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Acidity-attenuated heteropolyacid catalysts: Acidity measurement using benzonitrile-TPD and catalytic performance in the skeletal isomerization of *n*-heptane

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Abstract

Difficulty in measuring acidic characters of heteropolyacid due to absorption of common bases such as ammonia and pyridine was circumvented using benzonitrile as an adsorbate. Acidity-attenuated and Pd-promoted heteropolyacid catalysts catalyzed *n*-heptane skeletal isomerization with high activity and high selectivity to branched heptanes, which are useful as clean high-octane fuels. Acidic characters measured by benzonitrile-TPD were well correlated with the catalytic performances.

Keywords: Benzonitrile-TPD; Isomerization of *n*-heptane; Heteropolyacid

1. Introduction

Catalysis by heteropolyacids (HPAs) and related compounds is a field of increasing importance worldwide. Some of HPAs are characterized by their stronger acid strength than conventional liquid and solid acids, and also by their definite pore structures. Due to these characters, HPAs such as $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ (abbreviated to H3PW and H4SiW, respectively) and silica-supported HPAs exhibit high activity and selectivity to various acid-catalyzed reactions such as alkylation, esterification, and acylation, as summarized in review articles [1–2] and other reports [3–10]. However, two problems are arising: one is unavailability of reliable method for measuring surface acidity and acid strength because of absorption of common bases, such as ammonia and pyridine, into the bulk of HPAs, and the other is prevailing side reactions over the desired reaction because of excessive strong acid strength. The skeletal isomerization of *n*-pentane in the presence of hydrogen is such that the high selectivity is realized only when the acid strength of H4SiW is controlled [5].

The skeletal isomerization of heavy alkanes, such as *n*-heptane and *n*-octane, is an industrially important reaction because the produced branched alkanes are useful as clean high-octane fuels. A number of reports have described the skeletal isomerization of *n*-heptane in the presence of hydrogen over such bifunctional catalysts as Pt- or Pd-H-β zeolite, Pt–Y zeolite, Pt–SO_4^{2-}/ZrO_2, and Pt–MoO_3 [11–17]. Among them, Pd- or Pt–Hβ zeolite is considered to be the most efficient catalyst for the isomerization of *n*-heptane [11].

Here, we report the new characterization method for surface acidic properties of HPA-derived catalysts, the improvement of branched heptane yields from *n*-heptane by controlling the acid strength of Pd-HPA bifunctional catalysts [18].

The surface acidic properties were determined using temperature programmed desorption (TPD) method of benzonitrile (BN), which has mild basicity (gas phase basicity = 780.9 kJ mol^{-1} and donor number = 49.8 kJ mol^{-1}) [19,20]. Preliminary experiments showed [5] that a tiny amount of benzonitrile was adsorbed on crystals of H4SiW, reflecting small surface area of the HPA crystals, ca. 5 m^2 g^{-1}. The result also suggests that benzonitrile does not absorb into the HPA

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bulk but does adsorb on acidic surface. To attenuate the acid strength of H4SiW and to improve yield of branched heptanes, H4SiW was supported on silica or was diluted with silica. The H4SiW on silica was modified with 2 wt.% palladium. In addition, Pd or Pt-promoted bifunctional catalysts of 2 wt.% Pd–Hβ and 2 wt.% Pt–SO_4^{2-}/ZrO_2 (Pt–SZ) were used as reference catalysts. Further, Pt-promoted $Cs_{2.5}H_{1.5}SiW_{12}O_{40}$ (Cs2.5SiW) and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs2.5PW) were tested in the skeletal isomerization of *n*-heptane. The cesium ion-exchanged HPAs have micropores while H4SiW on silica does not. The catalytic performances on these catalysts were discussed in conjunction with their pore sizes and acidic characters.

2. Experimental

2.1. Catalysts

Silica-supported H4SiW catalysts were prepared by an incipient wetness method, as reported previously [5]. Silica (aerosil 300, 274 $m^2 g^{-1}$) was used as a support. The loadings of H4SiW on silica were varied in the range from 10 to 60 wt.% by changing the concentration of the HPA in water. The resulting solids were calcined at 523 K in air for 5 h and denoted as $H4SiW/SiO_2$. Pd was loaded on $H4SiW/SiO_2$ using an aqueous solution of $PdCl_2{\cdot}6H_2O$. The loading of Pd was adjusted to 2.0 wt.%. These catalysts are denoted as Pd–$H4SiW/SiO_2$.

