Synthesis and Catalytic Performance of a Dual-Sites Fe–Zn Catalyst Based on Ordered Mesoporous Al₂O₃ for Isobutane Dehydrogenation

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Abstract

Ordered mesoporous Zn/OMA-Fe materials were easily prepared via one pot evaporation induced self-assembly (EISA) method in combination with incipient wetness strategy. Dehydrogenation of isobutane to isobutene were carried out on these materials, the isobutane conversion of 50.7% and the yield of 37.8% were obtained over 13Zn/OMA-10Fe catalyst at 580 °C with 300 h⁻¹ GHSV. The synthesized materials with large specific surface areas and uniform pore sizes were characterized by XRD, N₂ adsorption–desorption, TEM, XPS, H₂-TPR, Mössbauer and NH₃-TPD. A portion of Fe species were highly dispersed on the support surface and others incorporated into Al₂O₃ frameworks, Zn species existed in the form of hexagonal ZnO phase. The total acidity of these catalysts was increased by the introduction of Zn, facilitating the conversion of isobutane. Moreover, the conversion of Fe species might play a major role in improving isobutene selectivity.

Graphical Abstract



Keywords Isobutane dehydrogenation · Zinc · Iron · Mesoporous alumina

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1 Introduction

Isobutene is extensively used as chemical intermediate for producing many kinds of industrial products, such as butyl rubber, para-xylene, MTBE (methyl tert-butyl ether) and methacrylonitrile [1, 2]. In the early industrialized production stages, fluidized catalytic cracking and naphtha steam cracking are two main ways to produce isobutene [3, 4]. However, along with the rapid development of petrochemical industry, the growing demand for isobutene follows, and the production came from such processes is insufficient. In addition, the C₄ hydrocarbon resources from petroleum cracking increased greatly in the recent years. These have resulted in considerable interest in direct dehydrogenation of isobutane to isobutene because of its lower energy demand, lower cost and higher selectivity [5, 6]. In this reaction, Cr and Pt based catalysts are the most widely studied catalysts, which has been commercialized in industrial production for decades [7–9]. However, some problems are still remained such as the pollution of Cr-based catalysts to environment or the higher cost of Ptbased catalysts, which will limit their further applications to some degree. Therefore, it is important for isobutane dehydrogenation to exploit benign and cheap catalysts. By comparison, the abundant and non-noble elements such as iron, nickel, molybdenum, vanadium and cobalt are very attractive candidates that can form various heterogeneous catalysts. Tian et al. reported the yield of isobutene over V-K/ γ -Al₂O₃ catalysts in the isobutane dehydrogenation improved significantly after sulfidation [10]. Wang et al. investigated the effects of support over Co-based catalysts for isobutane dehydrogenation, silica-supported catalysts with no acidity exhibited the best catalytic performance [11].

Recently, Fe-based catalysts are drawing great interest in alkanes dehydrogenation, which are environmentalfriendly and inexpensive [12, 13]. These studies focused on improving the catalytic activity of Fe-based catalysts by exploring various supports, preparation methods and pretreatments [14–16]. Yun et al. employed different silicate zeolites (ZSM-5, beta zeolite) as support for the dehydrogenation of propane, and found that isolated framework Fe sites played a key role in propane selectivity [14]. Xu et al. compared Fe/Al₂O₃ catalysts prepared by vapor deposition with impregnation method. The former presented a much higher activity in oxidative dehydrogenation of ethane [15]. Sun et al. investigated the impact of hydrogen reduction on Fe₂O₃/Al₂O₃ catalysts, which achieving 24% propane conversion and 83% propene selectivity [16]. However, these catalysts exhibited relatively low activity or deactivated rapidly. None of these can be compared to commercial catalysts at the reactivity levels. Therefore, to

afford high catalytic activity and stability on the green and economical Fe-based catalysts is still a challenging work.

