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1 **Isobutane dehydrogenation over high-performanced**
2 **sulfide V-K/ γ -Al₂O₃ catalyst: modulation of vanadium**
3 **species and intrinsic effect of potassium**

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20

21 **Abstract**

22 Compared with industrial used Pt- and Cr-based catalyst in dehydrogenation (DH) of light
23 alkanes, the sulfide V-K/ γ -Al₂O₃ catalyst reported in this study shows lower cost and toxicity,
24 and significant DH performance. The yield to isobutene reached as high as 52.9%, which is
25 among the highest reported to date. We attribute such high isobutene yield to the precise
26 modulation of polymerization degree for vanadium species via doping of potassium and
27 indicating that the synergy between vanadium species and acid sites is critical to enhance the
28 DH performance. Our previous work showed sulfidation promoted the increase of DH
29 performance for vanadium-based catalyst, and we go further in this study to explore the
30 correlation between increased range of DH performance and the added potassium. The
31 different loaded potassium leads to variation in sulfidation degree, affecting the properties of
32 vanadium species and acid properties consequently. The potassium was distributed uniformly
33 on surface of the sulfide vanadium-based catalyst and was predominantly bonded with the
34 vanadium species rather than with the γ -Al₂O₃ support. With increasing the potassium amount
35 from 0 to 3 wt.%, the acid amount kept decreasing, and some specific strong acid sites
36 appeared once adequate sulfur was introduced in the V-K/ γ -Al₂O₃ catalyst. The
37 characterization and DFT results both revealed that the doped potassium contributes to
38 regulating the vanadium species in the oligomeric state. The synergy between vanadium
39 species and acid properties was regulated by the added potassium simultaneously, and thus
40 the DH performance was enhanced. This study provides promising strategy for preparation of

41 environment-friendly model industrial DH catalyst.

42 **Keywords:** isobutane dehydrogenation, modulation, vanadium species, potassium, intrinsic
43 effect.

44 **1. Introduction**

45 Light alkenes have been widely used as building blocks in chemical industry to produce
46 various important compounds including polypropylene, propylene oxide, butyl rubber, methyl
47 methacrylate, and so on. In comparison with the low-selectivity and energy-inefficient
48 conventional methods like fluid catalytic cracking (FCC) and steam cracking of oil
49 byproducts, dehydrogenation (DH) of light alkanes is becoming an attractive on-purpose and
50 environmental friendly process to produce light alkenes [1-4]. Although Pt- and Cr- based
51 catalysts have been applied in commercial DH processes, the high-cost and environmental
52 concerns restricted their further application. While, vanadium-based catalysts are attracting
53 ever-increasing attention in the DH of alkanes due to the lower cost, less environmental
54 issues and considerably high activity [5-8]. Besides, the vanadium-based catalysts reduce
55 risks to environment and human health.

56 To modify the structure of DH catalysts and to enhance the DH performance, various
57 promoters were introduced in. Sn was commonly added in Pt-based catalysts, and its
58 promoting effect on both geometric and electronic aspects was extensively studied [1, 9-11].
59 It was reported that the Sn additives led to creation of smaller Pt ensembles by formation of
60 Pt-Sn alloy and/or partial coverage of Pt. Besides, the electron density of Pt increased after
61 the electrons transferred from tin to platinum atoms. Consequently, the structure-sensitive

62 side reactions like coking and hydrogenolysis were inhibited, and the olefins easily desorbed
63 from the surface of Pt-based catalysts. The Sn increased the selectivity to olefins, while the
64 conversion of alkanes decreased. The DH activity of Cr-based catalysts was known to be
65 influenced by alkali metals, but the promoting role of alkali metals is still under debate
66 [12-15]. The alkali metal promoters could assist the formation of CrO_3 complexes which
67 transformed to catalytically active Cr_2O_3 under reducing atmosphere [12, 13]. The acidity of
68 Cr-based catalyst was also modified, which inhibited side reactions like cracking and
69 isomerization. The activity and selectivity to product alkenes were consequently promoted.
70 On the other hand, Cavani et al. reported that the potassium added in the $\text{Cr}/\text{Al}_2\text{O}_3$ catalyst
71 led to the formation of potassium chromate, which consumed the dispersed Cr^{3+} active
72 species [14, 15]. The DH activity of isobutane was generally inhibited by the added
73 potassium. The potassium was also doped in vanadium oxide catalysts to modify the structure
74 and properties [16-19]. It was indicated that the terminal $\text{V}=\text{O}$ bond was weakened [16, 17].
75 The acid-base characteristic of the system was changed, which accounted for better
76 selectivity in propane ODH. However, the selectivity to propene increased at the expense of
77 propane conversion [16, 18, 19].

78 In our previous study, sulfur was first introduced in oxide vanadium-based DH catalysts,
79 and the DH performance was promoted remarkably. Different increased range of DH
80 performance was observed after sulfidation, however, what influence the increased range
81 remains to be determined [20]. Besides, the oligomeric vanadium species were also proven to
82 present the highest DH activity [6, 20]. How to modulate the vanadium species at the

83 oligomeric state in the complicated sulfide system are yet challenging subjects.

84 Based on the above issues, we report on the precise modulation of DH performance and
85 polymerization degree for vanadium species via doping of potassium in this study. The
86 intrinsic effect of potassium on synergy between vanadium species and acid sites was also
87 investigated deeply. The added potassium was generally considered to elevate the selectivity
88 to product alkenes, however, the DH activity was inhibited simultaneously [16, 18, 19]. Still
89 the challenge in this study is to maintain the DH activity at a high level after the addition of
90 potassium. The ultimate goal is to prepare an ideal environment-friendly DH catalyst with
91 both high yield and selectivity to isobutene.

