorption cumulative volume of pores of $ZrLa_0 _2O_x$ and $Co/ZrLa_0 _2O_x$ were shown in Figure S1. Based on the IUPAC classification, the isotherms were both type II.52 The area of hysteresis loop below 0.48 P/P₀, which comes from small micropore, disappeared after Co loading, indicating that the Co occupied or blocked all the micropores. These micropore may form from surfactant removing. The gently rising section between 0.6-0.8 P/P₀ in ZrLa_{0.2}O_x revealed a wide distribution of pore size. These micropores were typically formed by stacking of $ZrLa_0 _2O_x$ particles. After Co loading, the slope in the hysteresis loop indicated a relatively uniform distribution of pore size. Considering about the BJH adsorption cumulative volume of pores, after Co loading, the decrease of pore volume is 0.239-0.142=0.097 cm³/g, which is much larger than the volume of supported Co ($0.0881/8.9=0.0099 \text{ cm}^3/g$). Besides the possible collapse of stacking, Co might be loaded at some openings of stacking pores. For ZrLa_{0.2}O_x without surfactant, after Co loading, the surface area decreased remarkably. It was due to the sintering of ZrLa_{0.2}Ox without surfactant. The chemical titration by O2 was carried out to measure the average particle size of Co, as shown in Table 1. The $Co/ZrLa_{0.2}O_x$ had the smallest average particle size of 1.1 nm, which was inversely with specific surface area.

To observe the morphology clearly, the TEM images of all Co-based catalysts were presented in Figure 2. From Figure 2a and b, it is hard to see the difference between $Co/ZrLa_{0.2}O_x$ and $ZrLa_{0.2}O_x$. In order to recognize the metal Co, the fresh reduced sample was investigated by HAADF-STEM. Unfortunately, we could not distinguish

Co clusters definitely (Figure 2c). The energy dispersive spectrometer mapping image (Figure 2d) was then taken. It confirmed that Co and La were both existent and dispersed well on $ZrLa_{0.2}O_x$. In the morphology, $Co/ZrLa_{0.2}O_x$ was similar to Co/ZrO_2 except for the carrier size. With La doping, the carrier size was decreased, which could exhibit an increase in the specific surface area, as discussed before. For the Co/ZrLaO_x and Co/LaO_x, the Co nanocluster could be recognized by TEM. At least 150 particles were measured and the Co average particle sizes were estimated as 3.5 nm and 2.7 nm for Co/ZrLaO_x and Co/LaO_x, respectively. Those results were basically consistent with O₂ titration measurement (Table 1). In Figure 2g, the La₂O₃ supported Co particles were also highly dispersed.



Figure 2. TEM images of (a) $Co/ZrLa_{0.2}O_x$, (b) $ZrLa_{0.2}O_x$, (c) High-angle annular dark-field STEM image of $Co/ZrLa_{0.2}O_x$, (d) EDS mapping image of $Co/ZrLa_{0.2}O_x$, (e) Co/ZrO_2 , (f) $Co/ZrLaO_x$, (g) Co/LaO_x , and (h) $Co/ZrLa_{0.2}O_x$ -N.



Figure 3. H₂-TPR profiles Co/ZrO₂, Co/ZrLa_{0.2}O_x, Co/ZrLaO_x, and Co/LaO_x.

Temperature-programmed reduction with hydrogen (H₂-TPR) is a powerful tool to study the reduction of the oxide phase and the interaction between the carrier and supported metals.⁵³ H₂-TPR profiles of various Co-based catalysts after calcination are presented in Figure 3. The peak-fit had been be performed in order to clearly explain the attribution of the partly overlapped reduction peaks in the different samples. At low temperature, two reduction peaks in the overlapping were assigned to the reduction of Co_3O_4 to CoO and the subsequent reduction of CoO to $Co^{0.22,54}$ The tailing peak after 450 °C in the TPR profiles of Zr-based catalysts implied that there was a certain interaction between Co metal and Zr carrier.^{55,56} The extent of tailing was maximal in Co/ZrLa_{0.2}O_x and declined with less or more La addition. No similar tailing existed in Co/LaO_x. The reduction temperature of Co⁰ also changed. When small amount of La doped in the ZrO₂, the reduction temperature decreased. With further addition of La, a new reduction peak was found at high temperature (~690 °C). Based on the previous report, it could be attributed to the reduction of carbonate and hydroxyl species in the LaO_x matrix.⁵⁷

3.2 Hydrogenation of Furfural

Table 2. Hydrogenation of Furfural^a

Entry	Catalyst	Conversion (%)	Yield (mol%)	

