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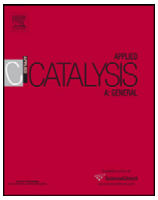

A new solid acid for specifically cleaving the $C_{ar}—C_{alk}$ bond in di(1-naphthyl)methane

Xiao-Ming Yue[a], Xian-Yong Wei[a,*], Bing Sun[a], Ying-Hua Wang[a], Zhi-Min Zong[a], Xing Fan[a], Zi-Wu Liu[a,b]

[a] *Key Laboratory of Coal Processing and Efficient Utilization (Ministry of Education) and Low Carbon Energy Institute, China University of Mining & Technology, Xuzhou 221008, Jiangsu, China*

[b] *School of Chemistry and Chemical Engineering, South China University of Technology, Wushan 381, Guangzhou 510640, Guangdong, China*

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ABSTRACT

Three catalysts were prepared by impregnating the same volume of pentachloroantimony (PCA), trimethylsilyl trifluoromethanesulfonate (TMSTFMS), or isometric PCA and TMSTFMA into an activated carbon (AC). Di(1-naphthyl)methane (DNM) was used as a coal-related model compound to evaluate their catalytic activity. The results show that $C_{ar}—C_{alk}$ bond in DNM can be specifically cleaved over each catalyst to afford naphthalene and 1-methylnaphthalene under pressurized hydrogen at temperatures up to 300 °C, but as a new solid acid (NSA), PCA–TMSTFMS/AC is significantly more active for DNM hydrocracking than the other two catalysts. FTIR and SEM analyses reveal the strong interactions among PCA, TMSTFMS, and the AC in the NSA. NH_3-TPD analysis suggests that the NSA should exhibit appreciably stronger acidity than the other two catalysts. The strong interactions may result in the appreciably stronger acidity of the NSA than that of the other two catalysts and thereby facilitate DNM hydrocracking. It is presumed that H_2 was heterolytically cleaved to immobile H^- and mobile H^+. The addition of mobile H^+ to *ipso*-position of DNM should be crucial step for DNM hydrocracking.

1. Introduction

The cleavage of bridged bonds (BBs), especially C—C bridged bonds, in coals is one of the most important reactions for direct coal liquefaction (DCL) [1–3]. Conventional DCL is usually conducted at temperatures higher than 450 °C, leading to severe increase in the yields of both gases and heavy products [4] with huge energy consumption in addition to significant increase in investment cost [3,5] caused by the requirement for the equipments capable of withstanding high temperature and pressure. Preparing active catalysts for effectively cleaving BBs in coals is needed for developing low-temperature DCL process to solve the above problems.

Rapid improvements in the area of carbocation chemistry have been achieved since the pioneering work of Olah, who used pentafluoroantimony as a strong Lewis acid [6]. However, such a strongly corrosive liquid acid erodes equipments and cannot be effectively recycled. Solid acids have the advantages of low corrosion, larger specific surface area (SSA) and good retrievability [7].

Since coal structures are still not clear, studies on the reactions of coal-related model compounds have become powerful tools to reveal the mechanisms of coal liquefaction on the molecular level [8–13]. In general, thermal cleavage of $C_{ar}—C_{alk}$ bond is much more difficult than that of $C_{alk}—C_{alk}$ bond. Consequently, selective cleavage of $C_{ar}—C_{alk}$ bond at a lower temperature in the presence of a proper catalyst is the key of hydrocracking in DCL and model reactions. Wei et al. found that the metal catalysts such as Fe, Ni, and Pd/C mainly catalyzed di(1-naphthyl)methane (DNM) hydrogenation via biatomic hydrogen transfer, whereas their sulfides predominantly promoted DNM hydrocracking via monatomic hydrogen transfer, i.e., radical hydrogen transfer (RHT) [14,15]. RHT to DNM also occurred over an activated carbon (AC) and promoted by adding sulfur [16]. The hydrogenation of aromatic rings is inevitable in addition to the release of hydrogen sulfide either over metal sulfides or over AC/sulfur, although the total selectivity of hydrogenated products was very low from the reaction of DNM. Specifically cleaving $C_{ar}—C_{alk}$ BBs in coals under mild conditions is of great importance both for understanding coal structures (especially the types of aromatic units and BBs connecting the units) and for facilitating the separation of reaction products.