Furthermore, it is well known that promoters could improve the catalytic property of catalysts in dehydrogenation of light alkanes [17, 18]. ZnO can be acted as a promoter in catalysis for the character of n-type semiconductor and strong interaction with other metal [19, 20]. Zhang et al. studied the catalytic performance on Zn-doped Pt/ZSM-5 catalyst in propane dehydrogenation, indicated that the introduction of Zn increased the Pt dispersion and the interaction of Pt with support, thus improved catalytic activity and stability [21]. Silvestre-Albero reported that PtZn/MCM-41 catalysts showed a superior behavior in isobutane dehydrogenation with 100% isobutene selectivity [22]. In addition, the results from DFT calculations showed the addition of Zn to Pt weakened C=C bond, which helped to increase isobutene selectivity [23].

In our previous work, ordered mesoporous material exhibited better catalytic stability than traditional support, but the activity was not satisfied [24, 25]. Herein, a series of Fe-Zn dual-sites catalysts based ordered mesoporous Al₂O₃ (OMA) were explored to catalyze the dehydrogenation of isobutane. First of all, OMA-Fe materials with different Fe content were facilely synthesized via evaporation induced self-assembly (EISA) strategy, then the loading of Zn via incipient-wetness impregnation method. The fresh and some used catalysts were characterized by XRD, N2 adsorption-desorption, H₂-TPR, Mössbauer and so on. Particular emphasis was focused on the interaction of metals, the forms of Fe (Zn) species and surface acidity of the catalysts. And all the characterizations were associated with relevant catalytic reactions. As a result, the inexpensive and pollutionfree catalyst of 13Zn/OMA-10Fe showed the promising prospect for dehydrogenation of light hydrocarbon.

2 Experimental

2.1 Catalyst Preparation

During the synthesis of Fe–Zn dual-sites catalysts, the main reagents included ferric nitrate (Fe(NO₃)₃·9H₂O, \geq 99.0%), zinc nitrate (Zn(NO₃)₂·6H₂O, \geq 99.0%), aluminum isopropoxide (C₉H₂₁AlO₃, \geq 98.0%), Pluronic P123 (EO₂₀PO₇₀EO₂₀, Mw = 5800), nitric acid (HNO₃, 67 wt%) and absolute ethanol (C₂H₅OH). All the chemicals were A.R. grade and directly used without purification.

OMA-Fe materials were synthesized via EISA strategy with fine control according to the previous literatures [26]. Typically, 1 g P123 was dissolved 20 ml absolute ethanol. Then *a* mmol Fe(NO₃)₃·9H₂O, *b* mmol aluminum isopropoxide (a+b=10 mmol) and 1.6 ml nitric acid was added. After 6 h of stirring, the mixed solution was shifted to a culture dish, then transferred the culture dish into a 60 °C drying oven for 2 days. Finally calcined at 600 °C with a ramping rate of 1 °C min⁻¹ for 5 h. The catalysts were denoted as OMA-xFe, where x refers to Fe/(Al+Fe) molar ratio in initial precursor.

Ordered mesoporous Zn/OMA-Fe materials were synthesis via incipient wetness method. The OMA-xFe materials were impregnated with the relevant amount of zinc nitrate solution and calcined at 600 °C for 5 h. The obtained catalysts were denoted as yZn/OMA-xFe, where y stands for wt% of ZnO.

For comparison, ordered mesoporous alumina (OMA) was prepared by the same via EISA strategy. And the 13Zn/ OMA material was prepared on the same incipient wetness method, where 13 stands for wt% of ZnO.

2.2 Catalytic Dehydrogenation

The experiments for isobutane dehydrogenation were conducted in fixed-bed. Before the test, the catalyst (900 mg) was sieved at 60–80 mesh, and loaded in quartz tube diluted with quartz grain. Then catalyst bed was programmed up to desire temperature (560–620 °C) under N₂ flow, pure isobutane gas was switched in fixed flow at gas hourly space velocity (GHSV) of 300 h⁻¹. The reactants and products were analyzed using gas chromatography equipped with a flame ionization detector and thermal conductivity detectors.

2.3 Characterization

The specific surface areas, pore volumes and average pore diameters were determined by N_2 adsorption and desorption on Autosorb-iQ analyzer.

X-ray diffraction (XRD) was operated on X'Pert Pro diffractometer system with Cu K α radiation ranging from 10.0 to 80.0° and 0.6 to 5.0°.

Transmission electron microscopy (TEM) was carried out on the TECNAIG 2 F20 instrument.