			FA	THFA
1	Co/ZrO ₂	86	85	1
2	Co/ZrLa _{0.2} O _x	95	92	3
3	Co/ZrLaO _x	84	82	2
4	Co/LaO _x	80	79	1
5	Co/ZrLa _{0.2} O _x -N	66	56 ^b	0
6 ^c	Co/ZrLa _{0.2} O _x	98	95	3
7	ZrO ₂	5.5	5.5	0
8	ZrLa _{0.2} O _x	9.2	9.2	0

(a) Reaction conditions: 100 mg furfural, 50 mg catalyst in 10 mL water, 80 °C, 2 MPa H₂, 2 h. (b) The loss of carbon balance came from undetected polymerization. (c) Reaction conditions: 40 °C, 2 MPa H₂, 10 h.

To test the catalytic activity of the Co catalysts, the hydrogenation of furfural in water with H_2 was used as a probe reaction for aromatic aldehydes and ketones hydrogenation. Usually, furfural could proceed the hydrogenation of C=O bond, the hydrogenation of C=C bond, the hydrogenolysis C=O bond, decarbonylation, rearrangement and polymerization. 58,59 As shown in Table 2, when the reaction was carried out with Co catalysts at 80 °C, 2 MPa H₂ in 2 h, furfuryl alcohol was the predominant product along with very small amount of over-hydrogenation by-product, tetrahydrofurfuryl alcohol (THFA). The conversion was increased from 86% to 95% by doping small amount of La to Co/ZrO_2 and then decreased to 84% by increasing the ratio of La to Co as 1:1. The conversion with Co/LaO_x was even lower, which was 80%. Co/ZrLa_{0.2}O_x-N showed a 66% conversion and 10% carbon loss coming from undetected polymerization.⁶⁰ When the reaction temperature was reduced to 40 °C, the catalyst could achieve 95 mol% yield of furfural alcohol in 10 h, which should be the lowest reaction temperature for the reported heterogeneous none precious metal catalyst. Control reactions for hydrogenation of furfural over carriers were also performed. La₂O₃ did not show any activity and ZrO₂ showed a low activity for the reaction. After doping La, the conversion of furfural changed from 5.5% to 9.2%.

In the hydrogenation reaction, the activity and selectivity could be affected by the solvent. Solvents including dichloromethane, n-hexane, ethyl acetate and ethanol were employed for furfural hydrogenation by using Co/ZrLa_{0.2}O_x as catalyst (Table S3).

Only 12% of furfural alcohol was produced in dichloromethane, which could be due to the impact of chlorine on the catalyst. 60% of furfural alcohol was produced in n-hexane. Interestingly, 92% of furfural alcohol was produced in ethyl acetate, ethanol and water, respectively. Combining the advantage such as cheaper, more available and environment-friendly, water should be the best solvent for our catalytic system.

3.3 Interactions among the elements of catalysts

The specific reaction activity revealed La doping significantly affected the distribution of Co nanoparticles. To study the interaction between La doped carrier and Co, H₂ temperature programmed desorption (H₂-TPD) was employed to characterize the strong metal-support interactions (SMSI) by calculating the amount of H₂ absorption of the catalyst.^{22,61,62} The results are displayed in Table 3.

Table 3. The H_2 adsorption of the catalysts by H_2 -TPD.

Catalysts	Co/ZrO ₂	Co/ZrLa _{0.2} O _x	Co/ZrLaO _x	Co/LaO _x	Co/ZrLa _{0.2} O _x -N
H_2 adesorption (mmol g ⁻¹)	0.556	0.503	0.653	0.770	0.608

Tauster et al had explained that the SMSI could suppress of hydrogen chemisorption over the catalysts.⁶³ It was clear that the H₂ desorption, which was assigned to the amount of H₂ absorbed at lower temperature, changed. Co/LaO_x obtained the maximum H₂ absorption. With the decline of La ratio, the suppression was more significant. Specially, Co/ZrLa_{0.2}O_x revealed the minimum H₂ absorption, and thus, Co/ZrLa_{0.2}O_x possessed the strongest SMSI, thereby allowing the Co paticle size to be smaller and stable. Therefore, the SMSI can be maximized with a suitable Zr/La ratio.