Sulfated zirconia, SO_4^{2-}/ZrO_2, was obtained from sulfuric acid and zirconium hydroxide, and followed by calcination at 893 K for 5 h, as reported in literature [21]. Pt was loaded on SO_4^{2-}/ZrO_2 by an incipient wetness method using aqueous H_2PtCl_6 solution. The Pd–Hβ was prepared from Hβ zeolite (Süd-Chemie; $SiO_2/Al_2O_3 = 25$) by an ion-exchange method using an aqueous solution of $[Pd(NH_3)_4]Cl_2$ [22].

Pt-promoted Cs2.5SiW and Cs2.5PW were prepared by a titration method, where an aqueous solution of Cs carbonate was added dropwise with vigorous stirring at ambient temperature to a mixture of aqueous solutions of H_2PtCl_6 and H3PW or H4SiW, as described previously [23,24]. Water was removed off using a rotary evaporator from the resulting colloidal solution after aging overnight. Prior to use, resulting solids were evacuated at 523 K for 2 h.

2.2. Catalytic reaction

The skeletal isomerization of *n*-heptane in the presence of hydrogen was conducted in a flow reactor (Pyrex, 10 mm inner diameter) at 453 K under atmospheric pressure. After placing 0.1–0.5 g of the bifunctional catalyst (mixed with 0.3–1.5 g granular quartz) in the reactor, the catalysts were reduced in a flow of H_2 at 573 K for 2 h and, then, the reactant gas (*n*-heptane: H_2 = 4.8: 95.2 vol.%) was fed at 453 K. The catalytic reaction was conducted under various W/F, where W and F represent catalyst weight in g and total flow rate in mol h^{-1}, respectively. The composition of the gas at the outlet of the reactor was analyzed using a gas chromatograph (Shimadzu GC-14B) equipped with a flame ionization detector (FID) and a capillary column (CHROMPACK; WCOT fused silica squalane, 100 m). Catalytic performance was expressed as conversion and selectivity of isomerization, which are defined as follows.

$$\text{conversion} = 1 - \frac{(\text{concentration of } n\text{-heptane at outlet})}{(\text{concentration of } n\text{-heptane at inlet})}$$

$$\text{selectivity} = \frac{(\text{sum of concentration of branched heptanes})}{(\text{concentration of reacted } n\text{-heptane})}.$$

2.3. Other measurements

Ammonia-temperature programmed desorption (NH_3-TPD) profiles were obtained by a multi-task TPD system (BEL Japan), equipped with a quadrupole mass spectrometer (ANELVA; M-QA100S). The catalyst was pretreated at 523 K under He flow, exposed to ammonia of 13 kPa (100 Torr) for 20 min at 373 K, and the excess ammonia was removed under a He flow for 0.5 h at 373 K. The temperature of the sample was raised at a rate of 10 K min^{-1} to 973 K, and the desorbed gas was monitored using Q-mass at $m/z = 16$. The desorbed water was also monitored at $m/z = 18$, which will arise from the dehydration of silica support, the dehydration of heteropolyacid and the decomposition of heteropolyacid. Comparing peak heights at $m/z = 16$ and 18, we omitted the contribution of water to $m/z = 16$ because of a minor (less than 5%) effect of water to the peak height at $m/z = 16$.

Benzonitrile-temperature programmed desorption (BN-TPD) profiles were obtained using a homemade TPD system, equipped with a FID detector. The catalyst was pretreated at 523 K under N_2 flow, exposed at 373 K for 1 h to N_2 flow bubbled through BN bath held at ambient temperature and then the excess BN was removed under N_2 flow at 373–393 K. The temperature of the sample was raised at a rate of 10 K min^{-1} to 973 K under N_2 flow while FID signal of the exit gas was monitored. In both TPD measurements, samples were pretreated at 523 K, where all of water of crystallization will be removed. In fact, a sole sharp peak of water at $m/z = 18$ was observed on pure H4SiW at ca. 800 K, where heteropolyacid decomposes [2] but no peak was detected in a temperature range between 420 and 623 K.

The BET surface area was determined from a nitrogen adsorption isotherm at 78 K using a BELSORP 28SA apparatus (BEL Japan Inc.). Micropore-size distribution was estimated from argon isotherm measured at 87 K using Saito-Foley method [25,26].