92

93 **2. Experimental section**

94 **2.1 Preparation of catalyst**

95 A series of V-K/ γ -Al₂O₃ catalysts with the same amount of vanadium (13.5 wt.%) were
96 prepared by incipient wetness impregnation. Initially, NH₄VO₃ (Alfa Aesar Chemical Co.
97 Ltd., 99.9% purity) was dissolved in an aqueous solution of oxalic acid (Sinopharm Chemical
98 Reagent Co. Ltd., 99.5% purity), with a molar ratio of 1:2. Then different amount of KNO₃
99 (Sinopharm Chemical Reagent Co. Ltd., 99.0% purity) was added into the former solution
100 that serves as a precursor of potassium. Pseudo-boehmite (Zibo Lituo Composite Co. Ltd.)
101 was subsequently impregnated with the solution under mechanically stirring. Finally, the
102 mixture was dried in water bath at 70 °C for 4h, and then kept in oven at 120 °C for 12h. The
103 calcination of the catalyst was conducted at 550 °C for 10h in air with a heating rate of

104 2 °C/min. For further catalytic evaluation, the as-prepared catalysts were pelleted, crushed
105 and sieved with 20-60 mesh. As for the preparation of sulfide V-K/ γ -Al₂O₃ catalysts, the
106 oxide catalysts were pre-sulfided at 560 °C for 3h in a 5% H₂S/H₂ gas with a flow rate of 30
107 mL/min. The catalysts after sulfidation are denoted as xK-S, where “x%” is the nominal K₂O
108 content by weight.

109 **2.2 Characterization**

110 XRD measurements were performed using an X’Pert PRO MPD diffractometer, equipped
111 with Cu K α radiation (40 kV, 40 mA). Raman spectra were recorded on a Thermo Fisher
112 Scientific DXR Raman spectrophotometer at ambient conditions with an excitation
113 wavelength of 532nm. N₂ adsorption–desorption isotherms were recorded with a
114 Quantachrome Autosorb iQ3 Gas Sorption Analyzer at liquid nitrogen temperature. The
115 as-prepared catalysts were outgassed at 300 °C for 4h to remove the adsorbed impurities. The
116 morphology of sulfide vanadium-based catalyst was examined with a JEOL JSM-7900F
117 scanning electron microscope (SEM), and the distribution of the elements was measured by
118 EDS-SEM using JEOL-7900F SEM equipped with an Oxford Instruments X-MaxN
119 Energy-Dispersive Spectroscopy. The FT-IR spectra were recorded on a Nicolet 6700
120 spectrometer. The samples were put in the atmosphere of pyridine for adsorption with 24h,
121 then the physisorbed pyridine desorbed under vacuum at 150 °C for 2h. The spectra were
122 collected by accumulating 64 scans at a 4 cm⁻¹ resolution. NH₃-TPD was conducted on a
123 Micromeritics Autochem 2920 apparatus. During the NH₃-TPD test, the samples (0.1g) were
124 pretreated in a helium flow at 600 °C for 1h, and then the NH₃ was adsorbed on samples at

125 70 °C for 0.5h. After the adsorption, the gas was switched to helium and the physisorbed NH₃
126 was desorbed at 110 °C for 0.5h. The temperature then increased to 700 °C with a ramp of
127 10 °C/min. The NH₃-TPD signal was recorded with a TCD detector. Afterwards, the
128 calibration between the desorption peak area and various concentration of NH₃ was
129 performed on the same apparatus. The acid content was calculated according to this standard
130 curve. XPS was conducted on a Thermo Fisher ESCALAB 250 spectrometer with a
131 monochromatic Al K α source. The pass energy was 20eV, and the energy step size was set to
132 be 0.05eV. The XPS spectra were obtained under CAE mode operation, meaning that both the
133 energy resolution and pass energy remain constant during the scan. The binding energy of
134 C1s at 284.8 eV for adventitious carbon was adopted as the energy reference.

135

136 **2.3 Catalytic evaluation**

137 The DH activity was evaluated at atmospheric pressure and at 610 °C in a conventional
138 bench-scale fixed-bed reactor. Typically, 1.0 g of the catalyst with a 20-60 mesh size was
139 loaded in a stainless steel tubular reactor with an internal diameter of 10 mm and a length of
140 500 mm. As for the catalytic evaluation of sulfide vanadium-based catalysts, the as-prepared
141 oxide catalyst was first heated to 560 °C in 60min under N₂ with a flow rate of 20 mL/min.
142 The gas was then switched to 5% H₂S/H₂ of 30 mL/min, and kept for 3h at 560 °C.
143 Subsequently, the temperature was elevated to 610 °C, and the H₂/isobutane with a volume
144 ratio of 4:1 was introduced. The composition of products was analyzed online with an Agilent
145 7820A GC equipped with a flame ionization detector and a column of Al₂O₃. The conversion

146 of isobutane, selectivity to isobutene, and yield to isobutene were determined as follows:

147 (1) Conversion of isobutane = **Erreur !**

148 (2) Selectivity to isobutene = **Erreur !**

149 (3) Yield to isobutene = **Erreur !**

150 **2.4 DFT calculations**

151 The Vienna Ab initio Simulation Package (VASP) was used for the density functional
152 theory (DFT) calculations of the V-clusters [21, 22]. The geometry optimizations were
153 performed with the projector augmented wave (PAW) pseudopotential and the plane-wave
154 basis set with the cut-off energy of 500 eV [23]. Generalized gradient approximation with the
155 Perdew-Burke-Ernzerhof (PBE) form was used for the exchange-correction functional [24].
156 The Hubbard+U correction was used to describe the electronic on-site coulombic interactions
157 of V 3d orbital with the value of $U = 3.2\text{eV}$ [25]. Because periodic boundary condition was
158 used in VASP, the vacuum buffer spaces in three directions were set at least 12 Å. Atomic
159 structures were fully optimized until the forces were smaller than 0.02 eV/Å and the energy
160 was converged to less than 10^{-5} eV between two iteration steps.