(B) LaO_x , $ZrLa_{0.2}O_x$, Co/LaO_x , $Co/ZrLa_{0.2}O_x$ and $Co/ZrLa_{0.2}O_x$ -N; (C) Co/ZrO_2 , $Co/ZrLa_{0.2}O_x$, $Co/ZrLa_{0.2}O_x$ -N and Co/LaO_x

In situ XPS was also used to study the interactions of various elements among the catalysts, and the results were shown in Figure 4. The spectra of Zr revealed that the peaks at 182.0 and 184.4 eV were assigned to Zr 3d_{5/2} and Zr 3d_{3/2}, respectively.⁶⁴ After La doping, Co loading or no CTAB addition, the binding energies all increased, demonstrating that the Zr species were more likely to interact with other elements via electron donation. However, the Zr local environment changed slightly in Co/ZrLa_{0.2}O_x, implying more complex interactions among each elements, especially between Co and La. In the spectra of La, the doublet peaks at 835.5 eV and 852.3 eV were assigned to La $3d_{5/2}$ and La $3d_{3/2}$.⁶⁵ A slight shift was observed when La doped in ZrO₂, which was due to the interaction of La and Zr and the migration of electric charge. Unlike Co/ZrLa_{0.2}O_x-N, there was a shift in both Co/LaO_x and Co/ZrLa_{0.2}O_x after the Co loading. This interaction may contribute to Co dispersion. The binding energy of Zr 3d decreased after La doping, while that of La 3d was higher in $ZrLa_{0.2}O_x$ than in LaO_x . It indicated that La donated electron to Zr to make a $Zr^{4-\delta}La^{3+\epsilon}_{0.2}O_x$ species. This interaction would not only stabilize the carrier, but also led to more coordinative unsaturated defects. From Co 2p spectra, we could find two different kinds of Co species exist. The peaks at 777.9 eV and 792.8 eV related to Co interacting with La, which could not be observed in Co/ZrO_2 catalyst. The peaks at 780.3 eV and 796 eV related to Co nanoclusters. So in these catalysts, the doping of La improved the interaction between Co and support. It could also explain why Co/LaO_X possessed such low specific surface area ($9.5m^2/g$) but still small Co average particle size (2.6 nm). In this catalyst, ZrO₂ was the main support, while La doping could not only modify ZrO₂ to reach high surface area, but also contribute to Co dispersion. These two effects jointly promoted high Co dispersion.

3.4 Adsorption Mechanism

Besides the high dispersion of Co, the interactions between feedstock and support could be a significant issue. As carbonyl group is a Lewis base, the surface acidity

ACS Catalysis

could promote the adsorption of aldehyde feedstock. The acidic properties of the synthesized carriers were investigated by NH₃-TPD, as shown in Figure 5. In general, the amount of acidic sites were affected by La addition.⁶⁶ The acidic sites in this kind of mixed oxides mainly come from the exposed metal cation, and can be classified depending on NH₃ desorption temperatures as weak acidic sites (<200 °C), medium acidic sites (200-400 °C) and strong acidic sites (>400 °C).⁶⁷ From the curves in Figure 5, all the carriers showed a broad peak from 80 to 200 °C, demonstrating the existence of weak acidic sites. No desorption peak was found when the temperature raised over 200 °C. The acidity was increased first and then decreased with the La-doping. Compared with ZrO₂, the improved acidity for ZrLa_{0.2}O_x could be explained by that (1) t-ZrO₂ had a stronger acidity than m-ZrO₂,⁶⁸ (2) the higher specific surface area could allow more acidic sites to be exposed to the surface (Table 1). Based on the XRD results, the $m-ZrO_2$ was disappeared after La addition which could affect the crystal structure or the electronic feature and then change the surface acidic properties. The decreased acidic sites in ZrLaO_x might be attributed to the declined molar ratio of Zr with La addition. As a typical solid base, LaO_x had very few weak adsorption of NH_3 . Therefore, the doping could alter the acidic property of the carrier, which would affect the absorption for carbonyl group.



Figure 5. NH₃-TPD patterns ZrO₂, ZrLa_{0.2}O_x, ZrLaO_x, and LaO_x.



Figure 6. FT-IR spectra of furfural, fresh reduced $Co/ZrLa_{0.2}O_x$ catalyst, furfural absorbed on $Co/ZrLa_{0.2}O_x$, furfural absord on $ZrLa_{0.2}O_x$, butyraldehyde, and butyraldehyde adsorbed on $Co/ZrLa_{0.2}O_x$.

