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Shape-selective isopropylation of naphthalene. Reactivity of 2,6-diisopropylnaphthalene on dealuminated mordenites

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Abstract

Shape-selective isopropylation of naphthalene over a hydrogen-mordenite (HM) catalyst is an effective route for the production of 2,6-diisopropylnaphthalene (2,6-DIPN). Our previous work on naphthalene isopropylation has shown that 2,6-DIPN selectivity is substantially increased by HM dealumination. An assessment of 2,6-DIPN reactivity on the catalyst would be useful in understanding factors that control product selectivity. We measured 2,6-DIPN reactivity on three HM catalysts (SiO_2/Al_2O_3 ratio 14, 38 and 74), under propylene pressure, in batch reactor tests at 200°C. The propylene pressure was varied to give propylene to 2,6-DIPN mole ratios of 4.0, 1.0 and 0.5. On HM14 and HM38 catalysts, 2,6-DIPN conversions were 12–27%, mostly to higher alkylates. Some isomerization of 2,6-DIPN occurred at the lowest propylene pressure, but was suppressed by increasing the propylene pressure. 2,6-DIPN is nearly unreactive on dealuminated mordenite (HM74). These results reveal that the high selectivity toward 2,6-DIPN in the isopropylation of naphthalene is partly attributable to the low reactivity of 2,6-DIPN on dealuminated mordenites.

Keywords: 2,6-Diisopropylnaphthalene; Propylene; Mordenite; Alkylation; Isomerization

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1. Introduction

There is a growing interest to produce 2,6-dialkylnaphthalenes (2,6-DANs) for making monomers of high-performance polyester fibers, molded plastics, thermotropic liquid crystalline polymers, and other advanced polymer materials [1–3]. Future expansion in the use of these materials depends on the development of an efficient method for production of 2,6-DANs such as 2,6-diisopropylnaphthalene (2,6-DIPN).

In earlier work, we showed that dealuminated hydrogen-mordenite (HM) catalysts give high selectivity for isopropylation at the β-positions of naphthalene [4–6]. The main products are 2-monoisopropylnaphthalene (2-MIPN), and two diisopropylnaphthalene (DIPN) isomers, 2,6- and 2,7- (Scheme 1). HM has non-interconnecting, twelve-membered ring elliptical pores of dimension 6.7 × 7.0 Å as its main pore structure. The high shape-selectivity of HM can be explained on the basis of two observations. First, main channel dimension of HM is intermediate between the critical diameters of the two MIPN isomers. Due to steric constraints on the transition state, 1-MIPN can not be formed within the HM channels; whereas, the critical

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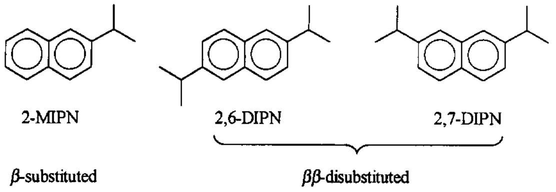


Scheme 1. β-Substituted mono- and diisopropylnaphthalenes.

diameter of the β-substituted isomer, 2-MIPN, is sufficiently smaller than the channel diameter. Diisopropyl substitution is even more inhibited, and only ββ-substituted isomers (2,6- and 2,7-DIPN) can result from reaction within the micropores [7]. Substitution at the more reactive α-carbons of naphthalene can only occur on external surface catalyst sites. The second shape-selectivity mechanism has to do with relative diffusion rates (product selectivity). A slightly smaller critical diameter and a more linear structure give 2,6-DIPN a lower barrier to diffusion in the micropores than 2,7-DIPN [4,8,9].

High catalytic selectivity for 2,6-DIPN requires two factors: its selective formation and its low reactivity on the catalyst once it is formed. Catalyst sites on the external surface of mordenite can promote non-selective reactions which decrease the 2,6-DIPN selectivity. Examples of such reactions are isomerization, transalkylation, and continued alkylation leading to tri- and tetraalkylnaphthalenes. We report here experiments designed to examine the reactivity of 2,6-DIPN on HM at 200°C, and how the reactivity changes with HM aluminum content and propylene pressure. This is a continuation of our effort to utilize the rich resource of polycyclic aromatic hydrocarbons found in coal-derived liquids and heavy oils to make value-added chemicals [1–6].