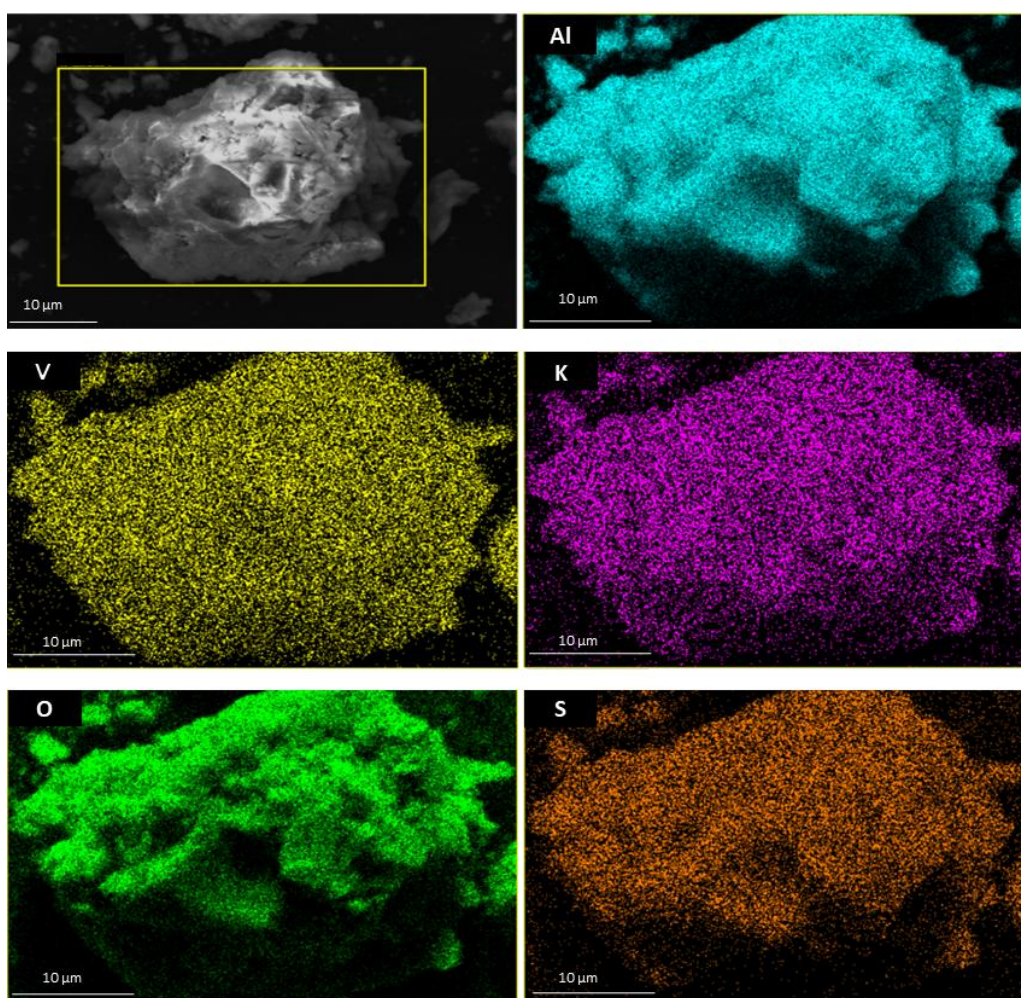
161 It is known that all the vanadium species exist in V^{4+} state during the preparation process
162 of catalysts due to the formation of the complex. The VO_4H_4 model was constructed to
163 represent the vanadium species in the preparation process. Besides, the vanadium loaded was
164 13.5 wt.% in this study, which mainly exist in polymeric state according to previous studies
165 [6, 26]. It is commonly accepted that polymeric vanadium clusters involve three to five

166 vanadium atoms [27]. The pentamer $V_5O_xH_y$ species were adopted in this DFT calculation.
167 The valence state of vanadium species also influenced the structure of vanadium species.
168 XPS was conducted to confirm the valence state of vanadium and the V2p XPS spectra were
169 deconvoluted (Fig. S1). It is demonstrated that the average oxidation state was about 4.0.

170

171 3. Results and Discussion

172 3.1 Modulating vanadium species via potassium



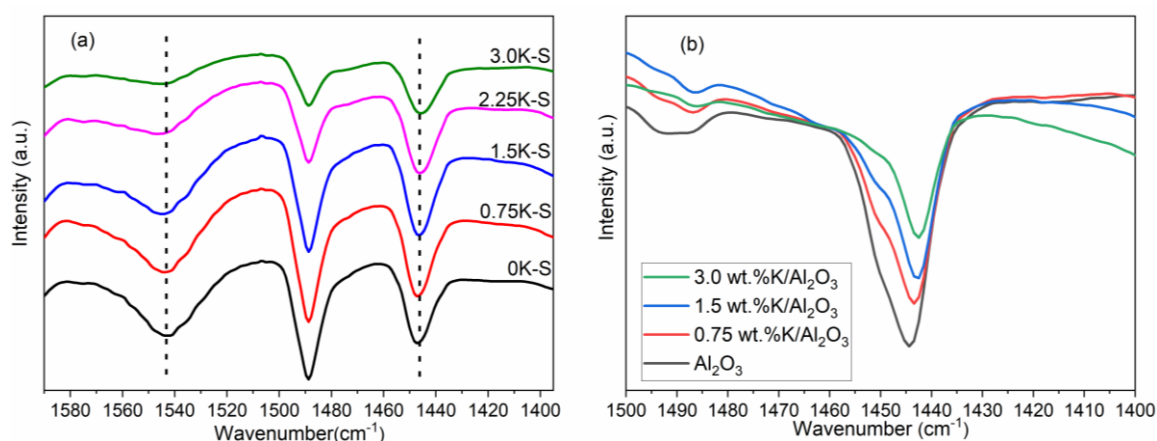
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174

Fig. 1 EDS-SEM images of sample 2.25K-S.

175 To realize the modulation of vanadium species by the doped potassium, it is crucial to
176 determine the existing form and bonding mode of potassium. EDS-SEM mapping was

177 performed to reveal the elements' distribution in sample 2.25K-S (Fig. 1). The results show
178 that both potassium and vanadium are distributed uniformly on sample 2.25K-S and no
179 obvious aggregation of specific species is observed. The potassium species might combine
180 with the Al₂O₃ support and/or vanadium species that require further experiments to determine
181 the bonding mode.