To further study the interaction between feedstock and carrier, the furfural adsorption experiments were carried out and characterized by Fourier transform infrared (FT-IR) spectroscopy (Figure 6). For the pure furfural sample, the characteristic of C=O vibration was at 1673 cm⁻¹. In the fresh catalyst, the band at 1630 cm⁻¹ was the characteristic of O-H banding mode which could be attributed to the stretching vibration mode of chemisorbed water.⁶⁹ This band presented in all the materials. When furfural absorbed on Co/ZrLa_{0.2}O_x, the characteristic of C=O vibration of furfural was disappeared at 1673 cm⁻¹. The band at 1751 cm⁻¹ was assigned to the physisorbed furfural.^{70,71} A new band was formed at 1572 cm⁻¹ which overlapped with the O-H banding mode. When furfural absorbed on ZrLa_{0.2}O_x, the

new band was at 1564 cm⁻¹. To identify whether this new band was related to the interaction between C=O bond and the catalyst, we took butyraldehyde with simple structure and functional group as the probe molecule. The standard band of C=O stretching vibration of butyraldehyde was at 1720 cm⁻¹, which was also disappeared and a new band was formed at 1553 cm⁻¹ over butyraldehyde absorbed Co/ZrLa_{0.2}O_x. This band probably be due to the absorption of C=O bond. Thus, the new band could be assigned to the absorption of C=O bond over both ZrLa_{0.2}O_x carrier and Co/ZrLa_{0.2}O_x catalyst. The reason for the decreased in wavenumbers over Co/ZrLa_{0.2}O_x could be related to the absorption of aldehyde group with Zr⁴⁺ (acidic site of ZrO₂) by lone pair electron rather than breaking the C=O, which could weaken C=O vibration.^{72,73} In Figure 6, a blue shift from 1564 cm⁻¹ to 1572 cm⁻¹ implied that Co could interact with C=O bond. With the establishment of this interaction, the electron could transform from the d-orbitals of Co to double bond π-orbitals to enhance the C=O bond.

Therefore, a possible reaction pathway was proposed: First, the C=O bond of furfural was interacted with both carrier and Co. Then, the C=O bond could be hydrogenated by hydrogen atoms and furfuryl alcohol was formed. In this catalyst, the small Co clusters could activate the hydrogen and C=O bond, while the carrier absorbed the C=O bond. They co-contributed to the interaction between catalyst and reactant, which can improve the catalytic activity even at lower temperature.

3.5 The effect of surfactant on the catalyst

Except for the doped ratio, the surfactant have a significant influence on the catalytic property. To understand the function of surfactant, we compared the properties of Co/ZrLa_{0.2}O_x-N with Co/ZrLa_{0.2}O_x through the XRD, BET, TEM, H₂-TPD, NH₃-TPD and XPS. Basically, from Figure S2d, the same phase (t-ZrO₂) of the catalysts implied that the surfactant didn't change the crystal structure. However, the surfactant could affect the specific surface area and average particle size. Compared with ZrLa_{0.2}O_x, the specific surface area of ZrLa_{0.2}O_x-N was decrease from 125.3 m²g⁻¹ to 107.9 m²g⁻¹ (Table 1). If no surfactant was used, the specific surface

area of catalyst was declined from 53.3 m²g⁻¹ to 15.5 m²g⁻¹ with the Co loading. As mentioned above, the carrier without surfactant could have lower stability and will sintered during Co loading. From the TEM image (Figure 2h), the morphology of the $Co/ZrLa_{0.2}O_x$. N was similar to the $Co/ZrLa_{0.2}O_x$. The poor contrast limited the recognition of Co from the carriers. However, the TEM images revealed an increase in the carrier size over the ZrLa_{0.2}O_x-N and the average particle size of Co over ZrLa_{0.2}O_x-N was increased form 1.1 nm to 5.9 nm by O₂ titration measurement, which was the largest in our catalysts. From the H₂-TPD result in Table 2, the SMSI was declined without the surfactant modification, and the H₂ adsorption was increased from 0.503 mmol g⁻¹ to 0.608 mmol g⁻¹. The interaction was weakened, thereby leading to much larger average particle size. From XPS spectra in Figure 4, the binding energy of both La 3d and Zr 3d in Co/ZrLa_{0.2}O_x-N were higher than that in Co/ZrLa_{0.2}O_x, indicating that the carrier without surfactant was more saturated. Most Co species in Co/ZrLa_{0.2}O_x-N revealed free Co particles. The acidity of ZrLa_{0.2}Ox-N was similar to ZrLa_{0.2}Ox, demonstrating the surfactant had almost no influence on the acidic sites (Figure S3). Thus, we speculated that the surfactant could improve the SMSI to achieve the highly dispersed Co nano-clusters.