2. Experimental

The mordenites, NaM14 and NH_4M38, were supplied as 10 μm average particle size powders from the PQ Corporation, Inc. The last two digits in the catalyst name specify the molar SiO_2/Al_2O_3 ratio. NaM14 was treated with 1 M NH_4Cl at reflux, washed free of chloride, dried and calcined to generate the proton-form (HM14). Dealuminated mordenites were prepared by stirring HM14 in 1 M HCl at reflux temperature for either 10 h (HM71) or 24 h (HM74). The sample was recovered onto a filter, washed free of chloride, dried and calcined. All catalyst were calcined in air at 465°C for 5.5 h. Catalyst samples were solubilized using lithium metaborate fusion for ICP-AES chemical analyses. Samples were outgassed at 400°C prior to BET sorption of N_2 to measure catalyst surface areas and total pore volumes. Micropore and mesopore volumes were calculated using the T-plot method.

All chemicals were of high purity and used as supplied. Naphthalene (99%) was obtained from Aldrich Chemical Co., Inc. 2,6-Diisopropylnaphthalene was obtained from TCI Chemicals, Ltd. (GR grade). Its purity was analyzed using GC. Propylene (99.5% minimum, polymer purity) was obtained from Matheson, Inc. and delivered to the reactor as a vapor.

Catalyst tests were done in a 30 cm^3, stainless-steel microautoclave reactor. For naphthalene alkylation, the reactor was charged with 1.0 g (7.8 mmol) naphthalene, 0.66 g (15.6 mmol) propylene, and 0.10 g catalyst. Reactivity of 2,6-DIPN was evaluated by charging the reactor with 1.0 g (4.7 mmol) 2.6-DIPN, 0.10 g catalyst, and propylene to make the desired propylene to 2,6-DIPN mole ratio (4.0, 1.0 or 0.5). The propylene-pressurized reactor was mounted on a holder and immersed in a fluidized sand bath heater. Mixing was accomplished by vertically agitating the reactor at 240 min^{-1}, with a 1 cm stroke. All runs were conducted at 200°C for 2 h.

At the end of the test, the reaction was quenched by immersing the reactor in cold water. The contents of the reactor were then washed with acetone onto a filter. Solution products were analyzed by GC-MS and GC-FID. For

Table 1
Properties of the HM catalysts

Catalyst [a]	Na_2O (wt%)	Surface area (m^2/g)			Pore volume (cm^3/g)		
		Total	Micro [b]	Meso [b]	Total	Micro [b]	Meso [b]
NaM14 [c]	6.24	466	457	10	0.312	0.174	0.138
HM14	0.19	na [d,e]	na	na	na	na	na
HM38 [c]	0.07	512	429	82	0.293	0.167	0.126
HM71	< 0.01	566	497	75	0.349	0.191	0.125
HM74	< 0.01	583	509	74	0.385	0.196	0.148

[a] Trailing digits specify the mordenite SiO_2/Al_2O_3 mol ratio.
[b] Pore diameters: meso 20–600 Å, micro < 20 Å.
[c] Data as reported by PQ Corp., Inc.
[d] Not available.
[e] HM14 and NaM14 are likely to have very similar pore structures, surface areas and sorption capacities.

both GC instruments, the column was 30 m × 0.25 mm DB-17 (J&W Scientific), and the oven temperature program was 40–280°C at 4°C/min.

3. Results and discussion

Sorption data and residual sodium contents for the catalysts are given in Table 1. The sodium content of NaM14 is reduced by approximately 97% by exchange with ammonium. Following dealumination with hydrochloric acid, residual sodium content is below the limit of detection (0.01 wt%). As shown here and in previous work [6,10], HM pore volume, especially mesopore volume, generally increases as a result of HM dealumination.