3. Results and discussion

3.1. BN- and NH_3-TPD on $H4SiW/SiO_2$

Fig. 1 shows the BN-TPD spectra of $H4SiW/SiO_2$ with various H4SiW loadings. Here, *x*% H4SiW refers to wt.% of H4SiW in H4SiW + silica. Three peaks were observed at around 460, 600, and 700 K. The BN-TPD spectra were

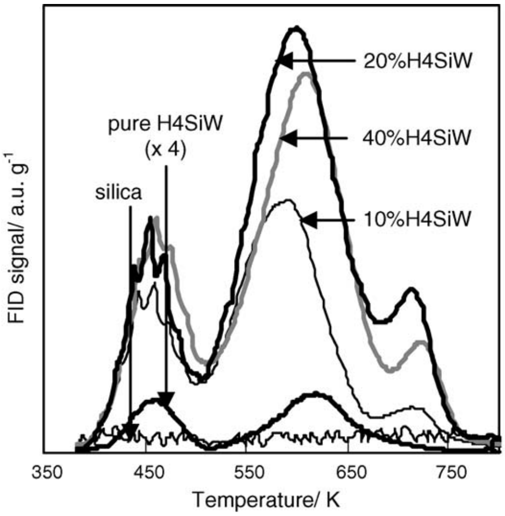

Fig. 1. BN-TPD spectra of $H4SiW/SiO_2$ with various H4SiW loadings.

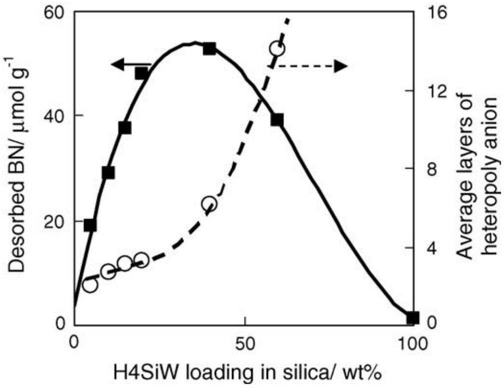

Fig. 2. Peak area of BN-TPD spectra at above 600 K and average layers of heteropoly anion on silica support calculated from 2 × (number of heteropoly anion)/(benzonitrile adsorbed).

deconvoluted using a peak-fitting program, Fityk, and such peak parameters as area, position and width were evaluated. Peak area of ca. 460 K peak did not vary with the H4SiW loadings while those of 600 and 700 K peaks varied with the H4SiW loadings. Sum of peak areas of 600 and 700 K peaks was plotted against H4SiW loading, as shown in Fig. 2. The sum of peak areas attained a maximum at 40 wt.% loading of H4SiW and, then, decreased. It is noteworthy that weakly acidic silica could not adsorb BN and that pure H4SiW adsorbed only a small amount of BN because of its small surface area, demonstrating no absorption of BN into the bulk of H4SiW but adsorption of BN at a top most surface. In Fig. 2, H4SiW loadings are also plotted against average layers of heteropoly anion, which were calculated by assuming adsorption of two benzonitrile molecules per heteropoly anion. Three to four layers of heteropoly anion would form on silica surface at low H4SiW loadings between 5 and 20 wt.% while layer thickness jumped up to 6 and 14 layers at 40 and 60 wt.% H4SiW loadings, respectively.

In preliminary experiments, the desorbed gas was analyzed with Q-mass, together with FID. In the three peaks in BN-TPD-FID, most of 460 and 700 K peaks resulted from BN ($m/z = 103$). It is reasonable to be assigned that physically or weakly adsorbed BN will provide a peak at 460 K. A small peak at 700 K may come from BN evolved at the decomposition of HPA since a broad peak of extra water ($m/z = 18$) was observed at around 700 K. In addition to BN, benzene ($m/z = 78$) was observed at 600–630 K. In the 600 K peak, formed benzene contributed about 5% to the total FID peak height of 5 wt.% $H4SiW/SiO_2$ while the remainder of FID peak (95%) was due to BN. The portion of benzene in the 600 K peak increased with H4SiW loadings. Eventually in pure H4SiW, all of FID peak at 630 K consisted of benzene.

In contrast to BN adsorption, a large amount of ammonia was absorbed into $H4SiW/SiO_2$ bulk, as shown in Fig. 3. Fig. 3A presents NH_3-TPD spectra. The spectrum of pure H4SiW showed a sharp and high peak at *ca.* 800 K while those of silica-supported H4SiW consisted of broad and ill separated peaks located below 800 K, suggesting the interaction between H4SiW and surface hydroxyl group of silica. Fig. 3B shows peak areas of the spectra linearly increased with H4SiW loadings, demonstrating the absorption of ammonia into H4SiW bulk. It should be noted that water ($m/z = 18$) and ammonia ($m/z = 16$) showed sharp peaks in their TPD spectra