3.6 The extension of the catalyst system

3.6.1 Hydrogenation over various doped Co/ZrREO_x catalysts

Other rare earth metals could also be doped into Zr matrix and worked for furfural conversion (Table 4). When different rare earth metals were added, they revealed the similar t-ZrO₂ crystal structure. No diffraction peak of Co was found in the catalysts as presented in Figure S3. It was worth mentioning that under the same ratio of doping metal, the Co average particle size was almost decreased with the increase of rare earth metals ions radius (La³⁺ > Pr³⁺ \approx Nd³⁺ > Ce⁴⁺). All the catalysts revealed good catalytic activity, and the conversion of furfural to furfuryl alcohol was higher than 90% under the selected conditions. The average particle size could affect the catalytic activity. Small Co nanocluster showed the best catalytic performance while the large average particle size led to the poor selectivity and conversion.

14010 111						
Entry	Catalyst	Average	Conversion (%) –	Yield (mol%)		
		size (nm) ^b		FA	THFA	
1	Co/ZrCe _{0.2} O _x	2.8	90	85	5	
2	Co/ZrPr _{0.2} O _x	2.2	94	89	5	
3	Co/ZrNd _{0.2} O _x	2.0	95	90	5	

Table 4. Hydrogenation over different rare earth doped Co/ZrRE_{0.2}O_x catalysts.^a

(a) Reaction conditions: 100 mg substrates, 50 mg Co/ZrLa_{0.2}O_x catalyst in 10 mL water, 80 °C, 2 MPa H₂, 2 h. (b) The average particle size was measured by O₂ titration.

3.6.2 Hydrogenation of biomass derived aromatic aldehydes and ketones

Other typical aromatic aldehydes and ketones were also tested as substrates under 40 °C and 2 MPa H_2 for 10 h. As shown in Table 5, 5-hydroxymethyl furfural, the product of hydrolysis of hexose over acid, could be hydrogenated to 2,5-dihydroxymethyl furan equivalently. Benzaldehyde and acetophenone were tested as model compounds of lignin derived aldehydes and ketones. The conversion both reached 100% yield to corresponding alcohol without any saturation of aromatic rings. These results revealed that this catalyst was efficient for hydrogenation of aromatic aldehydes and ketones at near ambient temperature.

Entry	Substrates	Conversion (%)	products	Selectivity (%)
1	но	100	но Он	100
2	0	100	ОН	100
3	° N	100	OH	100

Table 5. Hydrogenation of biomass derived aromatic aldehydes and ketones^a

(a)Reaction conditions: 100 mg substrates, 50 mg Co/ZrLa $_{0.2}$ O_x catalyst in 10 mL water, 40 °C, 2 MPa H₂, 10 h.



3.7 Recycling experiments



Figure 7. The effect of recycle time on the catalytic performance of the Co/ZrLa_{0.2}O_x catalyst.

Catalyst stability is an important parameter to evaluate its performance, which is crucial for large scale applications. Based on the above results, $Co/ZrLa_{0.2}O_x$ catalyst exhibited the best catalytic activity and was employed to investigate the stability at 80 °C for 2 h in water and 2 MPa H₂. As shown in Figure 7, the $Co/ZrLa_{0.2}O_x$ can be used for 4 times without apparent loss of selectivity. 95% of furfuryl alcohol selectivity remained in the whole recycling tests. The conversion slightly decrease which was not less than 90% at the run of 4. The used catalyst was analyzed by XRD. As shown in Figure S4, there was not obvious difference between the fresh and used catalyst. Determined by O₂ titration, the Co average particle size after reaction was 2.0 nm. The results illustrated that the catalytic activity was stable and efficient for the selective hydrogenation of furfural.

4. Conclusion

In summary, rare earth metals (including La, Pr,Nd, and Ce) doped ZrO₂ was prepared by surfactant-assisted co-precipitation/hydrothermal crystallization method and used to load Co by simple impregnation method. The rare earth metal doping Page 25 of 29

ACS Catalysis

could affected the crystal structure of catalysts, dispersed Co nanoparticles by strong metal-support interactions (SMSI) and increased the acidic sites. The adsorption mechanism exhibited that both carrier and Co adsorbed the carbonyl groups. The surfactant addition during support preparation also improved SMSI to stabilize the catalyst and increase Co dispersion. Furfural was hydrogenated to furfural alcohol in water with up to 95% yield over Co/ZrLa_{0.2}O_x at 40 °C, 2 MPa H₂ in 10 h. Other typical aromatic aldehydes and ketones (such as 5-hydroxymethyl furfural, benzaldehyde and acetophenone) were all completely hydrogenated to corresponding alcohols. Therefore, this rare earth metal oxides doped ZrO₂ supported nano Co ternary catalyst showed a great potential in the hydrogenation reaction.