X-ray photoelectron spectroscopy (XPS) were performed on Thermon ESCALAB 250xi spectrometer. The binding energies were calibrated against at 284.8 eV of C1s.

 H_2 temperature-programmed reduction (H_2 -TPR) was performed on ChemBET Pulsar Analyzer. About 100 mg catalyst was loaded, pretreated at 600 °C in He flow for 45 min. After cooling to room temperature, then raised temperature to 800 °C in 10% H_2 -Ar mixed flow.

 NH_3 temperature-programmed desorption was performed on ChemBET Pulsar analyzer combined with mass spectroscopy. After being pretreated at 600 °C in He flow, the catalyst (150 mg) was adsorbed to saturation by NH_3 at 120 °C. The profile was detected from 50 to 600 °C.

The ⁵⁷Fe Mössbauer were measured by a MA-260 (Bench MB-500) Mössbauer spectrometer at room temperature and the Doppler velocity was calibrated against α -Fe foils.

3 Results and Discussion

3.1 Nitrogen Adsorption–Desorption Analysis

Nitrogen adsorption–desorption characterization is used to study textural properties of OMA-xFe and yZn/OMA-10Fe catalysts and the results are shown in Fig. 1. Each sample exhibited IV type isotherm with H1 hysteresis loop, indicated the presence of mesopore in these catalysts [27]. The textural properties of above samples were listed in Table 1. The specific surface areas and pore volumes of OMA-xFe materials were not clearly change (around 200 m² g⁻¹) with



Fig. 1 Nitrogen adsorption-desorption analysis of the fresh catalysts: (a) OMA-3Fe; (b) OMA-5Fe; (c) OMA-7Fe; (d) OMA-10Fe; (e) 5Zn/OMA-10Fe; (f) 7Zn/OMA-10Fe; (g) 10Zn/OMA-10Fe; (h) 13Zn/OMA-10Fe; (i) 20Zn/OMA-10Fe

Table 1 The textural data of the fresh catalysts

Samples	$S_{BET}(m^2~g^{-1})$	$V_{P} (cm^{3} g^{-1})$	d _P (nm)
OMA-3Fe	209.0	0.33	9.5
OMA-5Fe	207.1	0.32	9.5
OMA-7Fe	203.4	0.31	9.5
OMA-10Fe	205.3	0.32	9.5
5Zn/OMA-10Fe	186.7	0.31	9.6
7Zn/OMA-10Fe	184.6	0.29	9.5
10Zn/OMA-10Fe	190.4	0.35	9.5
13Zn/OMA-10Fe	183.7	0.30	9.5
20Zn/OMA-10Fe	178.8	0.36	9.6

the increment of iron content up to 10%, which implying similar pore structural properties of these OMA-xFe materials. It has been known larger surface area contributed to the dispersity of Fe active sites, which could restrain the metal sintering. Thus, the big specific surface areas of these fresh OMA-xFe catalysts were conducive to catalytic stability [28, 29]. Furthermore, it is reasonable that the specific surface areas of yZn/OMA-10Fe catalyst decreased slightly after the introduction of Zn, illustrating that it was successfully impregnated on the pore channel of OMA-10Fe materials [30].

3.2 XRD Analysis

For characterizing the pore symmetry and crystalline structure, the XRD patterns of all the fresh samples are displayed in Fig. 2. The low-angle XRD patterns of OMA-xFe (Fig. 2A) indicated that all these samples presented an intense (100) peak at 0.8° and a very weak (110) peak around 1.3°, which were the characteristics of P6mm hexagonal symmetry, indicating that these samples are all typical

of well-ordered mesoporous structure [27, 31]. Moreover, it should be noted that the diffraction peak around 0.8° and 1.3° was still maintained after the introduction of Zn, suggesting that the ordered mesoporous yZn/OMA-10Fe with different Zn contents were successfully synthesized. The wide-angle XRD patterns of abovementioned materials are shown in Fig. 2B. No diffraction peaks for Al₂O₃ or iron species were visible in the OMA-xFe materials, implying Fe species were highly dispersed on support surface or incorporated into amorphous Al₂O₃ frameworks [22, 32]. However, the hexagonal crystalline ZnO (ICDD No. 89-1397) was apparently observed on the yZn/OMA-10Fe catalysts more than 7%Zn and the diffracted intensity increased distinctly with increasing Zn content.

