

MOR/SBA-15 Composite Catalysts with Interconnected Meso/Micropores for Improved Activity and Stability in Isopropylation of Naphthalene

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The isopropylation of naphthalene with isopropyl alcohol was studied over composites of MOR/SBA-15 in a high-pressure, fixed-bed reactor. The MOR catalyst showed a high 2,6-/2,7-diisopropyl naphthalene (DIPN) ratio of 1.75, but a low naphthalene conversion (54%) and fast deactivation of the catalyst. The composites of MOR/SBA-15 were prepared by a hydrothermal recrystallization process to obtain hierarchical micro/mesopores. During the process, MOR recrystallized in the mesopores of SBA-15, the structure of which was stabilized by carbon

Introduction

Zeolites function as shape-selective catalysts in isopropylation of naphthalene to obtain selectively 2,6-diisopropylnaphthalene (2,6-DIPN), which is an important raw material for synthesizing new polyesters such as polyethylene naphthalate.^[1] However, the micropores of the zeolites limit the diffusion of large reactant and product molecules, and they are easily blocked by coke deposition leading to catalyst deactivation. A popular method developed recently to avoid this problem is to introduce mesopores into the zeolite crystals. The combined meso- and micropores have the advantages of fast diffusion and accessibility of bulky molecules to the reaction sites located in the micropores of the zeolite, which would provide high reaction rates and catalyst stability. The isopropylation of naphthalene is usually studied with zeolites such as USY, BEA, and MOR.^[2] The large-pore USY catalyst shows high conversion and high stability, but it is less selective to 2,6-DIPN.^[3] The small-

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coating formed on the pore walls as a template. The best prepared MOR/SBA-15 catalyst achieved a high conversion of 85%, high stability, and less coking, while maintaining the high 2,6-/2,7-DIPN ratio (\approx 1.8). The modified micro/mesopore structure allowed facile diffusion of bulky molecules to and from active catalytic sites located in the small MOR pores as a result of the connection between the two types of pores in the MOR/SBA-15 composite.

pore MOR catalyst gives a high shape selectivity for 2,6-DIPN relative to 2,7-DIPN of similar size, but with lower conversion and lower stability accompanied with more coke formation as a result of the bulky intermediate molecules blocking the mouth of its straight-channel pores. Hence, if we provide mesopores to MOR, the naphthalene conversion and catalyst stability can be improved while still maintaining the high shape selectivity to 2,6-DIPN.

There are several approaches to form hierarchical mesoporous/microporous zeolite composite structures. The first approach involves the conventional dealumination or desilication of zeolites by acid leaching, steaming, or alkaline treatments to create mesopores in zeolite crystals.^[4] Second, a mesoporous carbon matrix is used as a template to grow zeolite crystals with a uniform mesopore system.^[5] The last approach involves recrystallization of a zeolite into a mesoporous material by hydrothermal reaction in the presence of a surfactant.^[6] In the previous works on alkylation of naphthalene with mesoporous MOR, however, catalyst stability and shape selectivity for 2,6-dialkyl naphthalenes have still been in need to improve.^[2c-h,4a]

In the present work, we prepared MOR/SBA-15 composites by a modified hydrothermal (HT) recrystallization method to obtain combined micro/mesopore structures. We discovered that the formation of stable carbon coating on the walls of SBA-15 (SBA-15C) was essential in the process, which helped recrystallization of MOR while retaining the mesopore structure of SBA-15 as a template during the HT treatment. The activity, selectivity, and stability of the MOR/SBA-15 composite catalysts were studied for isopropylation of naphthalene with isopropyl alcohol. Thus the properly fabricated MOR/SBA composite catalyst achieved significantly higher naphthalene conversion, im-



proved stability, and increased 2,6-DIPN yield relative to the commercial MOR alone.

Results and Discussion

Fabrication of hierarchical MOR/SBA-15 composite catalysts

We prepared three types of MOR/SBA-15(C) composite catalysts by varying calcination conditions of SBA-15 synthesis process; the carbon-free SBA-15 calcined in air at 550°C, SBA-15C-550/N₂ with unstable carbon calcined in N₂ at 550°C, and SBA-15C-900/Ar with stable carbon calcined in Ar at 900°C. The hierarchical micro/meso porous zeolite composite structures were formed by the recrystallization of MOR into SBA-15 pores under HT conditions. Our recrystallization procedure was distinguished from reported ones^[6] in that we did not use any structure-directing surfactant or alkaline pH in the recrystallization solution. Thus, the homogenized aqueous solutions of MOR and SBA-15 or SBA-15C were hydrothermally treated for recrystallization at 130°C for 48 h, and the precipitate was calcined at 550°C for 5 h.