Supporting Information

The Supporting Information is available free of charge.

N₂ Adsorption–desorption isotherm, XRD, NH₃-TPD, H₂-TPD patterns of the samples and some experimental details.

Acknowledgments

This work supported from the NSFC (21572213), program for Changjiang Scholars and Innovative Research Team in University of the Ministry of Education of China and the Fundamental Research Funds for the Central Universities (wk 2060190040).

Reference

(1) Corma, A.; Iborra, S.; Velty, A. Chem Rev. 2007, 107, 2411-2502.

(2) Tuck, C. O.; Pérez, E.; Horváth, I. T.; Sheldon, R. A.; Poliakoff, M. *Science* **2012**, 337, 695-699.

(3) Nair, B. Int. J. Toxicol. 2000, 20, 23-50.

(4) Villaverde, M.; Bertero, N.; Garetto, T.; Marchi, A. Catal. Today 2013, 213, 87-92.

- (5) Okamoto, M.; Hirao, T.; Yamaai, T. J. Catal. 2010, 276, 423-428.
- (6) Kong, X.; Chen, L. Appl. Catal., A 2014, 476, 34-38.
- (7) Sitthisa, S.; Resasco, D. E. *Catal. Lett.* **2011**, 141, 784-791.
- (8) Taylor, M. J.; Durndell, L. J.; Isaacs, M. A.; Parlett, C. M.; Wilson, K.; Lee, A. F.; Kyriakou, G. *Appl. Catal.*, *B* **2016**, 180, 580-585.

(9) Yuan, Q.; Zhang, D.; van Haandel, L.; Ye, F.; Xue, T.; Hensen, E. J.; Guan, Y. J.
Mol. Catal. A: Chem. 2015, 406, 58-64.
(10) Srivastava, S.; Mohanty, P.; Parikh, J. K.; Dalai, A. K.; Amritphale, S.; Khare, A.
K. Chin. J. Catal. 2015, 36, 933-942.
(11) Wei, S.; Cui, H.; Wang, J.; Zhuo, S.; Yi, W.; Wang, L.; Li, Z. Particuology 2011,
9, 69-74.
(12) Li, H.; Luo, H.; Zhuang, L.; Dai, W.; Qiao, M. J. Mol. Catal. A: Chem. 2003,
203, 267-275.
(13) Yang, X. W.; A.; Qiao, B.; Li, J.; Liu J.; Zhang. Acc. Chem. Res. 2013, 46, 1740-1748.
(14) Zhang, X.; Shi, H.; Xu, B. Q. Angew. Chem. Int. Ed. 2005, 44, 7132-7135.
(15) Liu, W.; Zhang, L.; Yan, W.; Liu, X.; Yang, X.; Miao, S.; Wang, W.; Wang, A.;
Zhang, T. Chem. Sci. 2016, 7, 5758-5764.
(16) van der Lee, M. K.; van Dillen, J.; Bitter, J. H.; de Jong, K. P. <i>J. Am. Chem. Soc.</i> 2005 , 127, 13573-13582.
(17) Wang, Z.J.; Skiles, S.; Yang, F.; Yan, Z.; Goodman, D. W. Catal. Today 2012, 181, 75-81.
(18) Melaet, G.; Lindeman, A. E.; Somorjai, G. A. Top. Catal. 2014, 57, 500-507.
(19) Yang, J.; Tveten, E. Z.; Chen, D.; Holmen, A. Langmuir 2010, 26, 16558-16567.
(20) Rane, S.; Borg, Ø.; Rytter, E.; Holmen, A. Appl. Catal., A 2012, 437, 10-17.
(21) Riva R · Miessner H · Vitali R · Del Piero G <i>Appl. Catal.</i> A 2000 196
111-123
(22) Lee L. Burt S. P. Carrero, C. A. Alba-Rubio, A. C. Ro, I. O'Neill, B. I. Kim
H L Lackson D H \cdot Kuech T F \cdot Hermans L <i>L Catal</i> 2015 330 19-27
(23) Turlier P : Martin G React Kinet Catal Lett 1982 21 387-390
(24) Chen K : Fan V : Van O L Catal 1997 167 573-575
(25) Vamaguchi T. Ton. Catal 1004 20, 100, 217
(26) Wu V Vie H · Tian S · Tsubaki N · Han V · Tan V I Mol Catal A · Cham
2015 206 254 260
2013, 590, 234-200. (27) Dark S. H.: Chun D. H.: Kim S. H. Kongan I. Cham. Eng. 2011, 28, 402, 408
(27) Faik, S. H., Chull, B.H., Killi, S. H. Korean J. Chem. Eng. 2011, 26, 402-406.
(28) Zhao, Z., Ran, J. <i>Appl. Calal.</i> , A 2015 , 505, 77-85.
(29) Xu, G. Y.; Guo, J. H.; Qu, Y. C.; Zhang, Y.; Fu, Y.; Guo, Q. X. Green Chem.
2010, 18, 5510-5517. (20) Takaguahi T. Eugelkowa, S.N., Irona, M. I. Catal 2001, 202, 14, 24
(30) Takeguchi, T.; Furukawa, S.N.; Inoue, M. J. Catat. 2001, 202, 14-24.
(31) Hernandez-Kamirez, E.; Wang, J.; Chen, L.; Valenzuela, M.; Dalal, A. Appl. Surj.
Sci. 2017, 599, 77-65.
(32) Gong, Y., Chen, H., Chen, Y., Cui, X., Zhu, Y., Zhou, A., Shi, J. <i>Microporous</i>
Mesoporous Maler. 2013, 175, 112-120. (22) Naily M. A. Michen, D. C. Dubay, A. Callaida Sturf 2009, 217, 224, 228
(33) Naik, M. A.; Mishra, B. G.; Dubey, A. Couolas Surf. 2008, $517, 234-238$.
(54) Stefanic, G.; Grzeta, B.; Nomura, K.; Irojko, K.; Music, S. J. Alloys Compd.
2001 , <i>527</i> , 151-160.
(35) Hussein, G. A. J. Anal. Appl. Pyrolysis 1996, 37, 111-149.
(36 Chen, Y.Z.; Liaw, B.J.; Kao, C.F.; Kuo, J.C. Appl. Catal., A 2001, 217, 23-31.
(37) Hou, T.; Yu, B.; Zhang, S.; Zhang, J.; Wang, D.; Xu, T.; Cui, L.; Cai, W. Appl.
<i>Catal., B</i> 2015 , 168, 524-530.