3.3 TEM analysis

TEM characterization is one of the most effective techniques to further confirm the ordered mesoporous structure of the samples. OMA-10Fe and 13Zn/OMA-10Fe were chosen as representatives of abovementioned OMA-xFe and yZn/ OMA-10Fe materials (Fig. 3). As we can see, these two materials both presented one-dimensional parallel channels along [1 1 0] (Fig. 3a, c) and hexagonal pores along [1 0 0] (Fig. 3b, d), which directly verified the presence of ordered meso-structure and accorded with SXRD and N₂ adsorption–desorption analysis.

3.4 XPS Analysis

The Fe (Zn) 2p XPS patterns of fresh catalysts are in Fig. 4. Fe $2p_{3/2}$ peaks for all the OMA-xFe catalysts appeared at 711.7 eV with a satellite peak around 719 eV. It demonstrated that Fe species were Fe(III), as proved by 13.5 eV between Fe $2p_{1/2}$ and $2p_{3/2}$ peaks in spin–orbital



Fig. 2 XRD patterns of the fresh catalysts: (a) OMA-3Fe; (b) OMA-5Fe; (c) OMA-7Fe; (d) OMA-10Fe; (e) 5Zn/OMA-10Fe; (f) 7Zn/OMA-10Fe; (g) 10Zn/OMA-10Fe; (h) 13Zn/OMA-10Fe; (i) 20Zn/OMA-10Fe



Fig. 3 TEM images of the fresh catalysts: a and b OMA-10Fe; c and d 13Zn/OMA-10Fe



Fig. 4 Fe2p (**A**) and Zn2p (**B**) XPS spectra of the fresh catalysts: (a) OMA-3Fe; (b) OMA-5Fe; (c) OMA-7Fe; (d) OMA-10Fe; (e) 5Zn/OMA-10Fe; (f) 7Zn/OMA-10Fe; (g) 10Zn/OMA-10Fe; (h) 13Zn/OMA-10Fe; (i) 20Zn/OMA-10Fe

splitting theory [33–35]. Moreover, the bands of Zn $2p_{3/2}$ were located at the BE = 1021.7 eV, in consistent with the standard Zn(II) [36, 37]. Significantly, the Fe $2p_{3/2}$ peaks of yZn/OMA-10Fe catalysts exhibited a slight negative

shift, while the Zn $2p_{3/2}$ peaks exhibited a diminutive positive shift. It suggested the very weak electron-transport between Fe and Zn species, and the two metals might may function independently in dehydrogenation reaction.

3.5 H₂-TPR Profiles

H₂-TPR experiment is an effective method for testing the reduction behaviors of the heterogeneous catalysts. TPR profiles of OMA-xFe and yZn/OMA-10Fe catalysts are shown in Fig. 5. As shown, all the OMA-xFe catalysts with different Fe contents exhibited similar profiles, which presenting three hydrogen reduction peaks. The low temperature region in 445–480 °C belong to the reduction of Fe_2O_3 to Fe_3O_4 , the high temperature region around 570 °C was linked with the reduction of Fe_2O_3 to FeO, and the higher reduction peak around 740 °C was the reduction to Fe [23, 38, 39]. After introducing 5% ZnO to OMA-10Fe catalyst, the TPR profile still exhibited three reduction peaks. However, it was worth noting that only one reduction peak appearing around 460 °C in the profiles of 7~20Zn/OMA-10Fe catalysts with the introduction of more zinc. Combining with the profile of 13Zn/OMA, the only reduction peak in 561 °C assigned to the reduction of Zn^{2+} [40]. It is speculated that the reduction of Fe³⁺ in Zn/OMA-10Fe catalysts was easily to Fe₃O₄ after doping more Zn, because its existence can promote the



Fig.5 H_2 -TPR profiles of the fresh catalysts: (a) OMA-3Fe; (b) OMA-5Fe; (c) OMA-7Fe; (d) OMA-10Fe; (e) 5Zn/OMA-10Fe; (f) 7Zn/OMA-10Fe; (g) 10Zn/OMA-10Fe; (h) 13Zn/OMA-10Fe; (i) 20Zn/OMA-10Fe; (j) 13Zn/OMA

 Table 2
 ⁵⁷Fe Mössbauer

 parameters of the
 catalysts before and after

 dehydrogenation

reduction of metal oxides deriving from the semi-conductor feature of ZnO itself [41].