Table 2 shows a comparison of naphthalene isopropylation data reported in our preliminary communication [6], including data for the catalysts used in the present study. Selective isopropylation at the β-positions of naphthalene occurs within the HM micropores. Non-selective alkylation, polyalkylation and isomerization reactions occurring on the catalysts external surface decrease 2,6-DIPN selectivity. It is apparent that increasing the HM SiO_2/Al_2O_3 ratio increases the β-selectivity to 2-MIPN and the ββ-selectivity to 2,6- and 2,7-DIPN. The 2,6-DIPN to 2,7-DIPN isomer ratio also increases by about 27% with dealumination, from 1.76 for HM14, to 2.29 for HM71 and 2.24 for HM74. In other words, the dealuminated mordenites (HM71 and HM74) have higher selectivities for 2,6-DIPN.

Table 2
Propylene addition to naphthalene over HM catalysts [a]

Catalyst	Conversion (%)				Isomer selectivity (mol%)			
		Pdt. distribution (mol%)			MIPN	DIPN		
		MIPN	DIPN	TrIPN + [b]	2-	2,6-	2,7-	2,6-/2,7-
HM14	76	63	32	3.6	60	33	19	1.76
HM38	73	60	34	4.4	58	39	19	1.99
HM71	74	60	37	2.3	64	51	22	2.29
HM74	47	75	23	0.6	71	55	25	2.24

[a] Batch reaction conditions: 1.0 g (7.8 mmol) naphthalene, 0.66 g (15.6 mmol) propylene, 0.10 g HM, 200°C for 2 h.
[b] Tri- and tetraisopropylnaphthalenes.

Table 3
Analysis of the 2,6-DIPN starting material

Component	Mol%
2-MIPN	2.4
1-MIPN	1.1
2,6-DIPN	95.5
2,7-DIPN	0.4
other-DIPN	0.3
TrIPN [a]	0.2
TeIPN [b]	0.0
RNAP [c]	0.2

[a] Triisopropylnaphthalene.
[b] Tetraisopropylnaphthalene.
[c] Alkylnaphthalenes, not solely isopropyl substituted.

To understand the enhanced selectivity for 2,6-DIPN with aluminum removal from HM, two factors require consideration. The first is the increased selectivity during the alkylation (product forming) steps. The second concerns the reactivity of the 2,6-DIPN product during the catalyzed alkylation reaction. Concerning selectivity during the alkylation step, we showed that dealumination causes an increase in the HM mesopore volume, and results in a small contraction of the HM micropore diameter (as determined by XRD) [6]. Intraparticle diffusion rate differences between 2,6- and 2,7-DIPN are magnified by reducing the channel dimension, and selectivity for 2,6-DIPN, the slimmer of the two isomers, increases [6]. We now turn attention to the issue of product reactivity on the catalyst. In the limiting case, once the desired product is formed, it would react no further. As we will show, this seems to be the case for 2,6-DIPN on dealuminated HM (HM74).

Purity of the 2,6-DIPN starting material is approximately 95.5% according to GC analysis as shown in Table 3. Monoisopropylnaphthalenes are the main impurities, with much smaller amounts of isomeric DIPNs (other than the 2,6-isomer), tri- and tetraisopropylnaphthalenes (TrIPN and TeIPN, respectively), and isomeric C_5-, C_7- and C_8-alkylnaphthalenes, $m/z = 198$, 226 and 240, respectively (RNAP). Components assigned to other-DIPN are those that give mass spectral data consistent with diisopropyl substitution, but the substitution patterns are not known. To a certain extent, impurities in the 2,6-DIPN stock complicate the interpretation of reaction results, but the presence of the impurities also enabled us to make some interesting comparisons of relative reactivities.

The results for reaction of 2,6-DIPN over the three HM catalysts, at the three different propylene/2,6-DIPN ratios, are shown in Table 4, Tables 5 and 6. 2,6-DIPN conversions can be positive or negative (see Table 6) depending upon whether the reaction results in a net decrease or net increase in the amount of 2,6-DIPN. The concentration (in mol%) of each component is given along with the change in its concentration vs. the starting material. This type of tabulation facilitates comparisons of relative reactivity and helps to identify reactant–product relationships between different compounds.