Taking the above importance into account, we tried to prepare a highly active catalyst for specifically cleaving $C_{ar}—C_{alk}$ BBs in coals. Here, we report our preliminary results using DNM as a coal-related model compounds.

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[*] Corresponding author. Tel.: +86 0516 83885951; fax: +86 0516 83885951.
E-mail address: wei_xianyong@163.com (X.-Y. Wei).

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2. Experimental

2.1. Materials

DNM was synthesized by heating naphthalene with 1-chloromethylnaphthalene over zinc powder. Solvent cyclohexane was commercially purchased and distilled before use. An AC, trimethylsilyl trifluoromethanesulfonate (TMSTFMS) and pentachloroantimony (PCA) were also commercially purchased. The AC was ground to <75 μm and dried in a vacuum at 80 °C for 24 h, then stored under a nitrogen atmosphere before use.

2.2. Catalyst preparation and characterization

The AC (8 g) and the same amount (30 mL in total) of one or two acidic species (ASs), i.e., PCA, TMSTFMS or isometric PCA and TMSTFMS, were placed into an 80 mL CEM Discover microwave reactor with a condenser and magnetic stirrer. After replacing air in the reactor with nitrogen three times, the reactor was heated to 80 °C and kept at the temperature for 20 min. Then it was cooled to room temperature and continuously stirred for 12 h. The catalysts, i.e., PCA/AC, TMSTFMS/AC and PCA–TMSTFMS/AC, were obtained by filtering the reaction mixtures through a membrane filter of polytetrafluoroethylene with 0.8 μm of pore size followed by desiccation at 120 °C for 24 h under the protection of nitrogen. Among the catalysts, PCA–TMSTFMS/AC was investigated with emphasis as a new solid acid (NSA).

Infrared spectra of the AC and catalysts were recorded on a Nicolet Magna IR-560 Fourier Transform infrared (FTIR) spectrometer using KBr pellets. Specific surface area (SSA), total pore volume (TPV) and average pore diameter (APD) of the samples were determined by nitrogen adsorption at −196 °C on an Autosorb-1-MP instrument. Scanning electron microscopic (SEM) observations of the samples and corresponding elemental analysis were performed with a Hitachi S-3700N scanning electron microscope operating at 200 kV combined with an energy dispersive spectrometer (EDS). The catalyst acidities were measured by temperature-programmed desorption of ammonia (NH_3-TPD) with a TP-5000 II adsorption instrument.

2.3. DNM hydrocracking and reaction mixture analysis

DNM (1 mmol), a catalyst (0–0.4 g) and cyclohexane (30 mL) were put into a 60 mL stainless, magnetically stirred autoclave. After replacing air in the autoclave with hydrogen, the autoclave was pressurized with hydrogen to a desired pressure, i.e., initial hydrogen pressure (IHP between 1 and 5 MPa), at room temperature (20 °C) and heated to an indicated temperature (150–300 °C) in 15 min. After reaction at the temperature for a prescribed period of time (1–10 h), the autoclave was immediately cooled to room temperature in an ice-water bath. The products and unreacted DNM in the reaction mixture taken out from the autoclave were quantified with a Hewlett-Packard 6890 gas chromatography and identified with a Hewlett-Packard 6890/5973 gas chromatography/mass spectrometry.