3.6 Mössbauer Spectra

Figure S1 shows the ⁵⁷Fe Mössbauer spectra of fresh and spent catalysts. The associated fitting data are in Table 2. The ⁵⁷Fe Mössbauer spectra of OMA-10Fe catalyst displayed a doublet peak: the IS of 0.33 mm/s was characteristic of Fe^{3+} in octahedral site with content of 100%; Same phenomenon was also found in 13Zn/OMA-10Fe [42]. These results were well consistent with the conclusion in XPS analysis, the Fe species on the fresh OMA-xFe and yZn/OMA-10Fe catalysts existed in a form of Fe³⁺. However, after reaction at 620 °C, the spent OMA-10Fe displayed two doublet peaks. A doublet peak with IS of 0.41 mm/s was ascribed to Fe³⁺ in octahedral site (54%), and another with IS of 1.06 mm/s was assigned to Fe²⁺ in octahedral site (46%), suggesting that sectional Fe³⁺ was reduced by the dehydrogenation products during reaction [42, 43]. Besides, compared with the spent OMA-10Fe catalyst, the content of Fe²⁺ in the spent 13Zn/ OMA-10Fe decreased, which resulted from the reduction of Fe^{3+} in yZn/OMA-10Fe catalysts was more prone to Fe_3O_4 rather than further reduction to FeO and Fe. These results are accorded with the conclusion in H₂-TPR analysis.

3.7 NH₃-TPD Analysis

The catalytic activity of the catalyst is strongly related to surface acidic properties of the catalyst. The effects of Zn on the amount of acid sites of the yZn/OMA-10Fe catalyst are determined by NH₃-TPD and the corresponding profiles are depicted in Fig. S2. As we can see, the catalysts presented a broad asymmetric desorption peak at 50–600 °C, which indicating the different kinds of acidic sites on these catalysts. The peak located between 50 and 200 °C, 200–450 °C and > 450 °C, could be accredited to weak, medium and strong acidic sites respectively [28, 30, 44]. All the NH₃-TPD results are de-convoluted using Gaussian functions and the corresponding the amount of acidic sites are presented in Table 3. The total acid amount of OMA-xFe catalysts with different iron contents and pure OMA support was very similar, even the weak, medium and strong acid amount was

Sample	IS (mm/s)	QS (mm/s)	LW (mm/s)	Area (%)	Remarks
Fresh-OMA-10Fe	0.33	1.22	0.51	100	Fe ³⁺ in Oh
Fresh-13Zn/OMA-10Fe	0.33	1.22	0.47	100	Fe ³⁺ in Oh
Spent-OMA-10Fe	0.41	1.19	0.58	54	Fe ³⁺ in Oh
	1.06	1.91	0.58	46	Fe ²⁺ in Oh
Spent-13Zn/OMA-10Fe	0.41	1.20	0.63	69	Fe ³⁺ in Oh
	1.06	1.99	0.58	31	Fe ²⁺ in Oh

Table 3The acidic propertiesand the results of isobutanedehydrogenation over thecatalysts

Samples	The amo	ount of acidic s	sites (mmol g	Activity ^a	TOF ^b (h ⁻¹)	
	Weak	Medium	Strong	Total	$(\text{mmol } \text{g}^{-1} \text{min}^{-1})$	
OMA	0.042	0.023	0.010	0.075	11.8	_
OMA-3Fe	0.041	0.023	0.009	0.073	_	-
OMA-5Fe	0.042	0.024	0.009	0.075	_	-
OMA-7Fe	0.043	0.024	0.010	0.077	_	_
OMA-10Fe	0.045	0.025	0.009	0.079	115.3	31.6
5Zn/OMA-10Fe	0.085	0.055	0.017	0.157	229.9	31.8
7Zn/OMA-10Fe	0.091	0.063	0.017	0.171	260.4	34.2
10Zn/OMA-10Fe	0.093	0.064	0.018	0.175	272.2	33.4
13Zn/OMA-10Fe	0.098	0.069	0.019	0.186	304.5	36.5
20Zn/OMA-10Fe	0.102	0.071	0.019	0.192	291.9	31.6
13Zn/OMA	0.097	0.068	0.024	0.189	287.5	36.8

