Effect of Pretreatment on the Adsorption Performance of Ni/ZnO Adsorbent for Dibenzothiophene Desulfurization

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ABSTRACT: Ni/ZnO was prepared by co-precipitation and used as adsorbent for reactive adsorption desulfurization (RADS) of dibenzothiophene. The effect of calcination temperature, precipitate washing solvent, and reduction temperature on the adsorption performance of Ni/ZnO was investigated. It is observed that Ni/ZnO adsorbent calcined at 350 °C, washed with ethanol, and unreduced or reduced at low temperature performed best. By the characterization of BET, XRD, TPR, FTIR, and in situ XAFS, the optimal calcination temperature leads to the small crystallite of NiO and ZnO species. Washing with ethanol enhances the surface area of adsorbent and decreases its particle size. The influence of reduction temperature on the RADS performance is stronger than that of calcination temperature, which is ascribed to high-temperature reduction that makes the adsorbent easier to sinter and form a Ni-Zn alloy. The high RADS activity is a result of the adsorbent pretreatment conditions, which can form small Ni and ZnO particles, and the synergism between precursors.

1. INTRODUCTION

Recently, more and more stringent regulations have been put into effect to control the sulfur content in transport fuels. This has forced refineries and researchers to develop new processes to produce cleaner fuels. The adsorption desulfurization has thus emerged as an alternative to replace the traditional hydodesulfurization (HDS). The adsorbents usually considered for adsorption desulfurization include carbon materials,1 zeolite-based materials,2 reduced metals,3 metal oxides,4 and microporous coordination polymers.5 Among them, Ni/ZnO adsorbent based on the reactive adsorption desulfurization (RADS) shows excellent performance for ultradepth desulfurization. It is an efficient alternative and is seen as a combination of catalysis and adsorption.6–21 RADS can be conducted under milder conditions compared to the conventional HDS, and the consumption and purity requirement of hydrogen are less.6 Employing the RADS principle, Phillips Petroleum patented the so-called S-Zorb technology to remove the sulfur impurity in gasoline and diesel.22 In RADS of Ni/ZnO adsorbent, the sulfur desulfurization reaction occurs on the surficial Ni, and at the same time, the metallic Ni is sulfided to NiS2, then by H2S intermediate, the sulfur in NiS2 is transferred to ZnO,23 so-called autoregeneration process, where the ZnO acts as both a sulfur acceptor and a co-catalyst.8

The preparation and pretreatment have an important influence on the final RADS performance of Ni/ZnO adsorbent. Comparing to impregnation, co-precipitation can produce fine particles of NiO (Ni) and ZnO and make good contact between nickel sulfide and ZnO. Reduction treatment was found to be important variables for optimizing the activities, but the reduction may lead to the low activity owing to the formation of Ni-Zn alloy and the sinter of Ni metals.11 In our previous article,18 we have found that the desulfurization capability of Ni/ZnO decreases apparently when the residue content of sodium increases in the adsorbent. It is observed that sodium is enriched on the surface of adsorbent during calcination and reduction, leading to formation of Na-
Zn alloy and NaZn(OH)₃. Meanwhile, the Na residue increased the active crystallite size and decreased the surface area and pore volume, as well as weakened the interaction of Ni with ZnO. To get high activity, the Ni/ZnO adsorbent should have a sufficient surface area and proper interaction between ZnO and NiO (Ni), which can be achieved using modified manufacture method, calculation, and reduction pretreatment.

Elucidating the dynamic structure change of adsorbent during pretreatment is a key issue to understand the activation process and to develop efficient materials. In situ technology can provide credible information, avoiding the oxidation of high reactive metal in air. In this respect, it is imperative to develop in situ techniques for studying the pretreatment of Ni/ZnO adsorbent, so that the relationship of RADS performance with structures of adsorbent can be established, facilitating the rational design and preparation of adsorbent with satisfied activity. However, this relationship is still not well-known for the Ni/ZnO adsorption system.

The preparation conditions directly change the composition, texture, and structures of Ni/ZnO adsorbents, which will influence RADS performance. Elucidation of intrinsic reason of pretreatment influence will provide important information for the improvement of Ni/ZnO-based adsorbents. In this work, we systematically investigated the influence of calcination and reduction temperature (from 250 to 450 °C) and precipitate washing solvent (deionized water and ethanol) on the RADS performances. Structure—activity relationships of the Ni/ZnO adsorbents prepared by co-precipitation were examined by BET, XRD, TPR, and FTIR. With the in situ XAFS technique, the dynamic structural change of Ni/ZnO adsorbents under real conditions is investigated in detail.