3. Results and discussion

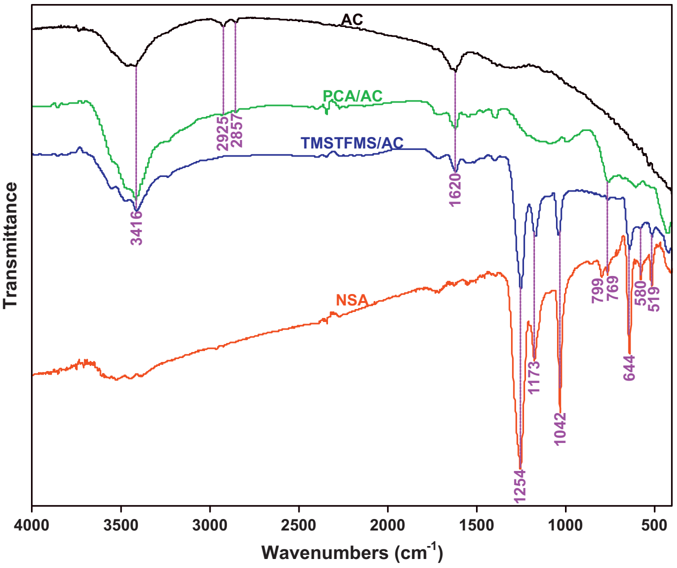


Fig. 1. FTIR spectra of the AC and catalysts.

As Fig. 1 shows, the absorbances of —OH at 3416 cm^{-1} and >C=C< moiety at 1620 cm^{-1} in the AC, PCA/AC and TMSTFMS/AC can be clearly observed but almost disappeared in the NSA, while the absorbances of $-CH_3$ and >C—C< moiety at 2925 and 2857 cm^{-1} observed in the AC almost disappeared in PCA/AC and completely vanished in TMSTFMS/AC and the NSA, although both TMSTFMS/AC and the NSA were prepared by impregnating TMSTFMS, which contains CH_3 groups. The appearance of C—Cl bonds at 769 cm^{-1} in PCA/AC suggests the reaction of PCA with the AC during the catalyst preparation. The formation of C—Cl bonds also occurred from the reaction of polyacetylene with PCA when PCA was used as a dopant [17]. Blue shift of the absorbance for some of C—Cl bonds from 769 [17] to 799 cm^{-1} [18] can be found by comparing FTIR spectrum of PCA/AC with that of the NSA. Many characteristic absorbances of $-CF_2-SO_2-O$ (asymmetric) [19] and Si—O [20] at 1254 cm^{-1}, $(CH_3)_3Si-O$ [21] at 1173 cm^{-1}, $O-SO_2-O^-$ [22] and F_3C-SO_2-O [23] at 1042 cm^{-1}, C—F [24] and $-SO_3$ (symmetric) [25] at 644 cm^{-1}, $-CF_3$ (asymmetric) [25] at 580 cm^{-1} and $-SO_3$ (asymmetric) [25] at 519 cm^{-1} from TMSTFMS were confirmed in the NSA in addition to the absorbance of C—Cl bonds at 769 and 799 cm^{-1}, as shown in Fig. 1 and Table 1. However, based on the absorbance intensity (AI) at 1254 cm^{-1}, the AI at 1173 cm^{-1} in the NSA is much weaker than that in TMSTFMS/AC, whereas the AIs at 1042, 644, 580 and 519 cm^{-1} in the NSA are significantly stronger than those in TMSTFMS/AC. Neither of the characteristic absorbances except for the absorbance at 799 cm^{-1} appeared in PCA/AC. The above results evidently indicate that there exist strong interactions among PCA, TMSTFMS and the AC in the NSA, although the detailed interaction mechanisms need to be further investigated.

As Fig. 2 displays, the surface of AC itself is smooth compared to the rough surface of three other samples. A number of spherical particles (SPs) with diameter less than 1 μm adhered to the AC surface can be clearly observed only in PCA/AC, while there are irregular grains (IRGs) with diameter less than 5 μm adhered to the AC surface in TMSTFMS/AC and the NSA. According to EDS analysis demonstrated in Fig. 3, the following elements were confirmed: (1) C and O from the AC, C, O, Sb and Cl in the SPs from PCA/AC; (2) C, O, F, Si and S in the IRGs from TMSTFMS/AC; (3) all the above elements in IRGs from the NSA. However, O/C ratio in the SPs from PCA/AC is far higher than that in the AC, although no O contains in PCA. The higher O/C ratio in the SPs from PCA/AC could be related to the reaction of PCA with oxygen-containing species in the AC and/or O_2 in air during the catalyst preparation. These observations further confirmed the strong interactions among PCA, TMSTFMS and the AC in the NSA.