The wide- and small-angle XRD patterns of calcined parents and MOR/SBA-15 composite catalysts in Figure S1 of Supporting Information revealed that the MOR/SBA-15 composite catalysts possess crystalline structures similar to those of original zeolites after the HT treatment. The small-angle XRD analysis showed a definite low-angle peak representing a hexagonal mesostructure after hydrothermal treatment except for MOR/ SBA-15C-550/N₂ catalyst. The N₂ adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) pore-size distributions of parent and prepared MOR/SBA-15 composite catalysts are presented in Figure S2. MOR zeolite showed a type I isotherm because of the microporosity. SBA-15 and SBA-15C showed a type IV isotherm corresponding to uniform mesoporosity. All the prepared MOR/SBA-15 composite catalysts showed type IV isotherms confirming the presence of ordered mesopore structure after the HT treatment. Furthermore, the P/P_0 value of SBA-15 (0.62) that showed steep rise in adsorption shifted to 0.41, 0.46, and 0.58 on MOR/SBA-15C-900/Ar, MOR/SBA-15C-550/N₂, and MOR/SBA-15 catalysts, respectively, indicating decreased pore sizes. This observation indicates that some of the SBA-15 mesopore channel is partly blocked with MOR, which provides evidence of the partial connection between mesopores and micropores. The similar trend has been observed in BJH pore size distributions in Figure S2b as well.

The textural properties derived from the N₂ adsorption isotherms are summarized in Table S1 (Supporting Information), including BET surface area, mesopore/micropore areas, and pore volume for all the prepared catalysts. Relative to SBA-15, the decreased mesopore area and pore volume for composite catalysts could be attributed to partial blocking of the mesopores by MOR zeolite. The external morphology of the parent MOR, SBA-15, and prepared MOR/SBA-15 composite catalysts were examined by SEM as shown in Figure 1. The MOR/SBA-15 composite catalysts did not show significant difference from the typical rope-like morphology of SBA-15 although they dis-



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Figure 1. SEM images of parent and MOR/SBA-15 composite catalysts.



Figure 2. HRTEM images of prepared composite catalysts. a, b) MOR/SBA-15; c, d) MOR/SBA-15C–550/N₂; e, f) MOR/SBA-15C–900/Ar.

played the presence of small MOR crystals intimately mixed with SBA-15.

The HRTEM images of prepared catalysts are presented in Figure 2. The MOR/SBA-15 catalyst images (Figure 2a,b) showed separate phases of MOR and SBA-15, but MOR/SBA-15C-550/N₂ (Figure 2c,d) and MOR/SBA-15C-900/Ar (Figure 2e, f) exhibited combined phases of MOR and SBA-15. In particular, the micrographs of Figure 2e, f show clearly that the domains of SBA-15 and MOR are superimposed with each other indicating the connection between the mesopores of SBA-15 and the micropores of MOR. The above results of textural characterization confirm the connection between mesopores of SBA-15 and micropores of MOR especially for MOR/SBA-15C-900/Ar, which is the objective of the composite formation in the present work. This modified micro/mesopore would facilitate diffusion of the large naphthalene molecules resulting in high activity and stability as discussed later.

The ²⁷Al NMR spectrum of commercial MOR and prepared composite catalysts are presented in Figure 3a. The parent MOR zeolite exhibited two peaks with chemical shifts of approximately 55 and 0 ppm corresponding to framework tetrahedral and extra-framework octahedral Al species, respectively. Similar peaks obtained for MOR/SBA-15 and MOR/SBA-15C–550/N₂ reveal that there were no structural changes during the HT treatment for these two composite catalysts. However, MOR/SBA-15C–900/Ar displayed decreased intensity of the



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on the carbon-coated walls of SBA-15, and the carbon is removed later by calcination in air to obtain the MOR/SBA-15 composite catalysts.