Table 4
Reaction of 2,6-DIPN on HM14 catalyst [a]

Propylene to 2,6-DIPN mole ratio	4.0	1.0	0.5
%2,6-DIPN conversion	27.1	25.4	23.9
Pdt. distribution (mol%, change)			
2-MIPN	0.0 (−2.4)	0.1 (−2.3)	0.4 (−2.0)
1-MIPN	0.0 (−1.1)	0.0 (−1.1)	0.0 (−1.1)
2,6-DIPN	69.6 (−25.9)	71.2 (−24.3	72.6 (−22.9)
2,7-DIPN	0.1 (−0.3)	0.3 (−0.1)	1.1 (0.7)
other-DIPN	0.3 (0.0)	1.9 (1.6)	4.6 (4.3)
TrIPN	26.1 (25.9)	23.4 (23.2)	19.1 (18.9)
TeIPN	3.7 (3.7)	2.8 (2.8)	1.9 (1.9)
RNAP	0.3 (0.1)	0.3 (0.1)	0.3 (0.1)

[a] Reaction at 200°C for 2 h. Propylene pressure varied.

Table 5
Reaction of 2,6-DIPN on HM38 catalyst [a]

Propylene to 2,6-DIPN mole ratio	4.0	1.0	0.5
%2,6-DIPN conversion	25.0	22.9	12.5
Pdt. distribution (mol%, change)			
2-MIPN	0.1 (−2.3)	2.0 (−0.4)	0.1 (−2.3)
1-MIPN	0.1 (−1.0)	0.2 (−0.9)	0.0 (−1.1)
2,6-DIPN	71.6 (−23.9)	73.6 (−21.8)	83.5 (−11.9)
2,7-DIPN	0.1 (−0.3)	0.2 (−0.2)	0.2 (−0.2)
other-DIPN	0.3 (0.0)	1.2 (0.8)	1.2 (0.9)
TrIPN	24.9 (24.7)	19.6 (19.4)	13.4 (13.3)
TeIPN	2.7 (2.7)	1.9 (1.9)	1.2 (1.2)
RNAP	0.2 (0.0)	1.2 (1.1)	0.3 (0.1)

[a] Reaction at 200°C for 2 h. Propylene pressure varied.

Conversions of 2,6-DIPN are quite high on HM14 and HM38, ranging from 12–27%. TrIPN and TeIPN products increase when propylene/2,6-DIPN is increased, especially on HM38 catalyst (Table 5). Increased propylene pressure drives the reaction toward higher alkylates (TrIPN and TeIPN). Propylene pressure has only a mild effect on alkylation for 2,6-DIPN reaction on HM14, but decreasing the propylene pressure causes 2,7- and other-DIPN products to increase (Table 4). Two factors may contribute to the decrease in selectivity for 2,6-DIPN: isomerization and transalkylation reactions involving 2,6-DIPN, and a change in MIPN isopropylation selectivity. It is difficult to judge for certain which factor is most important, but we can conclude that at least some of the original 2,6-DIPN is isomerized on HM14. With propylene/2,6-DIPN ratios of 4.0 and 1.0, production of TrIPN and TeIPN exceeds conversion of 2,6-DIPN. Isopropylation of MIPN impurities makes up for the imbalance. But at the lowest propylene/2,6-DIPN ratio, the situation is reversed: 2,6-DIPN decreases by 22.9 mol%, but the sum of TrIPN and TeIPN increases by only 21.0 mol%. MIPNs do not increase so no dealkylation of 2,6-DIPN occurs, rather 2,6-DIPN is isomerized.

It should be restated that only β-substituted isopropylnaphthalenes can be formed within the HM micropores. Reactions leading to α-substituted isopropylnaphthalenes must occur on external surface catalyst sites. At the higher propylene pressures, alkylation of 2,6-DIPN is increased, but its isomerization is suppressed for HM14 (Table 4) and HM38 (Table 5) catalysts. Both reactions of 2,6-DIPN produce α-substituted naphthalenes. Formation of the iso-

Table 6
Reaction of 2,6-DIPN on HM74 catalyst [a]

Propylene to 2,6-DIPN mole ratio	4.0	1.0	0.5
%2,6-DIPN conversion	0.8	−1.3	−1.5
Pdt. distribution (mol%, change)			
2-MIPN	0.0 (−2.4)	0.0 (−2.4)	0.0 (−2.4)
1-MIPN	0.0 (−1.1)	0.0 (−1.1)	0.0 (−1.1)
2,6-DIPN	94.7 (−0.7)	96.7 (1.2)	96.9 (1.4)
2,7-DIPN	0.1 (−0.3)	0.1 (−0.3)	0.1 (−0.3)
other-DIPN	0.1 (−0.2)	0.1 (−0.2)	0.2 (−0.1)
TrIPN	4.4 (4.2)	2.6 (2.4)	2.3 (2.2)
TeIPN	0.5 (0.5)	0.3 (0.3)	0.2 (0.2)
RNAP	0.2 (0.1)	0.3 (0.1)	0.2 (0.1)

[a] Reaction at 200°C for 2 h. Propylene pressure varied.