^aActivity was defined as mmol of produced isobutene per gram of catalyst per min

^bTOF was defined as total moles of isobutane converted/total moles of acid sites per hour

The activity and TOF was calculated over the isobutane dehydrogenation at T = 580 °C, GHSV = 300 h⁻¹

almost identical, suggesting the introduction of iron didn't increase the acidity of OMA-xFe catalysts. The three types of acid sites of OMA-xFe catalysts originated from surface coordinatively unsaturated Al sites on pure OMA support [45]. However, the amount of acid sites of yZn/OMA-10Fe catalysts significantly enhanced due to the introduction of Zn. The three types acidic amount of 5Zn/OMA-10Fe catalysts was almost twice that of OMA-10Fe catalysts. And with the increasing of Zn loadings, the amount of acid sites of these catalysts increased gradually. It is generally accepted that Zn species can provide acid sites, combined with XRD analysis, the increased acid sites of yZn/OMA-10Fe catalysts derived from ZnO crystal [46]. In addition, it was well established that the presence of total acidity could facilitate alkane conversion, which may be beneficial for the catalytic dehydrogenation of isobutane [47]. Therefore, the introduction of Zn on yZn/OMA-10Fe catalysts may have a promoting effect on the catalytic performance of isobutane dehydrogenation.

3.8 Catalytic Performance in the Isobutane Dehydrogenation

The reactivity of isobutane dehydrogenation over different OMA-xFe catalysts is shown in Fig. 6a. As we can see that the OMA-xFe catalysts with different Fe contents presented similar initial isobutane conversion and different initial isobutene selectivity. However, with increasing reaction time, the isobutane conversion of these catalysts slightly increased and isobutene selectivity enhanced rapidly, which may result from the partial conversion of Fe³⁺ to Fe²⁺. Finally, the isobutane conversion and isobutene selectivity of OMA-xFe catalysts was similar <u>at</u> 120 min time on stream suggesting that isobutane dehydrogenation within the scope of this paper. In

other words, the highly dispersed Fe_2O_3 species were excellent active sites for isobutane dehydrogenation. the optimal conversion of isobutane reached 36.6% and the selectivity of isobutene attained 64.8% at 620 °C over OMA-10Fe catalyst. Furthermore, isobutane conversion and isobutene selectivity increased gradually with time on stream, indicating the great stability of the OMA-10Fe catalyst.

Isobutane dehydrogenation is an endothermic reaction in thermodynamics, which need relatively high temperature to obtain excellent isobutene yield [48]. For exploring the influence of reaction temperature, the dehydrogenation reaction was carried out at 580-640 °C (Fig. 6b). The conversion of isobutane was 18.7% and the selectivity of isobutene was 76.9% at 580 °C after 30 min. With increasing the reaction temperature to 640 °C, the conversion of isobutane increased to 49.1% and selectivity of isobutene decreased to 55.2% at the same reaction time, which was very conformed to the characteristic of alkane dehydrogenation reaction [49]. In consideration of raising reaction temperature, too much undesired by-products followed. Furthermore, isobutane would suffer serious homogeneous conversion after the reaction temperature above 600 °C (Fig. S3). Thus, to minimize homogeneous reaction and by-products, 580 °C was selected to further determine the catalytic performance of yZn/OMA-10Fe catalysts.

The reactivity of isobutane dehydrogenation over different yZn/OMA-10Fe catalysts is shown in Fig. 6c. It could be seen that the 5Zn/OMA-10Fe catalyst exhibited a notably high isobutane conversion (37.2%) and isobutene selectivity (about 77%) at 580 °C after 30 min. With increasing the Zn contents, the isobutane conversion gradually increased to the maximum, then slightly decreased thereafter, however isobutene selectivity changed little. Over the 13Zn/OMA-10Fe catalyst, the isobutane



Fig. 6 The reactivity of isobutane dehydrogenation over the fresh catalysts: a OMA-xFe; b OMA-10Fe; c yZn/OMA-10Fe; d OMA and 13Zn/OMA

conversion reached 50.7%, the selectivity of isobutene attained 74.7%. The isobutane conversion and isobutene yield slowly declined with the increasing reaction time, which was due to the coke formation or the change of active species over the catalyst [50, 51].