1	
2	
3	(38) Wang, D.; Astruc, D. Chem. Soc. Rev. 2017, 46, 816-854.
4	(39) Chirik, P. J. Acc. Chem. Res. 2015, 48, 1687-1695.
5	(40) Tokmic, K.; Jackson, B. J.; Salazar, A.; Woods, T. J.; Fout, A. R. J. Am. Chem.
6	Soc. 2017, 139, 13554-13561.
/	(41) Audemar M : Ciotonea C : De Oliveira Vigier K : Rover S : Ungureanu A :
8	Drazei D. Durnitain M. Kalang F. Chan Charles 2015 , 0, 1995, 1901
9	Dragoi, B.; Dumitriu, M.; Jerome, F. ChemsusChem 2015, 8, 1885-1891.
10	(42) Rösler, S.; Obenauf, J.; Kempe, R. J. Am. Chem. Soc. 2015, 137, 7998-8001.
11	(43) Jacobs, G.; Das, T. K.; Zhang, Y.; Li, J.; Racoillet, G.; Davis, B. H. Appl. Catal.,
12	A 2002 , 233, 263-281.
15	(44) Xiong H F · Thang Y H · Li I I · Gu Y Y I Cent South Univ Technol
14	1004 11 414 410
15	2004, 11, 414-418.
17	(45) Zhu, S.H.; Gao, X.; Zhu, Y.L.; Cui, J.L.; Zheng, H.Y.; Li, Y.W. Appl. Catal., B
18	2014 , 158, 391-399.
19	(46) Houlberg, K.; Bøjesen, E. D.; Tyrsted, C.; Mamakhel, A.; Wang, X.; Su, R.;
20	Besenhacher F. Iversen B.B. Cryst Growth Des 2015 15 3628-3636
21	(47) Klingenberg D: Vennice M A Chem Mater 1006 8 2755 2769
22	(47) Kingenberg, B., Vannice, M. A. Chem. Maler. 1990, 8, 2733-2708.
23	(48) Jia, L.; Fang, K.; Chen, J.; Sun, Y. <i>React. Kinet. Catal. Lett.</i> 2008 , 93, 351-358.
24	(49) Štefanić, G.; Musić, S. Croat. Chem. Acta 2002, 75, 727-767.
25	(50) Garvie, R.; Hannink, R.; Pascoe, R. Nature 1975, 258, 703-704.
26	(51) Li X · Li D · Tian H · Zeng L · Zhao Z J · Gong J Appl. Catal. B 2017 202
27	(e) 21, 11, 21, 21, 11, 2018, 21, 2100, 201, cons, or upper comm, 2 2011, 202,
28	(50) D C E (1) D L (C) C 1040 (0, 1720, 174(
29	(52) Brunauer, S.; Emmett, P. J. Am. Chem. Soc. 1940, 62, 1/32-1/46.
30	(53) Chen, L.; Zhu, Q.; Wu, R. Int. J. Hydrogen Energy. 2011, 36, 2128-2136.
31	(54) Liu, Y.; Hanaoka, T.; Miyazawa, T.; Murata, K.; Okabe, K.; Sakanishi, K. Fuel
32	Process. Technol. 2009, 90, 901-908.
33	(55) Men Y · Yang M Catal Commun 2012 22 68-73
34	(55) Mich, T., Tung, M. Cutut. Commun. 2012, 22, 00-75.