Data listed in Table 2 exhibit that the impregnation of either PCA or TMSTFMS or both the ASs significantly decreased SSA and TPV of the resulting catalysts and remarkably decreased APD of the resulting PCA/AC but appreciably increased APD of the resulting TMSTFMS and NSA. Especially, the decrease in SSA for the NSA is

Table 1
Comparison of intensity relative to the absorbance at 1254 cm^{-1}.

WN (cm^{-1})	Intensity relative to WN_{1254}		Assignment
	NSA	TMSTFMS/AC	
1254	1.0000	1.0000	$-CF_2-SO_2-O$ (asymmetric) [19], Si—O [20]
1173	0.1684	0.2408	$(CH_3)_3Si-O$ [21]
1042	0.3364	0.2272	$O-SO_2-O^-$ [22], F_3C-SO_2-O [23]
799	0.0598	0	C—Cl [18]
644	0.2624	0.2243	C—F [24], $-SO_3$ (symmetric) [25]
580	0.0193	0.0147	$-CF_3$ (asymmetric) [25]
519	0.0602	0.0436	$-SO_3$ (asymmetric) [25]

WN – wavenumber; intensity relative to WN_{1254} – peak area at an indicated wavenumber/peak area at 1254 cm^{-1}.

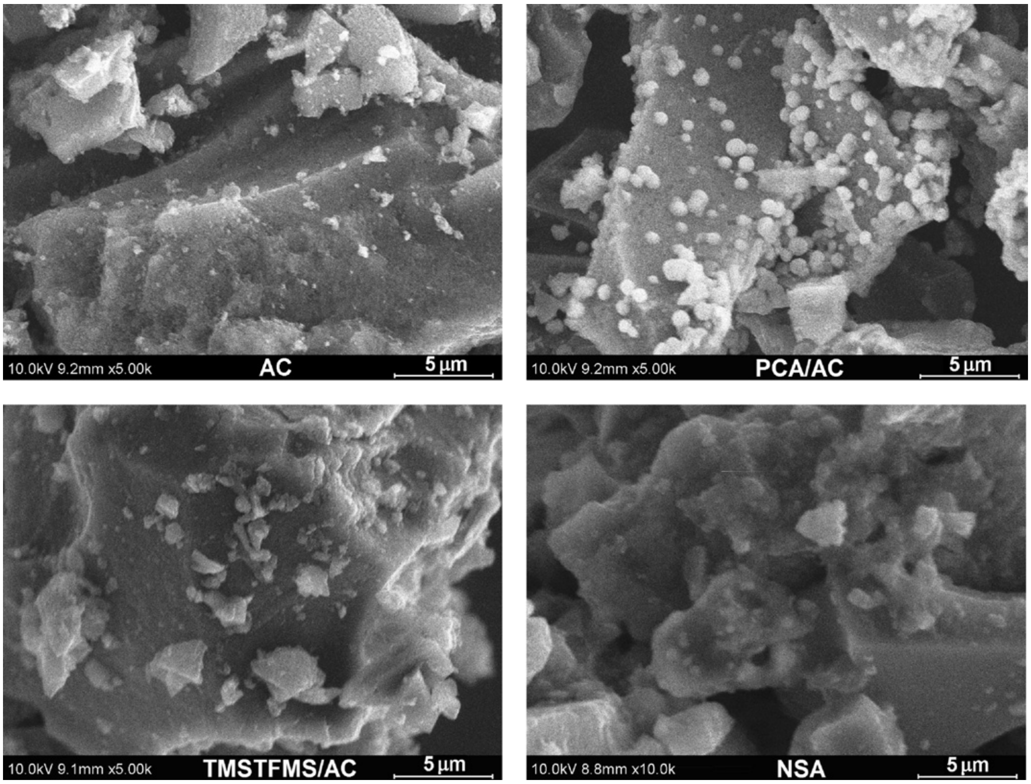


Fig. 2. SEM micrographs of the AC and catalysts.

the most significant. The results imply that significant amount of an AS or two ASs was impregnated into micropores in the AC and TMSTFMS expanded the micropores to some extent, especially by synergic interaction with PCA.