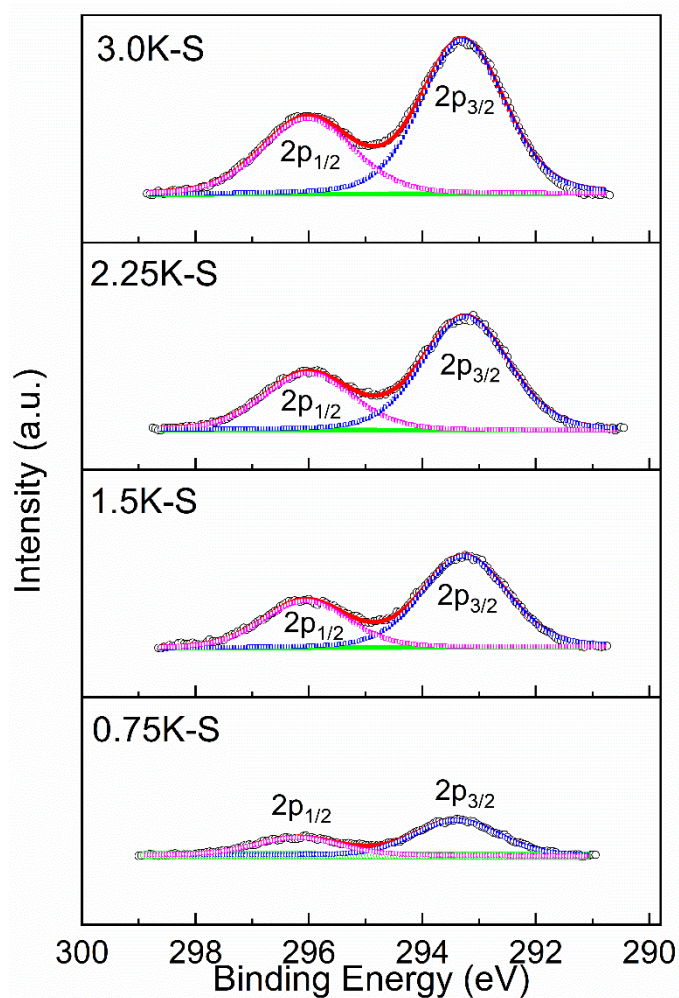


182
183 **Fig. 2 Py-FT-IR spectra of sulfide V-K/ γ -Al₂O₃ catalysts (a) and K/ γ -Al₂O₃ samples (b) with different**
184 **loading amount of potassium.**

185 As a traditional alkaline metal, the potassium would influence the acid properties of the
186 catalysts directly, and the distribution of potassium can be inferred by analyzing the variation
187 of acid properties. The acid type of sulfide vanadium-based catalysts was studied by FT-IR
188 using pyridine as a probe molecule (Fig. 2-a). Two bands at ~1542 and ~1445 cm⁻¹ are
189 present in the spectra of all samples and they are attributed to the pyridine adsorbed on
190 Brønsted and Lewis acid sites, respectively. The band at ~1490 cm⁻¹ is assigned to pyridine
191 co-adsorbed on both Lewis and Brønsted acid sites. It is commonly accepted that Lewis acid
192 sites on V/ γ -Al₂O₃ catalysts mainly originate from coordinative unsaturated Al³⁺ species
193 and/or V³⁺/V⁴⁺ species, while the Brønsted acid sites arise from V-OH groups [3, 28, 29].

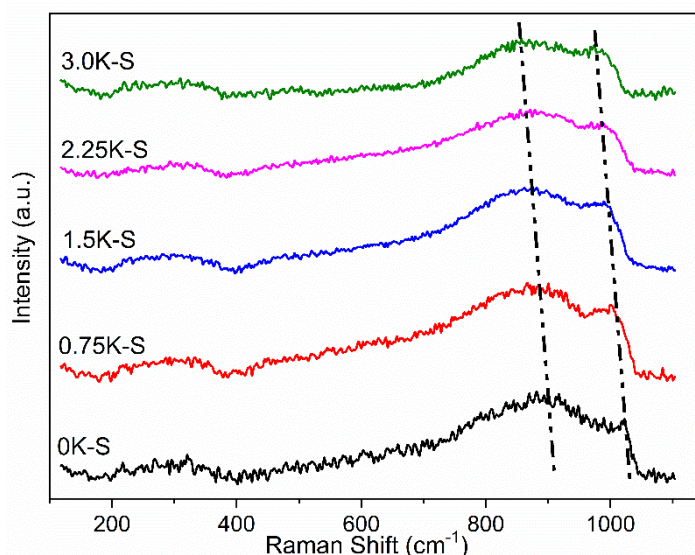
194 With potassium increase from 0 to 3 wt. %, the number of Lewis acid sites (NLS) changes
195 very little while the number of Brønsted acid sites (NBS) decreases visibly.

196 Additionally, different amount of potassium was directly loaded on bare γ -Al₂O₃ support,
197 and the Py-FT-IR spectra of K/ γ -Al₂O₃ samples are shown in Fig. 2-b. The peak at ~1445
198 cm⁻¹, which is attributed to the adsorption of pyridine on Lewis acid sites, is observed for all
199 samples. With increasing the potassium loading, the NLS is decreasing in comparison with
200 the pure γ -Al₂O₃. It is indicated that potassium could combine with γ -Al₂O₃ support directly
201 in the case of no vanadium, resulting in the NLS decrease. As Fig. 2-a shows, the NLS of
202 sulfide V-K/ γ -Al₂O₃ catalysts changes little while the NBS decreases obviously with the
203 increase of potassium. The above discussions jointly revealed that the potassium was inclined
204 to combine with vanadium species rather than with γ -Al₂O₃ in V-K/ γ -Al₂O₃ catalysts.



205
 206 **Fig. 3 Peak deconvolution for K2p XPS spectra of sulfide V-K/ γ -Al₂O₃ catalysts with different**
 207 **amounts of potassium.**

208 To further understand the bonding mode of potassium, the XPS analysis of the samples was
 209 carried out. The K2p XPS spectra for all samples are shown in Fig. 3. The peaks at binding
 210 energies of 293.1 eV and at 296.0 eV correspond at the K2p_{3/2} and K2p_{1/2} levels respectively
 211 and could be ascribed to K⁺ in potassium oxide [30, 31]. The K2p XPS and Py-FT-IR results
 212 jointly revealed that the potassium would bond with Brønsted acidic (V-OH) sites, which
 213 resulted in the formation of V-O-K/V-S-K bonds.