35	(50) Liu, Y., de Tymowski, B., Vigneron, F., Florea, I., Ersen, O., Meny, C., Nguyen,
36	P.; Pham, C.; Luck, F.; Pham-Huu, C. ACS Catal. 2013, 3, 393-404.
37	(57) Marcos, F.; Lucrédio, A.; Assaf, E. RSC Adv. 2014, 4, 43839-43849.
38	(58) Mariscal, R.; Maireles-Torres, P.; Ojeda, M.; Sádaba, I.; Granados, M. L. Energy
39	Environ Sci 2016 9 1144-1189
40	(50) Wowerko E M I Dohum Sei Deut A: Dohum Chom 1071 0 2702 2715
41	(59) we we ka, E. M. J. Folym. Sci. Fart A. Folym. Chem. 1971, 9, 2705-2715.
42	(60) Ma, Y.F.; Wang, H.; Xu, G.Y.; Liu, X.H.; Zhang, Y.; Fu, Y. Chin. Chem. Lett.
43	2017 , 26, 1153-1158
44	(61) Tauster, S. Acc. Chem. Res. 1987, 20, 389-394.
45	(62) Bertella, F.; Concepción, P.; Martínez, A. Catal. Today 2017, 289, 181-191.
40	(62) Tauster S: Fung S: Baker R: Horsley I Science 1981 211 1121-1125
47	(4) Anders T. Dirmetti M. Derseid S. Derse N. Eine D. Dirme D. Narrenski
40	(64) Andana, T.; Plumetti, M.; Bensald, S.; Russo, N.; Fino, D.; Pirone, R. Nanoscale
49 50	<i>Res. Lett.</i> 2016 , 11, 1-9.
51	(65)Hou, J. G.; Yang, C.; Wang, Z.; Jiao, S. Q.; Zhu, H. M. RSC Adv. 2012, 2,
52	10330-10336
53	(66) Shi W Catal Lett 2013 143 732-738
54	(67) Kumar D. Srivestava V. C. Michro I. M. Energy Eucle 2015 20 2664 2675
55	(07) Kumai, r., Silvastava, v. C., Iviisina, i. IVI. Energy Fuels 2015 , 29, 2004-2075.
56	(68) de Souza, P. M.; Rabelo-Neto, R. C.; Borges, L. E.; Jacobs, G.; Davis, B. H.;
57	Graham, U. M.; Resasco, D. E.; Noronha, F. B. ACS Catal. 2015, 5, 7385-7398.
58	
59	
60	ACS Paragon Plus Environment

(69) Keresszegi, C.; Ferri, D.; Mallat, T.; Baiker, A. J. Catal. 2005, 234, 64-75.

(70) Zhang, W.; Zhu, Y.; Niu, S.; Li, Y. J. Mol. Catal. A: Chem. 2011, 335, 71-81.

(71) Dimas-Rivera, G.; de la Rosa, J.; Lucio-Ortiz, C.; De los Reyes Heredia, J.; González, V.; Hernández, T. *Materials* **2014**, *7*, 527-541.

(72) Sharma, R. V.; Das, U.; Sammynaiken, R.; Dalai, A. K. Appl. Catal., A 2013, 454, 127-136.

(73) Loffreda, D.; Delbecq, F.; Vigné, F.; Sautet, P. Angew. Chem., Int. Ed. 2005, 44, 5279-5282.

TOC Graphic



Zr

La

Co