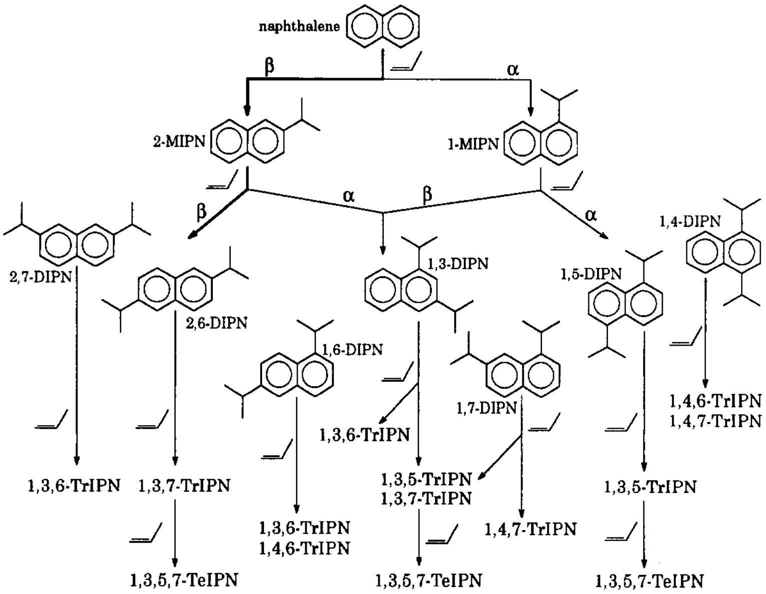
propyl cation increases with propylene pressure, so alkylation on the external surface is enhanced. The fact that there is little conversion of 2,6-DIPN on HM74 (Table 6) suggests that there are far fewer external surface active sites on HM74 than on HM14 and HM38. In collateral work, we found that higher 2,6-DIPN selectivity is achieved when isopropyl alcohol is used as the alkylating agent [4], or when water is added to the reaction with propylene [11]. In these cases, the selectivity enhancement is likely due to adsorption of water (added water or water produced by dehydration of isopropyl alcohol) on the external-surface catalyst sites.

Sugi et al. observed a similar effect for propylene adsorption in the isomerization of 4,4′-diisopropylbiphenyl (4,4′-DIPB) on HM [12–15]. A considerable amount of the 4,4′-isomer was isomerized to the 3,4′-DIPB at low propylene pressure, but the isomerization did not occur at high propylene pressure. The locus of isomerization activity was determined to be on the external surface of the catalyst.

In all of the tests, concentrations of RNAP products do not change much and are generally insensitive to propylene pressure. The one exception, which seems to be an anomaly, is found for reaction of 2,6-DIPN on HM38 with propylene/2,6-DIPN of 1.0 (Table 5). We previously reported that cracking and disproportionation reactions leading to RNAP products begin to increase at 250°C and above [5].

As shown in Table 6, reaction of 2,6-DIPN on dealuminated mordenite (HM74) is quite different than on HM14 and HM38. 2,6-DIPN is practically unreactive on HM74. Conversely, nearly the entire amounts of MIPN and isomeric DIPN impurities do react to form higher alkylates. Even 75% of the original amount of 2,7-DIPN reacts. There is, again, a small increase in 2,6-DIPN conversion with increasing propylene/2,6-DIPN ratio. These results reveal that the high selectivity toward 2,6-DIPN in the isopropylation of naphthalene is partly attributable to the low reactivity of 2,6-DIPN on dealuminated mordenites.