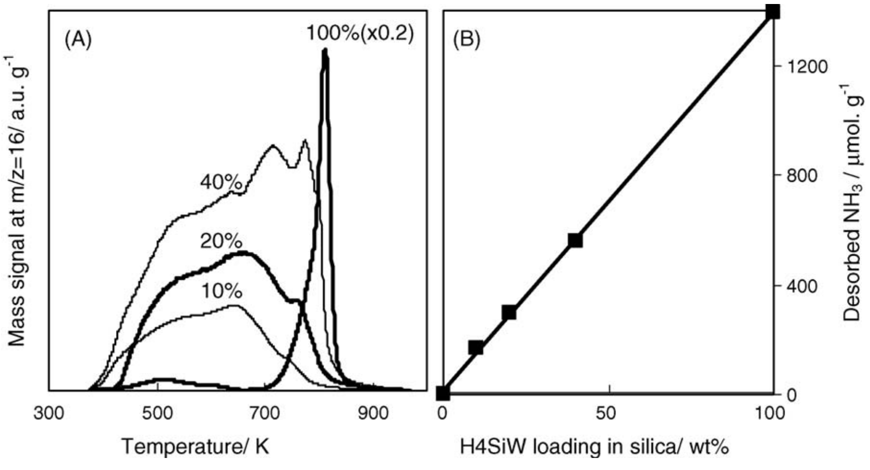

Fig. 3. (A) NH_3-TPD spectra and (B) amount of adsorbed NH_3 of $H4SiW/SiO_2$ with various H4SiW loadings.

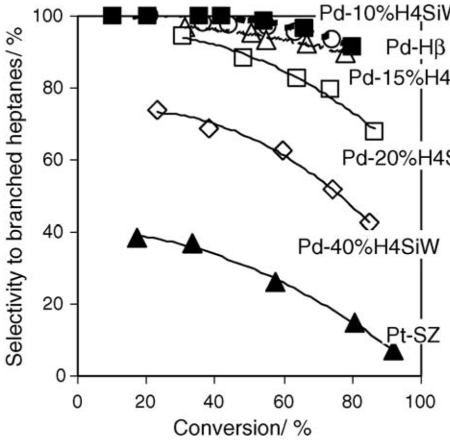

Fig. 4. Selectivity vs. conversion on Pd–H4SiW/SiO_2, Pd–Hβ and Pt–SZ, where one point represents a stable value at a set W/F and a curve for a catalyst was obtained by changing W/F.

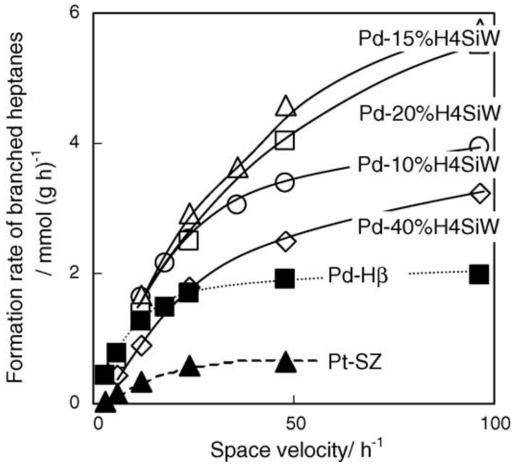

Fig. 6. Formation rate of branched heptanes on Pd–H4SiW/SiO_2 with various H4SiW loadings and on reference catalysts.

on pure H4SiW, suggesting desorption of ammonia at the decomposition of heteropolyacid.

3.2. Skeletal isomerization of n-heptane over Pd–H4SiW/SiO_2

n-Heptane could be isomerized into branched heptanes, such as methylhexanes, dimethylpentanes, and trimethylbutane. Some of these compounds are used as clean high-octane fuels. The isomerization of *n*-heptane was conducted on various catalysts. All of the catalysts except for Pd-40 wt.% H4SiW/SiO_2 gave stable conversions and selectivities for 5 h of time on stream and at various W/F. In the case of Pd-40 wt.% H4SiW/SiO_2, stable data was obtained at 5 h time on stream. Fig. 4 shows plots of sum of selectivities to branched heptanes against *n*-heptane conversions. A curve of selectivities versus conversions on a catalyst can be obtained by varying W/F. The figure shows that the selectivity of Pd-10 wt.% H4SiW catalysts was higher than 97% at 50% conversion, comparable to that of Pd-Hβ. The selectivities of catalysts decreased in the order as Pd–Hβ ≈ Pd-10% H4SiW > Pd-15% H4SiW > Pd-20% H4SiW ≫ Pd-40% H4SiW ≫ Pt-SZ at any conversion levels.