The temperature of calcination step during SBA-15 synthesis is important because it becomes the carbonization condition of remaining surfactant P123. Thus, carbon obtained at the high temperature of 900°C is very stable and preserves the mesopore structure of SBA-15 during the MOR recrystallization process by the HT treatment, whereas carbonization at 550 °C results in less stable carbon that cannot retain the mesopore structure as in the case of MOR/SBA-15C-550/N₂.

Figure 3. a) ²⁷Al and b) ²⁹Si NMR spectra of parent and MOR/SBA-15 composite catalysts.

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peak at 0 ppm, attributed to fewer amounts of extra-framework Al species present. The ²⁹Si NMR spectra in Figure 3b revealed well-resolved three peaks in SBA-15 at -91, -102, and -112 ppm attributed to Q2, Q3, and Q4 species in the mesoporous framework, respectively. MOR/SBA-15 and MOR/SBA-15C-550/N₂ exhibited spectra similar to that of MOR, whereas the spectrum of MOR/SBA-15C-900/Ar was similar to that of SBA-15. This confirms that the mesopore structure of SBA-15 is preserved well only in MOR/SBA-15C-900/Ar. The Q4/Q3 ratios of parent SBA-15 and H-MOR were 1.17 and 3.6, respectively. The MOR/SBA-15C-900/Ar catalyst possessed the same Q4/Q3 ratio value of 1.17, whereas MOR/SBA-15 and MOR/SBA-15C-550/N₂ catalysts possessed higher Q4/Q3 ratios 2.8 and 1.6. The higher Q4/Q3 ratios indicate higher degree of condensation of silanol (SiOH) groups in SBA-15.^[7] This result is another indication that the pore wall of SBA-15 is well preserved only for MOR/SBA-15C-900/Ar.

Physical characterization of the MOR/SBA-15 composite catalysts indicated that the desired hierarchical micro/mesoporous zeolite composite has been best fabricated by the recrystallization of MOR into the mesopores of SBA-15C–900/Ar. Thus in the recrystallization process, the formation of stable carbon coating on the pore walls of SBA-15 seems essential to obtain well-connected MOR/SBA-15 such as MOR/SBA-15C–900/Ar. The carbon is formed through carbonization under an inert gas of organic surfactant (P123) remained in SBA-15 from the synthesis step. Like a template, this carbon coating on the pore walls of SBA-15 helps prevent dissolution of the silica wall during HT treatment and stabilize the mesoporous SBA-15 structure, so that MOR could recrystallize into its mesopores. The process is schematically depicted in Scheme 1. During HT treatment the MOR initially partially dissolves and recrystallizes



Scheme 1. Schematics of formation process of MOR/SBA-15C-900/Ar composite catalysts during hydrothermal treatment.

Catalytic isopropylation of naphthalene over MOR/SBA-15 composite catalysts

The possible DIPN isomers produced from the isopropylation of naphthalene are α,α -(1,4- and 1,5-DIPN), α,β -(1,6-, 1,3- and 1,7-DIPN), and β,β -(2,6- and 2,7-DIPN), and their molecular sizes decrease in the order of $\alpha,\alpha > \alpha,\beta > \beta,\beta$. 2,6-DIPN and 2,7-DIPN are the slimmest products with dimensions of 0.661× 0.661×1.423 nm and 0.662×0.726×1.376 nm, respectively. Naphthalene isopropylation was first studied over commercial MOR zeolite catalyst at 250 °C, at 3.0 MPa and a weight hourly space velocity (WHSV) of 3 h⁻¹. As presented in Figure 4a and Figure S3, the naphthalene conversion was approximately 68% for the initial 1 h and it decreased gradually to approximately 54% after 6 h time on stream (TOS). The 2,6-DIPN selectivity





Figure 4. a) Naphthalene conversion on parent and MOR/SBA-15 composite catalysts versus TOS. b) TPO of used MOR parent and MOR/SBA-15 composite catalysts after isopropylation of naphthalene for 6 h. Reaction conditions: T = 250 °C; P = 30 bar; WHSV = 3 h⁻¹; isopropyl alcohol/naphthalene/decalin molar ratio: 1:2:7.5.