214

215 **Fig. 4 Raman spectra of sulfide V-K/ γ -Al₂O₃ catalysts with different amounts of potassium.**

216 The bond between V and K made it possible to modulate the vanadium species via doping

217 of appropriate potassium. Raman spectra were measured to reveal the influence of potassium

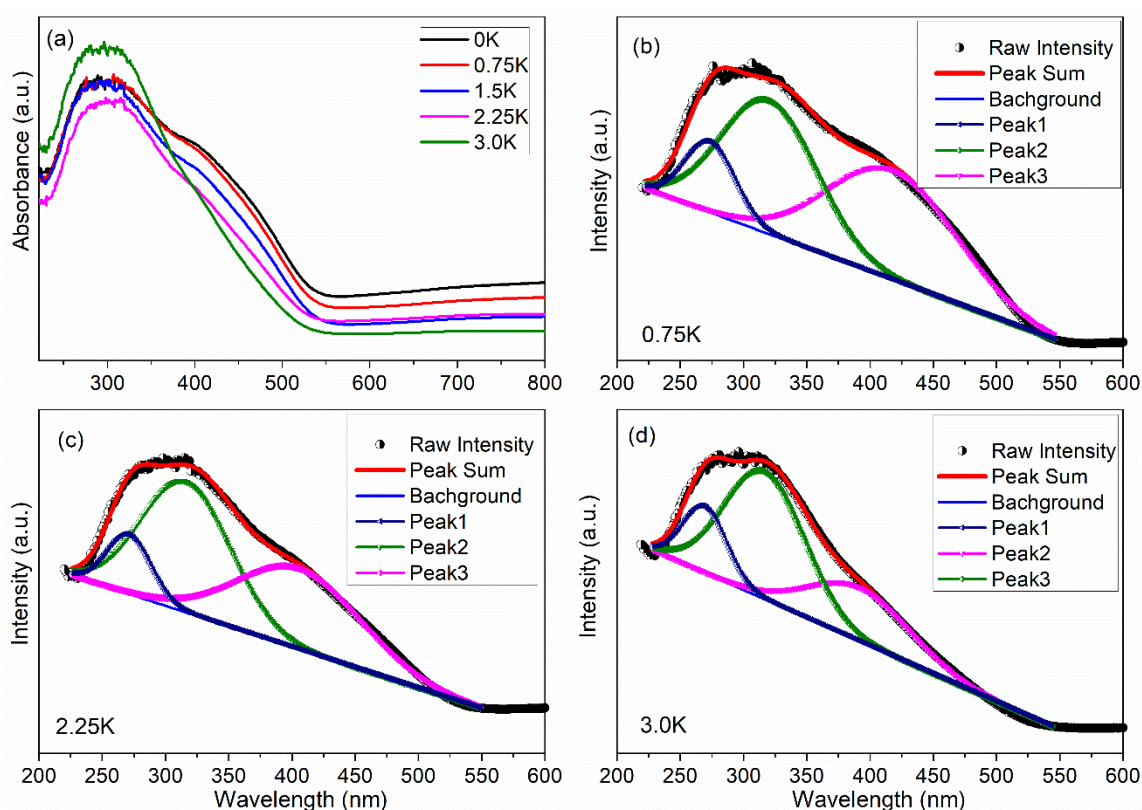
218 on the vanadium species. As shown in Fig. 4, two bands at around $\sim 1050\text{ cm}^{-1}$ and $\sim 900\text{ cm}^{-1}$

219 are observed, which are attributed to V=O/S and V-O-Al/V-S-Al vibrations, respectively [32,

220 33]. With the amount of potassium increased, the two characteristic Raman bands shift to

221 lower wavenumbers. The red-shift of the V=O bands is a signature for decrease of

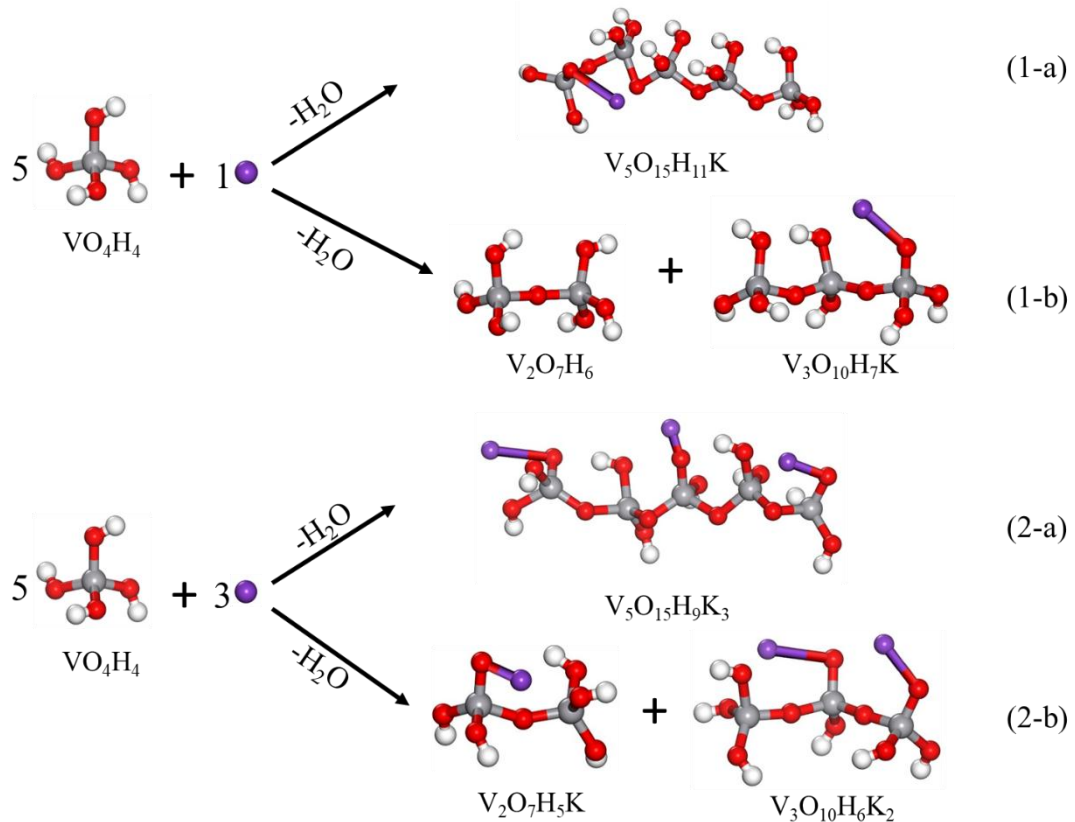
222 polymerization degree of vanadium species [34, 35].