NH_3-TPD is well used for measuring the surface acidity of porous samples and more NH_3 desorption at higher temperatures indicate stronger acidity of the samples [26]. As Fig. 4 illustrates, there are sharp desorption peak (SDP) in lower temperature region (LTR, <300 °C) and broad desorption peak in higher temperature region (HTR, 550–685 °C) for PCA/AC and the NSA, but only SDP can be observed for TMSTFMS/AC. The temperatures corresponding to maximum intensity in LTR for PCA/AC, TMSTFMS/AC and the NSA are 87.3, 185.2 and 216.1 °C, respectively, and those in HTR for PCA/AC and the NSA are 601.1 and 606.3 °C, respectively. In addition, the intensities of desorption peaks both in LTR and in HTR from the NSA are significantly stronger than those from PCA/AC. These results indicate that the acidity of NSA is substantially stronger than that of either PCA/AC or TMSTFMS/AC. The enhanced acidity should be closely related to the strong interactions among PCA, TMSTFMS and the AC in the NSA, which were characterized by FTIR, SEM and EDS analyses along with the surface property measurements mentioned above.

Table 2
Surface properties of the AC and catalysts.

Sample	SSA ($m^2\ g^{-1}$)	TPV ($cm^3\ g^{-1}$)	APD (nm)
AC	743.0	0.53	2.85
TMSTFMS/AC	637.7	0.46	2.91
PCA/AC	526.3	0.26	2.66
NSA	487.6	0.38	3.12

The results illustrated in Fig. 5 show that the activity of NSA for DNM hydrocracking is appreciably higher than that of PCA/AC and much higher than that of TMSTFMS/AC under the same reaction conditions. Dramatic increases in DNM conversion and the product yield can be observed over any catalyst. Noteworthily, all the catalysts specifically cleaved the BB in DNM, only affording naphthalene and 1-metyhylnaphthalene (1-MN). The yield of naphthalene is appreciably higher than that of 1-MN over any catalysts and the difference in yield between the two products increased with raising the reaction temperature, indicating that the 1-MN demethylation proceeded and became significant at

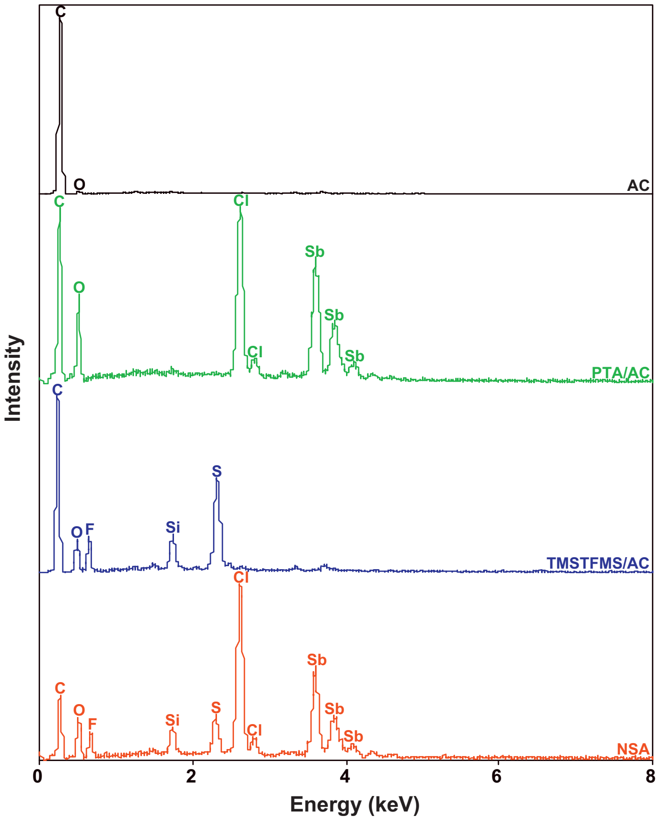


Fig. 3. EDS spectra of the AC and catalysts.

higher temperatures. Dramatic increase both in DNM conversion and in the product yields above 250 °C also deserves attention.