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ed to pre-adsorbed hydrocarbon species and the peak between 400-600 °C to the oxidation of deposited carbon species.[10] The MOR/SBA-15C-900/Ar produced a significantly lower amount of carbon than the other catalysts. The results corroborate well with the results of textural characterization discussed above. Thus the effective connection between mesopores of SBA-15 and micropores of MOR in MOR/SBA-15C-900/Ar would facilitate diffusion of the large naphthalene molecules without pore blocking, resulting in high activity and stability as observed. In Table 1, the acid-site distributions probed by temperature-programmed desorption (TPD) of NH₃ are listed. Notably, this acidity trend has only a weak correlation with the amount of the coke formation summarized in Table 1. This sug-

(100×2,6-DIPN moles produced per converted naphthalene moles), yield (100×2,6-DIPN moles produced per fed naphthalene moles), and 2,6/2,7-DIPN ratio were 7%, 4%, and ≈1.8, respectively, at 6 h time on stream. Thus MOR exhibited high shape selectivity but the reaction was slow and unstable as reported in many previous studies.^[2b-f,8] As presented in Figure 4a, the naphthalene conversions increased after 6 h on stream in the following order: SBA-15(0%) <MOR+SBA-15 (≈8%)<MOR (≈54%)<MOR/SBA-15 (≈61%) <MOR/SBA-15C-550/N₂ (≈66%)<MOR/

SBA-15C-900/Ar (\approx 85%). The reference SBA-15 catalyst of pure silicate framework did not show any activity because of no acid sites present. The apparent initial conversion originates from the adsorption of the naphthalene because no product was observed. Hence we can consider that the catalytic activity of all composite catalysts is derived solely from acid sites present in MOR. All composite catalysts showed improved stability compared to MOR, and in particular, MOR/SBA-15C-900/Ar exhibited the highest naphthalene conversion and the best stability. The physical mixture of MOR+SBA-15 showed less stability and lower conversion than parent MOR emphasizing the importance of pore connection between MOR and SBA-15.

The stability is correlated with the amount of coke formed during 6 h on stream as shown in Figure 4b and Table 1. The coke formation is caused by cracking, oligomerization, and dehydration side reactions occurring during isopropylation reactions when strong acid sites are present on the catalysts.^[9] The amounts of coke deposited on the used catalysts were determined by temperature-programmed oxidation (TPO) as presented in Figure 4b. The peak between 200–300 °C is attribut-

Table 1. Acidity based on NH_3 TPD and the amount of coke deposited on the used catalysts according to TPO analysis in Figure 4 b

| Samples | Concentrat [m | tion of acid s $mol g^{-1}$] | Amount of coke formed [wt%] | | | | | | |
|--------------------|------------------|-------------------------------|--------------------------------|-----|--|--|--|--|--|
| | Weak | Strong | Total | | | | | | |
| | (100–300 °C) | (>350 °C) | | _ | | | | | |
| MOR/SBA-15 | 0.014 | 0.411 | 0.425 | 7.9 | | | | | |
| MOR/SBA-15C-550/N2 | 0.003 | 0.470 | 0.473 | 6.8 | | | | | |
| MOR/SBA-15C-900/Ar | 0.006 | 0.342 | 0.348 | 6.3 | | | | | |
| H-MOR | 0.145 | 0.328 | 0.473 | 9.8 | | | | | |

gests that the coke formation and consequent catalyst stability are influenced mainly by the modified pore structure induced by forming a MOR/SBA composite catalyst instead of the acidity.

The mono-(IPN), di-(DIPN) and poly-(PIPN) isopropyl naphthalene products distributions in the naphthalene isopropylation reaction are plotted in Figure 5. The IPN, DIPN, and PIPN products obtained on MOR catalyst was 75%, approximately 25%, and 0% after 6 h TOS. The small and long pore channels of the MOR catalyst are easily blocked, which caused high selectivity for IPN and rapid deactivation. All the prepared MOR/ SBA-15 composite catalysts exhibited decreased amounts of IPN selectivity and increased catalyst stability.