2. RESULTS AND DISCUSSION

2.1. Textural Properties of the Adsorbents. Table 1 lists the BET surface area, pore volume, and averaged pore size of NiO/ZnO adsorbents with various pretreatments. Co-precipitated NiO/ZnO precursors were firstly dried (P-W) and then calcined at 250 (CW250), 350 (CW350), and 450 °C (CW450). It can be seen that, by increasing the calcination temperature from room temperature to 350 °C, the surface area and pore volumes of the Ni/ZnO adsorbents increase from 63.1 m²/g and 0.20 cm³/g to 101.7 m²/g and 0.46 cm³/g, respectively. However, further increasing the calcination temperature over 350 °C leads to the decrease of surface area and pore volume. On the other hand, the pore size presents the monotonically increase with the increment of calcination temperature. With the TG experiments of precipitating precursors, we observed that the transformation of Ni(OH)₂ and ZnCO₃ to NiO and ZnO occurred at the temperature range of 250–330 °C. Below 250 °C, the precursor had about 10% weight loss, which is attributed to the adsorbed water. It is postulated that the textural changes with calcination at 250, 350, and 450 °C are due to the release of adsorbed water, decomposition of the precursor, and sinter of oxides, respectively. The decomposition of the precursor leads to an increase of the BET surface area, pore volume, and pore size; the sintering of oxides during calcination leads to the decrease of the BET surface area and pore volume and then the decrease of the number of the active sites. The calcination at high temperature induces the shrinkage and agglomeration of adsorbent particles and collapse of the piled pores, leading to the increase of pore size.

After one time washing of the co-precipitated precursor with ethanol and then drying (P-E), the surface area, pore volume, and pore size increase. The ethanol-washed sample calcined at 350 °C (CE350) has the same effect, when compared with the no ethanol washing counterpart (CW350). It indicates that ethanol wash has a significant influence on the texture of the adsorbent. The water and ethanol surface tension is 72 and 22 dynes/cm at 25 °C, respectively; during calcination, the strong tension of water induces serious volume shrinkage and pore collapse. As a result, the surface area decreased. The surface tension of ethanol was less than that of water, and this weaker tension can keep the pore structures with less shrinkage. Zhang et al. reported similar results.

Table 1 also presents the surface area, pore volume, and averaged pore size of ethanol-washed and 350 °C calcined samples after reducing at 250 (CE350-R250), 350 (CE350-R250), and 450 °C (CE350-R250). After reducing the adsorbent at 250 °C, the surface area, pore volume, and the size of the Ni/ZnO adsorbent slightly decrease. The further increase in reduction temperature induces a remarkable decrease of its surface area and pore volume accompanied by the increase of pore size. It is suggested that the agglomeration of Ni and ZnO occurred in reduction process.

2.2. XRD. Figure 1 shows XRD patterns of dried P-W precursor and the calcined adsorbents. 3Ni(OH)₂·2H₂O and Zn₅(CO₃)₂(OH)₆ phases are detected in the P-W sample. But, the signal is weak, suggesting low crystallinity. After this, the P-W precursor was calcined at 250 °C; the XRD pattern had no apparent change, suggesting that little decomposition occurred. When the calcination temperature increased to 350 °C, NaCl-type NiO structure is distinguishable; in addition, wurtzite-type ZnO can be discerned. Further increasing calcination temperature to 450 °C, the XRD peaks of NiO and ZnO become sharper; the size of NiO and ZnO crystallite particles estimated by the Scherrer formula shows an apparent increase (Table 1). It concluded that the P-W calcined at 350 °C can form the oxide already while avoiding the growth of active particle.

As also shown in Figure 1, peaks of CE350 are broader than those of CW350, suggesting smaller crystallite particles, which is listed in Table 1. For reduced adsorbents, combined with the TPR results, well-dispersed amorphous Ni or small Ni crystalline size is formed for adsorbent reduced at 250 °C, because the size of Ni crystals was below the XRD limit of detection. The diffraction patterns of the adsorbents reduced at 350 °C show strong Ni lines, indicating most of NiO is...
Figure 1. XRD patterns of the adsorbent with various pretreatments. (a) Adsorbent precursor P-W; (b) CW250; (c) CE350; (d) CW350; (e) CW450; (f) CE350-R250; (g) CE350-R350; (h) CE350-R450. & 3Ni(OH)₂·H₂O; #, Zn₅(CO₃)₂(OH)₆; o, ZnO; *, NiO; %, Ni–Zn; ^, Ni.