Table 4, Tables 5 and 6 show that all of the DIPN isomers are potential precursors to higher alkylates. A general reaction pathway for propylene addition to naphthalene on mordenite cata-



Scheme 2. Possible reaction pathway for propylene addition to naphthalene over H-mordenites. Boldface path indicates β-selective substitution reactions occurring within the micropore channels.

lysts is shown in Scheme 2. Isomerization and transalkylation reactions have been excluded for simplicity. A schematic for MIPN and DIPN isomer interconversions was published by Sugi et al. [8]. Steric hinderance inhibits *ortho*-diisopropyl substitution on naphthalene, so it is possible to predict the substitution patterns of TrIPN and TeIPN isomers. Note that some TrIPN isomers, such as 1,3,6-TrIPN, do not react to give TeIPN since the only open substitution sites are *ortho* to isopropyl groups. 1,3,5,7-TeIPN is the only tetrasubstituted isomer that avoids *ortho*-substitution. Isopropylation of 2,6-DIPN, when it occurs, must give 1,3,7-TrIPN as the principle isomer. Since the HM channels will not accommodate this α,β,β,-TrIPN isomer, the reaction must occur on external surface catalyst sites. Further isopropylation of 2,6-DIPN to produce mainly TrIPN occurs on HM14 and HM38 catalysts. However, on HM74, only a small amount of 2,6-DIPN reacts, even at the highest propylene/2,6-DIPN ratios. Dealuminated mordenite (HM74) apparently has substantially fewer active sites on its external surface (for non-selective alkylation) than HM14 and HM38.

4. Conclusions

On low SiO_2/Al_2O_3 mordenites, 2,6-DIPN is both isomerized and further alkylated by propylene on the non-selective external surface of the catalyst. The extent of alkylation, the main reaction of 2,6-DIPN, increases with propylene pressure. Isomerization reactions are suppressed at high propylene pressure due to competitive adsorption of propylene on the catalyst which passivates external surface catalyst sites.

We have shown that all of the DIPN isomers are potential precursors to higher alkylates. However, on dealuminated mordenite (HM74), 2,6-DIPN is nearly unreactive while MIPN and isomeric DIPN impurities (including 2,7-DIPN) react to form higher alkylates. These results reveal that the high selectivity toward 2,6-DIPN in the isopropylation of naphthalene is partly attributable to the low reactivity of 2,6-DIPN on dealuminated mordenites.

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References

[1] C. Song and H.H. Schobert, Am. Chem. Soc. Div. Fuel Chem. Prepr., 37(2) (1992) 524.
[2] C. Song and H.H. Schobert, Fuel Process. Technol., 34 (1993) 157.
[3] C. Song and H.H. Schobert, Am. Chem. Soc. Div. Fuel Chem. Prepr., 40(2) (1995) 249.
[4] C. Song and S. Kirby, Microporous Mater., 2 (1994) 467.
[5] A.D. Schmitz and C. Song, Am. Chem. Soc. Div. Fuel Chem. Prepr., 39(4) (1994) 986.
[6] A.D. Schmitz and C. Song, Am. Chem. Soc. Div. Fuel Chem. Prepr., 40(4) (1995) 918.
[7] A. Katayama, M. Toba, G. Takeuchi, F. Mizukami, S.-i. Niwa and S. Mitamura, J. Chem. Soc., Chem. Commun., (1991) 39.
[8] Y. Sugi and M. Toba, Catal. Today, 19 (1994) 187.
[9] J.A. Horsley, J.D. Fellmann, E.G. Derouane and C.M. Freeman, J. Catal., 147 (1994) 231.
[10] G.S. Lee, J.J. Maj, S.C. Rocke and J.M. Garcés, Catal. Lett., 2 (1989) 243.
[11] A.D. Schmitz and C. Song, Catal. Lett., (1996) in press.
[12] X. Tu, M. Matsumoto, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim and Y. Sugi, Catal. Lett., 21 (1993) 71.
[13] Y. Sugi, J.-H. Kim, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu and M. Matsumoto, Stud. Surf. Sci. Catal., 84 (1994) 1837.
[14] Y. Sugi, X. Tu, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim and M. Matsumoto, Am. Chem. Soc. Div. Fuel Chem. Prepr., 40(4) (1995) 908.
[15] J.-H. Kim, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, S. Nakata, A. Kato, G. Seo and C. Pak, Appl. Catal. A: General, 131 (1995) 15.