The DIPN selectivity on MOR/SBA-15, MOR/SBA-15C–550/N₂, and MOR/SBA-15C–900/Ar catalysts were 30%, 34%, and 38%, respectively. The PIPN selectivity also increased in the same order because of increased conversions. The increased selectivity of DIPN and PIPN on prepared composite catalysts reflects the increased activity owing to the modified micro/mesopore structure that allows bulky molecules easy access to MOR



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Figure 5. Products distributions over parent and MOR/SBA-15 composite catalysts versus TOS; a) H-MOR; b) MOR/SBA-15; c) MOR/SBA-15C–550/N₂; d) MOR/SBA-15C–900/Ar. Reaction conditions: T = 250 °C; P = 30 bar; WHSV = 3 h⁻¹; isopropyl alcohol/naphthalene/decalin molar ratio = 1:2:7.5.

pores that contain the active catalytic sites. The hierarchical pore structure also minimizes coke formation and pore blocking by the formed coke to improve the stability. The monoisopropyl naphthalene (IPN) isomer distributions presented in Figure S4 also reflects the different pore structures. The commercial MOR zeolite with only small pores showed high selectivity to small 2-IPN (\approx 48%) relative to bulkier 1-IPN (27%). But for MOR/SBA-15 composite catalysts, the difference is minimized, indicating that there is no significant difference between the diffusion of 1-IPN and 2-IPN in the catalysts.

The time profiles of 2,6-DIPN selectivity and the 2,6-/2,7-DIPN ratio are presented in Figure 6. The 2,6-DIPN selectivity on MOR catalyst was initially highest (12%) and then stabilized at 8%



Figure 6. a) 2,6-DIPN selectivity and b) 2,6/2,7-DIPN ratio versus TOS for naphthalene isopropylation over parent and MOR/SBA-15 composite catalysts; Reaction conditions: $T = 250 \degree$ C; P = 30 bar; WHSV = 3 h⁻¹; isopropyl alcohol/naphthalene/decalin molar ratio = 1:2:7.5.

after 4 h on stream. The 2,6-DIPN selectivity on the MOR/SBA-15 composite catalyst was lower (\approx 4–5%), but it remained stable from the beginning. The 2,6/2,7-DIPN ratios representing the shape selectivity were all very similar (1.8–1.9) for MOR as well as for MOR/SBA-15 composite catalysts, indicating again that MOR is the active catalytic site for the composite catalysts as well. The isomeric distributions of DIPN other than 2,6- and 2,7-DIPN on MOR/SBA-15 composite catalysts are presented in Figure S5. Among the five minor isomers, 1,6-DIPN was produced as a major isomer of 7% on commercial MOR zeolite, whereas 1,3-DIPN was obtained in the highest amounts on MOR/SBA-15C-550/N2 (9%) and MOR/SBA-15C-900/Ar (8%) catalysts.

Conclusions

MOR has a channel-like pore structure of 6.7×7.0 Å and shows a high shape selectivity in isopropylation of naphthalene repre-



sented by a high 2,6/2,7-diisopropyl naphthalene (DIPN) ratio. However, the catalytic activity is low as a result of the restricted diffusion of reactant and product molecules through its small pores. In addition, the channel-like pores are easily blocked by coke deposition during the reaction and thus stability is poor. In this work, we attempted to form a hierarchical meso/micropore structure by combining micropores of MOR with mesopores of SBA-15 to improve naphthalene conversion and high stability with less coking, still maintaining the high 2,6/2,7-DIPN ratio characteristic of MOR. Thus the composites of MOR/SBA-15 were prepared by hydrothermal recrystallization process, by which MOR was recrystallized in the mesopores of SBA-15. For successful formation of the hierarchical meso/micro connection, the mesoporous SBA-15 structure should be stabilized by carbon coating formed on the pore walls as a template. The modified micro/mesopore structure allows facile diffusion of bulky molecules to and from active catalytic sites located in the small MOR pores as a result of the connection between the two types of pores in the composite MOR/SBA-15 crystal. Hence, our most successful MOR/SBA-15C-900/Ar catalyst achieved high conversion (85%) and high stability accompanied with less coking, and high 2,6/2,7-DIPN ratio (\approx 1.8). The hierarchical pore structure also minimizes coke formation and pore blocking by the formed coke to improve the stability.