2.3. TPR Results. TPR profiles of the pure ZnO, pure NiO, and calcined adsorbents are shown in Figure 2 (top). The onset temperature (Tₒ), the maximum temperature (Tₘ), and the quantity of hydrogen consumption are summarized in Table 2. Almost flat TPR profiles were obtained for pure ZnO, indicating that pure ZnO cannot be reduced. TPR profile of NiO as reference compound shows one peak centered at 338 °C. In NiO/ZnO adsorbents calcined at different temperatures, peaks around 430 °C belong to Ni²⁺, having strong interaction with the ZnO support. Calcined NiO/ZnO adsorbents display reduction profiles well above that of the standard bulk NiO, indicating that the NiO reduction is hindered by strong interaction between NiO and ZnO.

An increase in the lattice parameter of the NiO phase is observed for samples calcined at 350 °C, as presented in Figure 1; this is because ZnO dissolves in NiO, forming Ni₅ZnO₆ solid solution although it cannot be detected directly by XRD. However, the increase of calcination temperature from 350 to 450 °C does not lead to any increase in the lattice parameter of NiO, indicating that the dissolution of the components is in the process of precipitation and not in the decomposition of well-mixed precursors during the process of calcination. Rubinstein et al. also reported a similar observation. As shown in Table 2, the Tₒ of NiO/ZnO adsorbents increases from 412 to 445 °C, with increasing calcination temperature from 250 to 450 °C, because the adsorbent is sintered. Peaks around 600 °C in NiO/ZnO adsorbents can reasonably be attributed to reduction of surface ZnO. As listed in Table 2, it is observed that total hydrogen consumption increases slightly with the increase of calcining temperature up to 350 °C and then decreases with the further increase of calcination temperature to 450 °C. The amount of hydrogen consumption below 550 °C in NiO/ZnO adsorbents is close to the stoichiometric amount of NiO reduction, suggesting that NiO is fully reduced below 550 °C in the presence of 5% H₂ in Ar.

2.4. IR Results. Figure 3 shows the FTIR spectra with the calculation treatment. Bands around 3450 and 1624 cm⁻¹ are ascribed to the OH stretching and HOH bending, respectively, suggesting the existence of adsorbed water. The IR spectrum of the P-E compared to that of the P-W shows little difference except OH band shifts to higher frequency; this points to a possible decrease of the hydrogen-bonded hydroxyl groups. The strong bands at 1518, 1385, 1043, 837, and 711 cm⁻¹ due to the presence of carbonate in the precursor decrease with the further increase of calcination temperature, indicating the decomposition of the carbonate. The strong band at 451 cm⁻¹ increases with calcination temperature from 350 to 450 °C, indicating that NiO and ZnO appear. These results are consistent with those of XRD: 3Ni(OH)₂·2H₂O and Zn₅(CO₃)₂(OH)₆ are present over the precursor and the one calcined at 250 °C. Calcination of such precipitate above 350 °C yields NiO and ZnO.
2.5. XANES Spectra. Figure 4 shows Ni K-edge XANES of 350 °C calcined sample (the mixture of P-E and BN) reduced at 400 °C (1 MPa) under a flow of 5% H₂/95% He gas mixture from 0 to 230 min.

Figure 5. Phase composition and first-order fit for NiO conversion during reduction at 400 °C (1 MPa) under a flow of 5% H₂/95% He gas mixture from 0 to 230 min.

This is consistent with the pure NiO reduction reported by Richardson et al. However, Rodriguez et al. reported there was a longer induction period for NiO reduction. Meanwhile, there is no induction period in some reduction experiments. This discrepancy in behavior may result from differences in experimental conditions (temperature and H₂ pressure) and the morphology of the oxides. It is apparent that metallic Ni phase was detected with NiO phase loss simultaneously, indicating that there is no room for the intermediate phase. The induction period is postulated to produce oxygen vacancies on the NiO surface, which is necessary for H₂ dissociation. At low temperatures, this induction period will be longer. Once the Ni atoms are liberated, they will nucleate into clusters and grow in size until large enough, initiating the dissociation of H₂, where the reduction process can be accelerated autocatalytically.

The results suggest that NiO is reduced directly to Ni, consistent with those reported by Rodriguez et al. and Richardson et al.