In order to further investigate what species were active sites for isobutane dehydrogenation, we tested this reaction at 580 °C over pure OMA support and 13Zn/OMA catalyst as a contrast (Fig. 6d). It can be seen that the isobutane conversion and isobutene yield over pure OMA support were only 3.1% and 2.1%, respectively. It illustrated that ordered mesoporous alumina (OMA) was inactive to the dehydrogenation. When iron was introduced into OMA, the activity dramatically enhanced. For example, the isobutane conversion and isobutene yield over OMA-10Fe were 18.7% and 14.4%. In association with the XPS characterization and Mössbauer spectra of fresh OMA-Fe catalysts, Fe³⁺ species was concluded as probably active sites. In addition, with increasing reaction time, isobutene selectivity of OMA-xFe catalysts enhanced rapidly, which implied the conversion of Fe³⁺ to Fe²⁺ played an important role in improving isobutene selectivity.

In contrast to OMA. 13Zn/OMA showed better initial activity of isobutane dehydrogenation, the conversion was achieved about 55% and isobutene selectivity about 66%. Thus, ZnO can be deduced as a kind of active sites for isobutane dehydrogenation. In addition, the isobutane conversion of 13Zn/OMA-10Fe catalyst was 2.7 times that of OMA-10Fe catalyst at 580 °C after 30 min, indicating that ZnO was an effective promoter to the isobutane catalytic conversion, Zn^{2+} was indeed identified as another active site. In order to further understand the reactivity over different yZn/OMA-10Fe catalysts, the TOF values were calculated and listed in Table 3. TOF data indicated that the isobutane dehydrogenation activity depends on the acid sites to some extent. The maximum was obtained over 13Zn samples $(36.5-36.8 h^{-1})$ with higher total acid sites. Moreover, the activity decreased to 31.6 h^{-1} on 20Zn sample with the most acid sites, which implied that the acid sites from ZnO are not alone the active sites. It should be noted that the level of reactivity is usually the result of combined influence of multiple factors in heterogeneous catalytic system, which doesn't depend on a single factor, such as active component, catalyst acidity or the interaction of metal. Thus, the concept of "Activity" may be more accurate to reflect catalytic performance (Table 3). Compared with OMA support, the "Activity" of isobutene on OMA-10Fe catalyst showed noticeable growth. With the introduction of Zn, the "Activity" further improved up to the max of 13% Zn contents. These results intuitively reflected the level of catalyst performance over different catalysts.

3.9 The Characterizations of the Spent Catalysts

3.9.1 WXRD Analysis

The WXRD patterns of the fresh and corresponding spent catalysts are presented in Fig. S4. Compared with the fresh catalysts, the phase structure of spent OMA-10Fe and 13Zn/ OMA-10Fe catalyst was not changed. Moreover, there is no other iron carbide or Zn⁰ phase, illustrating that phase structure of Zn species was stable and the superficial Fe species were also highly dispersed during this dehydrogenation reaction.

3.9.2 XPS Analysis

The Fe 2p and Zn 2p XPS spectra of the fresh and corresponding spent catalysts are shown in Fig. 7. It can be observed that the Fe $2p_{3/2}$ peaks for the spent catalysts was 711.3 eV, which shifted 0.4 eV to lower BE values,