DNM conversion, the product yields and the difference in yield between naphthalene and 1-MN basically increased with the increases in the NSA feed (Fig. 6), reaction time (Fig. 7) and IHP (Fig. 8), but the increases with reaction time at 250 °C are insignificant (Fig. 7). There was almost no increase in 1-MN yield with the increase in IHP at 300 °C (Fig. 8). These facts suggest that the NSA activation at temperatures higher than 250 °C is needed and the increase in IHP facilitates 1-MN demethylation to naphthalene.

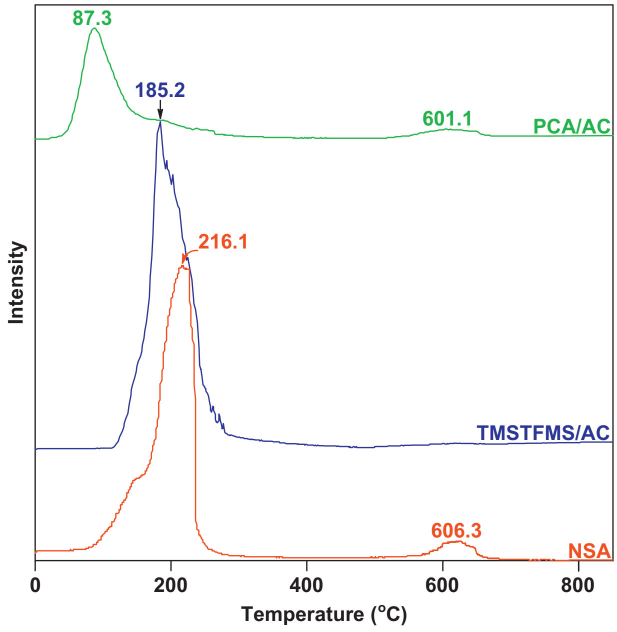


Fig. 4. NH_3-TPD profiles of the catalysts.