Figure 5 also demonstrates the experiment result and first-order fit for NiO conversion data at 400 °C and 1 MPa under a flow of 5% H₂/95% He gas mixture. Equation 1 is used for the first-order fit

\[ X_{\text{NiO}} = 1 - e^{-kt + t_0} \]  

where \( t_0 \) is the induction time correction. The results present that the real conversion is deviated from the fitted first-order kinetics at prolonged time with high conversion. The reasons are the following: First, NiO crystallites are surrounded by Ni metal and the formed H₂O molecules have difficulty in escaping. Second, ZnO strongly interacts with Ni species, hindering the reduction of NiO. Richardson et al. reported that NiO grains were isolated in supported adsorbents. Nickel atoms either move out from support to nucleation sites or self-aggregate to form small particles. More interestingly, the TPR results show the BN will influence the reduction of NiO. As shown in Figure 2 (bottom), contrary to the narrow peak at 419 °C of pure NiO/ZnO adsorbent, the TPR peak of the NiO/ZnO adsorbent with BN shifts to a higher temperature of 476 °C and becomes broader, indicating that BN improves the dispersed nickel species and the interaction between NiO and ZnO during heating treatment.

2.6. EXAFS Analysis. The Fourier transform Ni K-edge EXAFS spectra of the NiO/ZnO adsorbent reduced at 400 °C (1 MPa) are shown in Figure 6. The peaks at 1.5 and 2.5 Å reduce continuously. Simultaneously, a new peak at 2 Å
appears, and the peak intensity increases with increasing reduction time. Note that the distance scale in the Fourier transform spectra was not corrected for the phase shift. After 0.5 Å phase shift correction, the peaks located at 1.5, 2, and 2.5 Å agree with the Ni–O in NiO, Ni–Ni in metal Ni, and Ni–Ni in NiO coordinations. The EXAFS result, pointing to a direct transformation of NiO to Ni, is consistent with the XANES result.

2.7. Adsorption Tests: Dibenzothiophene (DBT) RADS. As shown in Scheme 1, the RADS of DBT model reaction proceeds through two ways: direct desulfurization (DDS) of DBT produces biphenyl (BP) and hydrogenation (HYD) process gives rise to tetrahydro- and hexahydrodibenzothiophene first and then the final product cyclohexylbenzene (CHB). The reaction mechanism of DBT desulfurization in RADS is similar to that of the HDS of Co/Mo or Ni/Mo catalyst. In this study, the conversion of DBT was used to measure RADS activity. DDS pathway was monitored by the BP selectivity (S_{BP}), and the hydrogenation pathway (HYD) was followed by the CHB selectivity (S_{CHB}).

The effect of calcining temperature on the DBT conversion on the Ni/ZnO adsorbent without reduction treatment and ethanol washing is shown in Figure 7. For all adsorbents, 100% DBT conversion was not obtained during the first few hours on-stream. The RADS activity of calcined samples augments with calcination temperature increasing from 250 to 350 °C and significantly decreases when calcining temperature further increases to 450 °C. The sulfur capacity at 100% DBT conversion increases from 0.16 to 0.18 g-S/g-NiO/ZnO and then decreases to 0.06 g-S/g-NiO/ZnO; these sulfur capacities are calculated by the difference of sulfur contents between the feed and product (Table 3). A maximum activity was achieved over the adsorbent calcined at 350 °C, owing to a synergism between the decomposition of the precursor and the small crystallite size of NiO (Ni) and ZnO species. Increasing calcination temperature results in the increase of the precursor decomposition, which is favored for DBT conversion; meanwhile, higher calcination temperature induced NiO and ZnO particle sintering and BET surface area reduction, which lead to decreased DBT conversion.

Figure 7 also plots the selectivity to investigate the HYD and DDS pathways. It is notable that selectivity markedly changes with the calcination temperature. For the Ni/ZnO adsorbent calcined at 250 and 350 °C, the main product is CHB before 25 h on-stream, indicating that the RADS takes place mainly through the HYD pathway. After 25 h, S_{BP} increases at the expense of S_{CHB} with time on stream increasing. For the HYD route, only trace tetrahydro- and hexahydrodibenzothio-
Phene were detected, suggesting that intermediate product is transformed to CHB product rapidly. The 350 °C calcined adsorbent shows higher HYD activity than 250 °C calcined adsorbent. For the adsorbent calcined at 450 °C, the dominant product is BP.