Experimental Section

Catalyst synthesis

Mesoporous SBA-15 was synthesized by following the standard procedures reported earlier.[11] The template, P123 (EO20PO70EO20, Aldrich; 4 g) was dissolved in a solution containing H₂O (30 g) and 2 M HCl at $40 \degree$ C. Tetraethyl orthosilicate (8.5 g) was added to the clear solution and the mixture was stirred at 40°C for 24 h. It was then aged at 100 °C for 48 h in a Teflon bottle, during which a precipitate was produced. The precipitate was recovered, washed, and air-dried at RT. Different calcination procedures were adopted to obtain SBA-15 and carbon-containing SBA-15C: i) Calcination in air at 550 °C for 5 h produced white SBA-15 powders. ii) Calcination in N₂ at 550 °C for 5 h yielded a gray sample, denoted as SBA-15C-550/N₂). iii) Calcination in Ar at 900 °C for 5 h yielded another gray sample, denoted as SBA-15C-900/Ar. During all calcinations, the temperature was raised from RT to 550 °C and 900 °C at a rate of 1°Cmin⁻¹. The gray color of SBA-15C samples was attributed to the formation of carbon films on the pore walls of SBA-15 because of the decomposition of the template (P123) during calcination in the presence of N_2 or Ar.

Commercial Na-MOR (CBV10A (SiO₂/Al₂O₃ = 13), Zeolyst) was ion exchanged with 1 multiplue NH₄NO₃ solution at 80 °C followed by drying overnight at 80 °C and calcination at 550 °C for 5 h in air to obtain H-MOR. The MOR/SBA-15 composite catalysts were prepared by the following synthesis procedure. H-MOR (3 g) in distilled water was sonicated for 30 min followed by addition of SBA-15 or SBA-15C (3 g). The MOR recrystallization process was performed by transferring the MOR/SBA-15 mixture into Teflon tube followed by aging at 130 °C for 48 h. The precipitate was recovered, washed, dried at 100 °C for 12 h, and calcined at 550 °C for 5 h. The prepared composite samples were denoted as MOR/SBA-15, MOR/ SBA-15C-550/N₂, and MOR/SBA-15C-900/Ar, respectively.

Physical properties of the catalysts

Powder X-ray diffraction (XRD) patterns were obtained by using a PW3040/60 X'pert PRO (PANalytical) with $Cu_{K\alpha}$ radiation. The surface area and pore volume of the samples were calculated from N_2 sorption isotherms (Micromeritics ASAP 2420). ²⁷Al NMR spectra were recorded at RT using a VNMRS 600 NB spectrometer (14.1 T) at a spin rate of 15 kHz. A resonance frequency of 156.3 MHz, a recycle delay of 0.5 s, and 7000 scans were applied. ²⁹Si NMR spectra were recorded at RT using a VNMRS 600 NB spectrometer with 1.6 mm HXY FastMAS Triple Resonance Probe at a spin rate of 7 kHz. A recycle delay of 0.5 s and a resonance frequency of 119.17 MHz were applied.

The morphology was determined using an FE-SEM XL30S FEG Phillips scanning electron microscope. The high-resolution transmission electron microscope (HRTEM) images were recorded on a JEOL JEM-2100F/CESCOR microscope operated at 200 kV. TPD of NH₃ was performed to find out the distribution of acidity in the prepared catalyst. TPO analysis (Micromeritics Auto Chem II) was performed to calculate the amount of coke deposited on the used catalysts. A 10% O₂-He mixture was flushed through the catalyst at RT for 1 h, and then the temperature was raised to 750 °C at a rate of 8 °C min⁻¹.

Isopropylation of naphthalene

All catalytic experiments were performed in a continuous, highpressure, fixed-bed reactor with an inner diameter of 1/2 inch. A reactant mixture of naphthalene and isopropyl alcohol dissolved in decalin was injected through a high pressure pump into a tubular stainless-steel reactor, the middle of which was loaded with catalyst (1.0 g) in the form of granules (20-40 mesh). A thermocouple placed near the center of the catalyst bed was used to measure the reaction temperature. Before the start of the reaction, the catalyst was activated in situ in N_2 flow at 550 $^\circ$ C for 4 h to drive off moisture and adsorbed hydrocarbons, if any. The typical reaction conditions were as follows: temperature, 250 °C; pressure, 3.0 MPa; WHSV (total liquid feed), 3 h⁻¹; TOS, 8 h; molar ratio of naphthalene, isopropyl alcohol, and decalin in liquid feed, 1:2:7.5. To keep the system at a steady high pressure, N₂ at 10 mLmin⁻¹ was introduced into the reactor along with the reaction feed. The reactor effluent was condensed in the sampler and sampled hourly. The products were analyzed by a gas chromatograph (model HP 7890) using a flame ionization detector and a 60 m \times 0.25 mm \times 0.25 μ m (HP Innowax) capillary column.

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