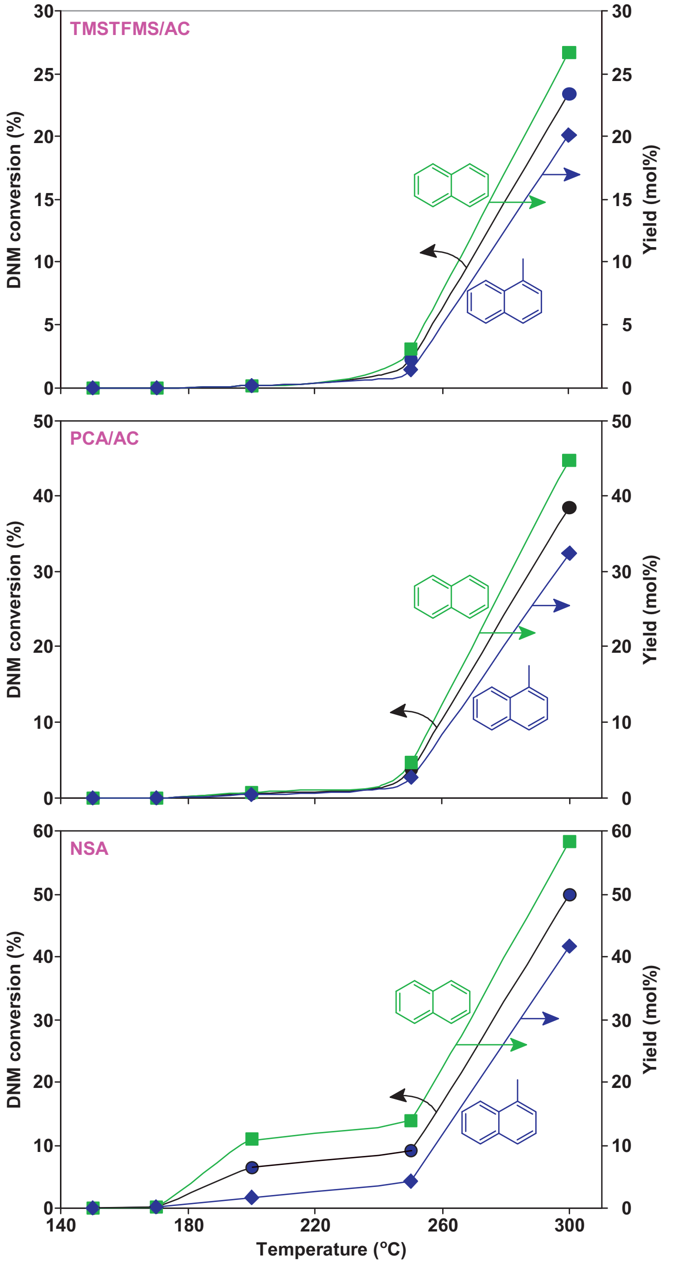
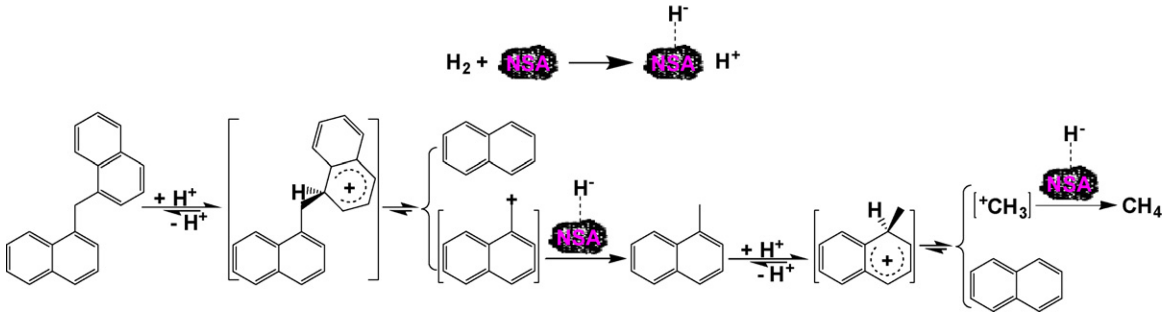


Fig. 5. DNM conversions and product yields over different catalysts at different temperatures (catalyst 0.4 g, IHP 5 MPa, 3 h).

Thermally cleaving the C_{ar}—C_{alk} bonds is very difficult because of the extreme lability of the resulting aryl radical. Hydrogen transfer either from $H^{\bullet}$ or from H^{+} is crucial for the C_{ar}—C_{alk} bond cleavage [27–31], because the addition of $H^{\bullet}$ or H^{+} to the *ipso*-position (IP) of an aryl group with a methylene linkage affords a stable aromatic molecule rather than a labile aryl radical. As mentioned above, synergic interaction of the electrophilic reagents PCA and TMSTFMS, which were impregnated into the AC in the NSA, substantially increased the NSA acidity. Strong acidity of the NSA facilitates heterolytical splitting of H_2 to an immobile H^{-} adhered to the NSA surface and a mobile H^{+}, as displayed in Scheme 1. The addition of mobile H^{+} to the IP of a naphthalene ring in DNM leads to specific cleavage of the BB in DNM, resulting in naphthalene and naphthalen-1-ylmethylium (NM). The resulting NM can abstract an



Scheme 1. Possible mechanism for the NSA-catalyzed hydrogen transfer to DNM.

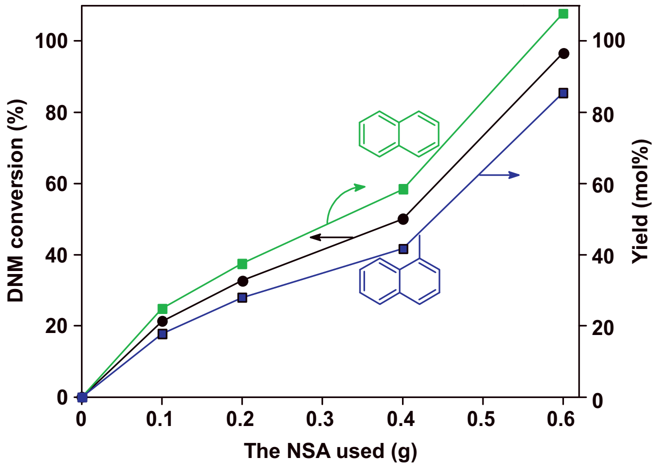


Fig. 6. Effect of the NSA feed on DNM conversion and product yield (IHP 5 MPa, 300 °C, 3 h).