indicating a part of Fe^{3+} was transformed to Fe^{2+} [52]. However, compared with the fresh 13Zn/OMA-10Fe catalyst, the Zn 2p3/2 peak of the spent 13Zn/OMA-10Fe catalyst exhibited an obvious positive shift, which resulted from the enhancement of the binding energy, the increase of the electron cloud density surrounding Zn atom and suggesting the reduction of the surface ZnO [53]. Meanwhile, in the XPS spectra of O 1s, there is no distinction between O1s XPS spectra of OMA-10Fe and the spent OMA-10Fe (Fig. S5). However, the O1s binding energy of 13Zn/OMA-10Fe catalyst exhibited a visible positive shift after reaction, which further verifying some Fe³⁺ were transformed to Fe²⁺ and the presence of surface ZnO reduction. In order to clarify the change of Fe, Zn species in the dehydrogenation reaction, the XPS data was listed in Table 4. We can see that the mole ratio of Fe/(Fe+Al) in the Fresh-OMA-10Fe and Fresh-13Zn/OMA-10Fe catalyst surface was similar and less than the total mole ratio value (10%), which was due to sectional Fe species incorporated into Al₂O₃ frameworks. These results are accorded with the result in wideangle XRD analysis. Furthermore, after the dehydrogenation reaction, it was worth noting that the Fe content of support surface increased, Zn content of support surface decreased, indicating some Zn species might migrate into bulk phase and slight Fe species in Al₂O₃ frameworks move out to support surface. The above results implied the surface Fe and Zn



Fig. 7 Fe2p (A) and Zn2p (B) XPS spectra of the catalysts before and after dehydrogenation: (a) OMA-10Fe; (b) the spent OMA-10Fe; (c) 13Zn/OMA-10Fe; (d) the spent 13Zn/OMA-10Fe

Table 4The percentage ofFe, Zn, Al, O element and Fe/(Fe+Al) mole ratio	Sample	Fe (%)	Zn (%)	Al (%)	0 (%)	Mole ratio of Fe and Fe+Al (%)
	Fresh-OMA-10Fe	2.13	-	35.20	62.67	5.7
	Fresh-13Zn/OMA-10Fe	1.92	7.16	33.17	58.37	5.5
	Spent-OMA-10Fe	2.49	-	37.00	60.50	6.3
	Spent-13Zn/OMA-10Fe	2.46	5.80	34.15	57.59	6.7

species underwent reconstruction during dehydrogenation such as reduction by the gas phase products.

seldom encountered oligomerization under this experimental condition.

3.9.3 TG-DSC Analysis

As we all know, coking is usually the main reason for catalyst deactivation in alkane dehydrogenation process. The TG-DSC is a very efficient technique to analyze the coking amount and the characterization results are shown in Fig. 8. The TG curves presented downtrend with the increase of temperature, which was divided into two stages. In the first stage, a slight weight losses in TG curves up to 300 °C, ascribed to the loss of physically adsorbed water. The second stage, located in the 350-500 °C range, the weight losses belonged to the removal of coke. It was worth noting that the coke content in spent OMA-10Fe was only 1.9%, but in the spent 13Zn/OMA and 13Zn/OMA-10Fe catalysts was about 5%. Combined with the stability of these three catalysts, the reason of catalyst deactivation may caused by coke. In addition, the carbon balance value of the three spent catalysts changed in the range of 94–98%, which suggested the lost carbon was mainly existed in the form of coke and isobutene

4 Conclusions

A series of Fe-Zn dual-sites catalysts based ordered mesoporous Al₂O₃ were easily prepared via one pot evaporation induced self-assembly in combination with postimpregnation method, while the pure OMA support and 13Zn/OMA catalyst were utilized for comparison. The obtained materials possessed large specific surface areas, big pore volumes and uniform pore sizes. A part of Fe species were highly dispersed on support surface and the others incorporated into Al₂O₃ frameworks, Zn species existed in the form of hexagonal ZnO phase. Mössbauer analysis indicated that Fe species were in a form of Fe³⁺ in octahedral site in the fresh catalysts. During the reaction, sectional Fe^{3+} in octahedral site was reduced to Fe^{2+} in octahedral site by by-products of the dehydrogenation. The conversion of Fe species played an important role in improving isobutene selectivity. After the introduction Zinc, the total acidity of the catalysts was also enhanced, which was benefit



Fig. 8 TG-DSC curves of the spent catalysts and carbon balance analysis: **a** the spent OMA-10Fe; **b** the spent 13Zn/OMA-10Fe; **c** the spent 13Zn/OMA, and **d** carbon balance over the three catalysts

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Compliance with Ethical Standards

Conflict of interest All authors declare no conflicts of interest.

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