223
 224 **Fig. 5 Diffuse reflectance UV-vis spectra of V-K/ γ -Al₂O₃ catalysts with different amounts of**
 225 **potassium (a), and peak deconvolution results for corresponding samples (b-d).**

226 Diffuse reflectance UV-vis spectra of V-K/ γ -Al₂O₃ catalysts were also recorded to show the
 227 specific changes in polymerization of vanadium species (Fig. 5). Two characteristic bands,
 228 including a broad band centered at ~300 nm and the other band at ~420 nm, could be
 229 observed for all the samples. After peak deconvolution, three peaks located at ~270 nm
 230 (Peak1), ~315 nm (Peak2) and ~420 nm (Peak3) were clearly shown for corresponding
 231 samples in Fig. 5(b-d), and the detailed deconvolution results were summarized in Table S1.
 232 It is commonly accepted that Peak1 and Peak2 are characteristic for monomeric and
 233 oligomeric vanadium species, while Peak3 corresponds to vanadium species with higher
 234 polymerization degree [36-38]. According to Table S1, as the potassium content increased, a
 235 progressive shift of Peak3 from 417.2nm to 391.1nm is observed, and the relative content of

236 Peak3 also decreases from 46.3% to 29.2%. Meanwhile, the content of Peak2 increases from
 237 41.9% to 55.1%. Obviously, the vanadium species transformed into oligomeric state
 238 progressively. The coherent Raman and UV-vis results reveal that the polymerization degree
 239 of vanadium species can be modulated gradually.



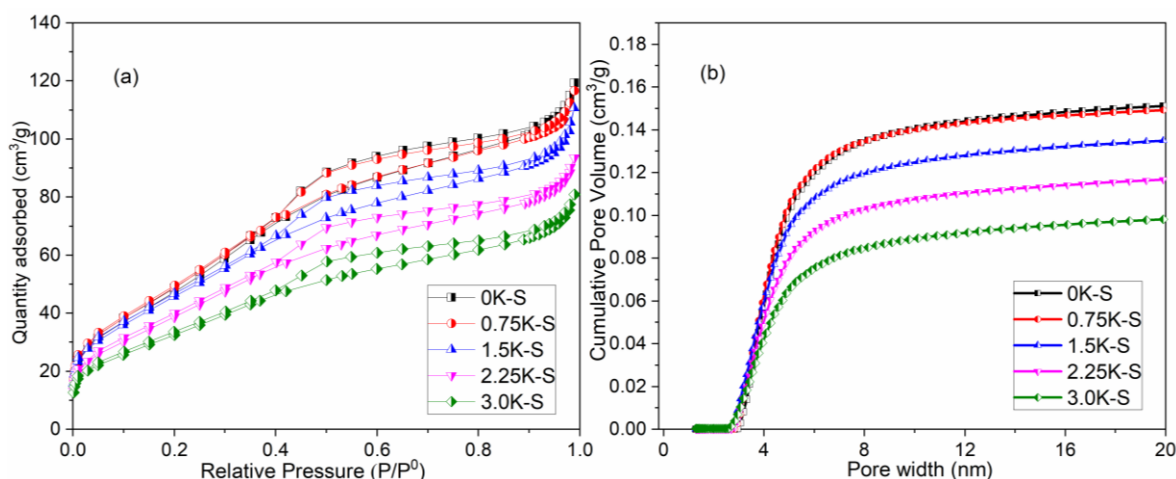
249 species were assumed to form either $V_5O_xH_y$ species, or trimer and dimer clusters. Different
250 amount of potassium was introduced during the formation processes, and the process is
251 schematically illustrated in Fig. 6. The energy change during the formation process were
252 calculated, as defined as $\Delta E = E_{\text{product}} - E_{\text{reactant}}$ (for more details concerning the calculation of
253 ΔE see Supporting Information).

254 According to the DFT calculations, ΔE_{1-a} and ΔE_{1-b} are 35.8 eV and 29.5 eV, respectively.
255 After the potassium atoms were increased to be three, ΔE_{2-a} and ΔE_{2-b} are calculated to be 55.9
256 eV and 24.4 eV. As shown, ΔE_{1-b} is lower than ΔE_{1-a} , and ΔE_{2-b} is also lower than ΔE_{2-a} . It
257 indicates that the VO_4H_4 species are easier to transform into trimer and dimer clusters than
258 pentamer vanadium species after potassium was added. Furthermore, ΔE_{2-b} is lower than
259 ΔE_{1-b} , confirming that the increased potassium content is beneficial for the formation of
260 trimer and dimer clusters. The DFT results clarify that potassium decreases the
261 polymerization degree of vanadium species, and the polymerization degree keeps decreasing
262 with increasing the amount of potassium. The DFT data are consistent with the experimental
263 results, further confirming that the vanadium species can be modulated by the doped
264 potassium.

265 **3.2 Effect of potassium on textural and acid properties**

266 The doped potassium contributes to modulate the vanadium species. Simultaneously, the
267 potassium would also influence acid and textural properties of sulfide V-K/ γ - Al_2O_3 catalyst.
268 The XRD patterns of samples with different potassium amount were measured, and the effect
269 of potassium on the dispersion of vanadium species was evaluated (Fig. S2). All samples

270 show three peaks at 36.7°, 45.7° and 66.5°, which are characteristic of γ -Al₂O₃ and consistent
 271 with the database standard (JCPDS No. 10-0425). This indicates that the added potassium
 272 does not cause aggregation of active vanadium species and formation of new phases.