immobile H⁻ from the NSA surface to afford 1-MN. The demethylation of 1-MN also proceeds via the addition of mobile H⁺ to the IP of the naphthalene ring in 1-MN and subsequent abstraction of an immobile H⁻ by the resulting ⁺CH₃ from the NSA surface, but the 1-MN demethylation is not easy compared to the BB cleavage in DNM due to less stability of ⁺CH₃ than NM.

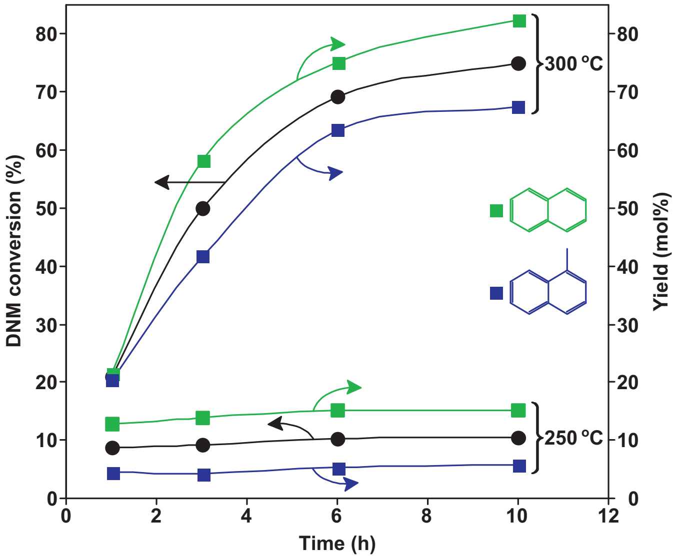


Fig. 7. Time profiles of DNM conversion and product yield at 250 and 300 °C (catalyst 0.4 g, IHP 5 MPa, 3 h).

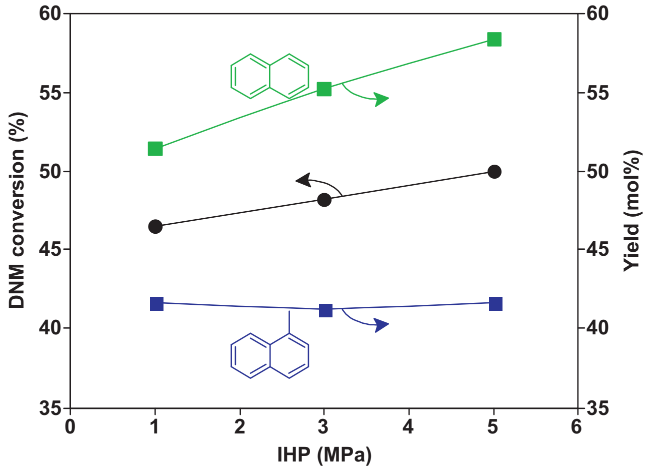


Fig. 8. Effect of IHP on DNM conversion and product yield (NSA 0.4 g, 300 °C, 3 h).

4. Conclusions

The strong interactions among PCA, TMSTFMS and the AC in the NSA were confirmed by FTIR, SEM and EDS analyses along with the surface property measurements. With stronger acidity than PCA/AC and TMSTFMS/AC, the NSA exhibited substantially higher activity than PCA/AC and even much higher activity than TMSTFMS/AC for specifically cleaving BB in DNM by the strong interactions. The high activity of NSA for the specific cleavage of BB in DNM could be ascribed to the catalysis of NSA in effective producing mobile H⁺ and immobile H⁻.

Acknowledgments

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