Figure 8 shows the effect of precipitate washing solvent on the C_{DBT} over the 350 °C calcined Ni/ZnO adsorbent without reduction treatment. Compared with the adsorbent without ethanol washing (CW350), the RADS activity enhances for ethanol washing (CE350), and the sulfur capacity at 100% DBT conversion enhances also from 0.18 to 0.21 g-S/g-NiO/ZnO (Table 3). Washing with ethanol led to an increased surface area and small NiO (Ni) and ZnO particles, resulting in higher RADS activity. The S_{CHB} and S_{BP} are also plotted in Figure 8. The time when the entire product is CHB increases from 25 h without ethanol washing to 32 h with ethanol washing, indicating the HYD activity increases after ethanol washing.

Figure 9 shows the C_{DBT} over the CE350 without reduction or with reduction at different temperatures. The high RADS activity was observed for unreduced adsorbent and 250 °C reduced adsorbent; the reason is presumably the small Ni particle formation. However, 100% DBT conversion is reached only after a few hours when the adsorbent is not reduced. It is probably that NiO is less active than Ni in the DBT RADS and a period of induction is necessary for the reduction of NiO/ZnO under the RADS condition. The RADS activity decreases with increasing reduction temperature, and S capacity at 100% C_{DBT} decreases from 0.20 to 0.02 and then to 0 g-S/g-NiO/ZnO (Table 3). Higher reduction temperature reduces BET surface area, increases the Ni and ZnO particle size, and forms Ni-Zn alloy, leading to a decrease of DBT conversion. The S_{CHB} and S_{BP} are also plotted in Figure 9. Comparing with the adsorbent without reduction, the HYD activity decreases after reducing at 250 °C and significantly decreases with a further increase in reduction temperature.

By comparing RADS activity and selectivity among NiO/ZnO adsorbents calcined at different temperatures, washed with or without ethanol, and reduced at different temperatures, we optimized the pretreatment conditions as 350 °C calcination temperature, ethanol washing, and without reduction or with reduction at a low temperature of 250 °C. Adsorbent with this optimized treatment gives rise to the highest DBT conversion and sulfur capacity with HYD route dominant.

Calcination transforms the 3Ni(OH)$_2$·2H$_2$O and Zn$_5$(CO$_3$)$_2$(OH)$_6$ phases in precipitated precursor to the NiO and ZnO component. XRD shows that this transformation is achieved between 250 and 350 °C. By TG and TG−MS, we observed that, in single-component precursor, ZnO or NiO was formed at about 250 or 310 °C, respectively. But, the formation of NiO/ZnO composite needs calcination above 320 °C. Kedesdy and Drukalsky reported that NiO does not dissolve in ZnO but ZnO can dissolve in NiO, forming Ni$_x$Zn$_y$O solid solution. This solid solution transforms to NiO and ZnO phases at higher temperature, but smaller NiO and ZnO crystallites are formed, which is beneficial for RADS reaction. The calcination at 350 °C is high enough for NiO/ZnO composite formation and avoids the sintering of oxide particles, thus giving rise to the excellent DBT RADS performance. When washing precipitated NiO/ZnO precursor with ethanol, ethanol replaced water remains in pores. Owing to the low surface tension of ethanol, the pore structures are retained when ethanol is released from pores by heating. Thus, calcined sample with ethanol washing has the highest surface and pore volume, leading to improved RADS performance.
activity. Pre-reduction transforms NiO to active Ni metal. Thus, induction period can be avoided in RADS reaction. But, the Ni-Zn alloy with low activity is formed by hydrogen reduction. A study shows that formation of Ni-Zn alloy seriously decreases RADS activity. The in situ reduction of NiO/ZnO avoids the formation of Ni-Zn alloy; thus, CE-350 without pre-reduction has the best RADS performance although a short induction period for Ni reduction is observed. The TPR and in situ XAFS results illustrate that the total reduction of NiO to metal Ni may require a temperature of over 400 °C. But, XRD presents that transformation of NiO to metallic Ni has been achieved at 350 °C for 6 h reduction. This can be attributed to the prolonged reduction time that compensates for the insufficient temperature. However, Ni/ZnO adsorbent with pre-reduction or in situ reduction at 250 °C showed the best RADS performance, suggesting the total reduction of NiO as unnecessary. The surficial reduction of NiO, avoiding formation of Ni-Zn alloy, is the best treatment for the DBT RADS reaction. Our comparison investigation about the pretreatment conditions for Ni/ZnO adsorbent presents the dynamic process of active phase formation, and the illustration of the effect of preparing and pretreating on the active structure and RADS property is beneficial for application of Ni/ZnO adsorbent.