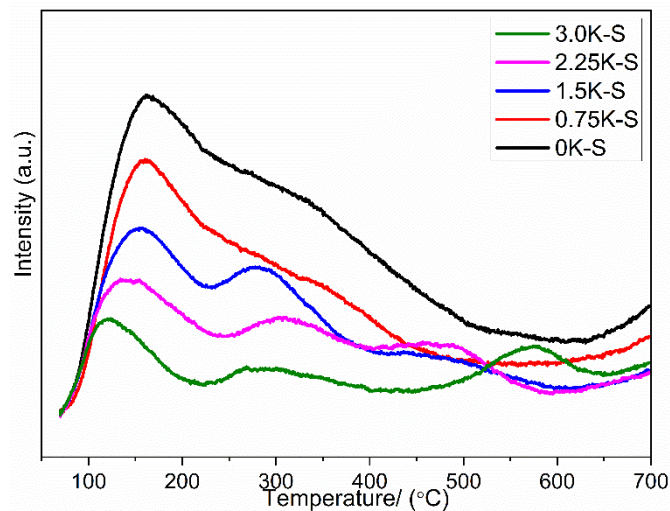
273
 274 **Fig. 7 N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of sulfide V-K/ γ -Al₂O₃**
 275 **catalysts with different amounts of potassium.**

276 **Table 1. Catalytic performance and physicochemical properties of different samples.**

Sample	S _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	Pore Width (nm)	Acid content (μ mol g ⁻¹)	Y _{Isobutene-1h} (wt.%)	S/V atomic ratio
0K-S	185	0.15	3.4	290.9	41.2	0.58
0.75K-S	180	0.15	3.4	221.9	50.4	0.64
1.5K-S	174	0.13	3.3	188.0	52.8	0.69
2.25K-S	143	0.11	3.2	148.9	52.9	0.85
3.0K-S	119	0.09	3.1	63.1	49.8	0.72

277 N₂ adsorption-desorption isotherms for all catalysts show the influence of potassium on the
 278 specific surface area and pore volume (Fig. 7-a). Type IV isotherms were obtained for all
 279 samples and the corresponding parameters are summarized in Table 1. With potassium

280 increasing from 0 to 3 wt.%, the BET surface area decreases from 185.4 (0K-S) to 119.2 m²
281 g⁻¹ (3K-S). The same trend is also observed for the pore volume (Fig 7-b). The pore volume
282 decreases with increasing the potassium loading, and the pore width is nearly the same. It was
283 demonstrated that potassium causes collapse of the pore structure, which resulted in a
284 decrease of both BET surface area and pore volume of catalysts [42, 43].

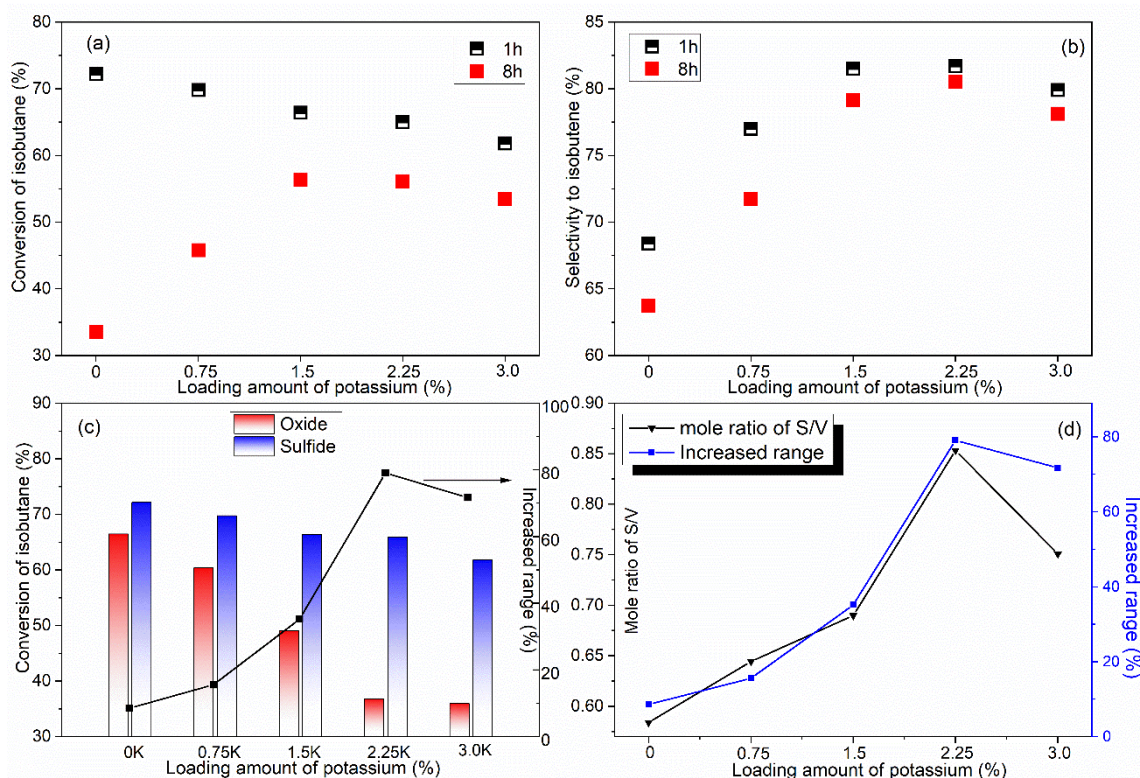


285
286 **Fig. 8 NH₃-TPD profiles of sulfide V-K/ γ -Al₂O₃ catalysts with different amounts of potassium.**

287 The variation of acid type for sulfide V-K/ γ -Al₂O₃ catalysts has already been illustrated in
288 Fig. 2-a. With potassium increase from 0 to 3 wt. %, the NLS changes very little while the
289 NBS decreases visibly. Besides, the NH₃ temperature-programmed desorption (NH₃-TPD)
290 was applied to show the effect of potassium on acid content and strength. As can be seen
291 from the NH₃-TPD profiles in Fig. 8, the acid amount keeps decreasing with an increase of
292 potassium loaded. The acid amount decreases from 290.9 μ mol/g (0K-S) to 63.1 μ mol/g
293 (3.0K-S) (Table 1). The peaks presented below 400 °C are attributed to the desorption of NH₃
294 from the weak and medium-strong acid sites of the catalysts. The strength of these two kinds
295 of acid sites decreased as the potassium increased. Some specific peaks above 400 °C
296 emerged for samples 1.5K-S, 2.25K-S and 3.0K-S, which originate from the desorption of

297 NH_3 from strong acid sites. In our previous work, it had been confirmed that the ionicity of
 298 V-S bonds is enhanced in comparison to that of V-O due to the lower electronegativity of
 299 sulfur, resulting in stronger interaction between VS_x species and NH_3 probe molecule [20].
 300 For samples 1.5K-S, 2.25K-S and 3.0K-S, the influence of potassium on acid strength
 301 gradually emerged after adequate sulfur was introduced in.

302 3.3 Precise promotion of dehydrogenation performance



303
 304 **Fig. 9 Evaluation of V-K/ γ -Al₂O₃ catalysts with different amounts of K in dehydrogenation reaction:**
 305 **Conversion of isobutane for sulfide catalysts (a), selectivity to isobutene for sulfide catalysts (b),**
 306 **increased range of conversion after sulfidation (c), and correlation between mole ratio of S/V and**
 307 **increased range of conversion (d).**

308 The above discussions show that the synergy between vanadium species and acid
 309 properties of vanadium-based catalysts can be influenced by the doped potassium, and the
 310 DH performance was affected accordingly. The DH performance for sulfide V-K/ γ -Al₂O₃

311 catalysts with different amount of potassium was evaluated using a conventional bench-scale
312 fixed-bed reactor for 8 hours. The DH performance selected at time-on-stream for 1h and 8h
313 is shown in Fig. 9 (a) and (b). With the increase of potassium from 0 to 3 wt.%, the
314 conversion of isobutane decreases from 72.2% (0K-S) to 61.8% (3.0K-S). The selectivity to
315 isobutene reaches as high as ~80% for samples 3K-S, 2.25K-S and 1.5K-S. The yield to
316 isobutene at time-on-stream for 1h is summarized in Table 1, and sample 2.25K-S presents
317 the highest yield to isobutene, reaching up to 52.9%, which is among the best reported to
318 date.

319 The DH performance for corresponding oxide catalysts without pre-treatment by H_2S/H_2
320 was also evaluated. The conversion of isobutane at time-on-stream of 1h for oxide and sulfide
321 V-K/ γ - Al_2O_3 catalysts are shown in Fig. 9 (c). The DH performance increases substantially
322 after sulfidation, and increased range of conversion was also calculated. Notably, different
323 amounts of potassium lead to various increased range. The increased range of conversion
324 shows a volcano shape with increasing the potassium loading, reaching a peak for sample
325 2.25K-S. After sulfidation, the conversion of isobutane for sample 2.25K-S increases from
326 36.8% to 65.9%, showing the biggest increased range.

327 Due to the special oxophilic character of vanadium oxide species, it was difficult to get all
328 the oxygen substituted by sulfur via O-S exchange [39-41]. The vanadium species in this
329 study actually are present as oxy-sulfide species after pretreatment by H_2S/H_2 . The S2p XPS
330 spectra of samples after treatment with H_2S/H_2 are presented in Fig. S3. It is shown that the
331 majority of introduced sulfur existed in the S^{2-} state, while a little amount of sulfur was

332 oxidized (SO_4^{2-} species) due to air exposure during the XPS test [44, 45]. We believe that the
333 sulfidation degree might lead to variation in the increased range of conversion. XPS was
334 carried out to characterize the relative atomic ratio of sulfur and vanadium. As the same
335 amount of vanadium was introduced in all samples, the atomic ratio of S/V was calculated to
336 indicate the degree of sulfidation. It is demonstrated in Fig. 9 (d) that the mole ratio of S/V
337 and the increased range of conversion both present volcano curve, reaching a peak for sample
338 2.25K-S. The correlation between increased range of DH performance and the added
339 potassium was clearly figured out, realizing the precise promotion of DH performance.

340 As stated above, the polymerization degree of vanadium species kept decreasing with the
341 potassium increasing from 0 to 3 wt.%. It implies that part of the bridge bonds between
342 vanadium ions broke down and consequently new chemical bonds between vanadium ion and
343 Al_2O_3 support are formed. Thus replacing oxygen by sulfur during the pre-sulfidation
344 treatment is becoming more difficult. Meanwhile, the increasing alkaline potassium would
345 react with H_2S to attract more sulfur to introduce. The combined effect is exemplified as a
346 volcano curve of sulfidation degree with potassium increase from 0 to 3 wt.% (Fig 9-d). It is
347 obvious that the different loading amount of potassium leads to variation in sulfidation degree,
348 affecting the vanadium species and acid properties ultimately.

349

350 **4.Conclusions**

351 This study reports on the precise modulation of vanadium species and DH performance via
352 the doped potassium with a simple coimpregnation process. It is also shown that the synergy

353 between vanadium species and acid sites plays a critical role in enhancing DH activity.
354 Ultimately, the yield to isobutene over sulfide V-K/ γ -Al₂O₃ catalysts reached as high as
355 52.9%, which is among the highest reported to date.

356 Combining characterization and DFT results, we revealed that the potassium was
357 predominantly bonded with the vanadium species, and the polymerization degree of
358 vanadium species depends significantly on the potassium. The doped potassium contributes
359 to regulating the vanadium species in the oligomeric state. Simultaneously, the bond between
360 K and Brønsted acidic (V-OH) species would also influence the sulfidation degree and acid
361 strength of V-K/ γ -Al₂O₃ catalysts. The intrinsic effect of potassium on synergy between
362 vanadium species and acid sites promotes the enhancement of DH activity obviously. This
363 study provides promising strategy for preparation of environment-friendly model industrial
364 DH catalyst.

365

366 **Conflicts of interest**

367 There are no conflicts of interest to declare.

368

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