3. CONCLUSIONS

Ni/ZnO prepared by co-precipitation was used as adsorbent for DBT RADS. Their adsorption performance is related to calcination temperature, precipitate washing solvent, and reduction temperature. The Ni/ZnO adsorbent calcined at 350 °C, washed with ethanol, and unreduced or reduced at low temperature performs best. The optimal calcination temperature is due to a synergism between the decomposition of the precursor and the small crystallite size of NiO and ZnO species. Washing with ethanol enhances the surface area and decreases its particle size. When the feed stream contains 500 ppm sulfur with DBT, the sulfur capacity for a complete conversion of DBT at 250 °C and 1 MPa is raised from 0.18 to 0.21 g-S/g-NiO/ZnO compared with the adsorbent without ethanol washing. The high RADS activity of the unreduced or low-temperature-reduced adsorbent is probably ascribed to the formation of small Ni and ZnO particles. The effect of reduction temperature on RADS performance is stronger than that of calcination temperature because of formation of low-activity Ni-Zn alloy during reduction treatment.

EXPERIMENTAL

Preparation of Adsorbent. The Ni/ZnO adsorbent precursor was prepared using the procedure described elsewhere, simply described as follows: A solution of 0.5 M Ni(NO₃)₂·6H₂O and 0.5 M Zn(NO₃)₂·6H₂O and a solution of 1M (NH₄)₂CO₃ were dropped simultaneously into a beaker containing deionized water at pH 7.0 and 90 °C with stirring and aged for another 2 h, followed by filtration and washing four times with deionized water under stirring for 30 min. The material was exchanged through washing one time with ethanol (assigned as P-E) or not (assigned as P-W). The dried P-E and P-W samples after calcining at temperature x is assigned as CEₓ. Then the material was exchanged through washing one time with ethanol (assigned as P-E) or not (assigned as P-W). The dried P-E and P-W samples after calcining at temperature x is assigned as CEₓ. Then the material was exchanged through washing one time with ethanol (assigned as P-E) or not (assigned as P-W). The dried P-E and P-W samples after calcining at temperature x is assigned as CEₓ. Then the material was exchanged through washing one time with ethanol (assigned as P-E) or not (assigned as P-W). The dried P-E and P-W samples after calcining at temperature x is assigned as CEₓ. Then the material was exchanged through washing one time with ethanol (assigned as P-E) or not (assigned as P-W). The dried P-E and P-W samples after calcining at temperature x is assigned as CEₓ. Then the material was exchanged through washing one time with ethanol (assigned as P-E) or not (assigned as P-W). Then the gas was switched to a He mixture (1 MPa). Ni K-edge was monitored using cubic spline fitting, and the amount and type of various phases under the reaction conditions were determined by least-square fitting procedure and PCA. The Fourier transform from k³-weighted EXAFS to R space was conducted by Gaussian window function in the k range of 3 to11.5 Å⁻¹.

RADS Reactions. The RADS of DBT was performed in a tube microreactor of 6 mm internal diameter. About 0.1 g of 40–60 mesh NiO/ZnO mixed with about 0.4 g of SiO₂ was loaded at the constant temperature region in each run. The reaction pressure was controlled by the back pressure regulator. The feed containing DBT (500 ppm S) in n-nonane was fed into the reactor by high-pressure liquid pump. For the reduction treatment, the oxide adsorbent was reduced in situ at temperatures of 250, 350, and 450 °C for 6 h in a H₂ flow of 9 mL/min and 1.0 MPa prior to the RADS reaction. Then, the reactor was cooled to 250 °C; the feed (1.8 mL/h) was admitted into the reactor. For the no reduction treatment, when the temperature was heated in N₂ to 250 °C (1 atm), the feed (1.8 mL/h) and H₂ (9 mL/min and 1.0 MPa) were admitted simultaneously into the reactor. The RADS experiment was carried out at 250 °C and 1 MPa with H₂/oil of 300 and LHSV of 13 h⁻¹. The feed and product were analyzed by a
Shimadzu GC-14B gas chromatograph with FID and J&W Scientific DB-1 60 m capillary column.

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ACKNOWLEDGMENTS

Thanks for the support from the National Natural Science Foundation of China (21473231 and 21603256).

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