Fig. 5 shows plots of conversions of *n*-heptane and selectivities to cracking products at W/F = 5.1 g h mol^{-1} against H4SiW loadings in Pd–H4SiW catalysts. The conversion passed through a maximum at Pd-20 wt.% H4SiW and the selectivity to cracking products progressively went up. As discussed on Fig. 2 for BN-TPD, the average layers of heteropoly anion jumped up at 40 wt.% H4SiW as H4SiW loadings increased. This may suggest the crystallite H4SiW, which does not interact with silica support, promotes the side reaction to cracking products.

As H4SiW loadings increased, conversions of *n*-heptane increased and selectivities to branched heptanes decreased. The formation rate of branched heptanes was calculated from (selectivity) × (conversion)/(W/F) × (concentration of *n*-hep-

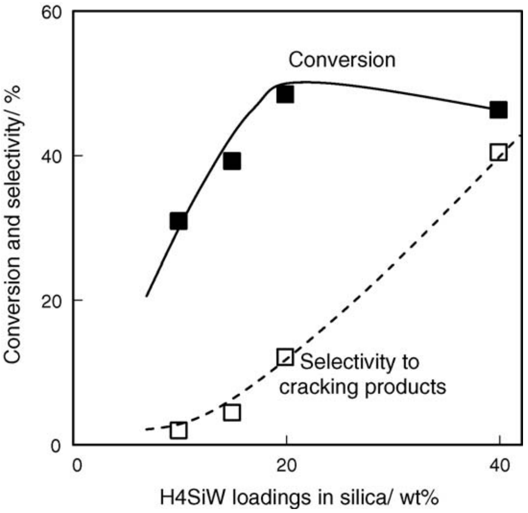

Fig. 5. Conversion and cracking selectivity on Pd–H4SiW/SiO_2 vs. H4SiW loadings in silica at W/F = 5.1 g h mol^{-1}.

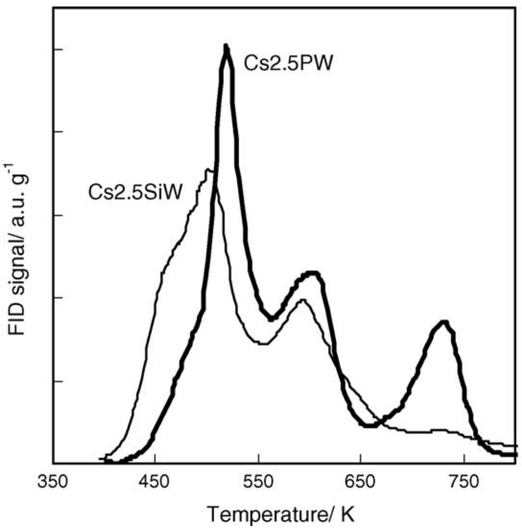

Fig. 7. BN-TPD spectra of Cs2.5SiW and Cs2.5PW.

Table 1
Catalytic performances on 2 wt.% Pt–Cs2.5PW and 2 wt.%Pt–Cs2.5SiW

Catalyst	W/F (g h mol^{-1})	Conversion (%)	Selectivity of cracking products (%)	Branched heptanes	
				Mono	Multi
Pt–Cs2.5PW	4.1	55.4	9.4	75.2	24.8
Pt–Cs2.5SiW	20.3	64.1	5.1	75.1	24.9

tane in the feed) and was plotted against space velocity, which was deduced from W/F and apparent specific gravity of catalyst (0.5), as shown in Fig. 6. The rates were followed in the order: Pd-15% H4SiW ≈ Pd-20% H4SiW > Pd-10% H4SiW > Pd-40% H4SiW ≫ Pd-Hβ ≈ > Pt–SZ. The rates on Pd-15% H4SiW and Pd-20% H4SiW were more than two times higher than that on Pd–Hβ, which has been known to be the best catalyst for this reaction. The results demonstrate the effectiveness of acidity attenuation of catalyst in increasing the formation rate of branched heptanes.

3.3. Catalytic properties of microporous HPAs

Nitrogen isotherms of Cs2.5PW and Cs2.5SiW were measured. A hysteresis was observed for adsorption and desorption isotherm in the case of Cs2.5PW, showing the presence of mesopores, while Cs2.5SiW has only micropores. Surface areas of Cs2.5SiW and Cs2.5PW were calculated to be 90–110 and 140 m^2 g^{-1} from BET analysis of nitrogen isotherms. Loading of 2 wt.% Pt on these HPAs caused a decrease of surface area: from 140 to 91 m^2 g^{-1} in the case of Cs2.5PW.

Fig. 7 shows BN-TPD spectra of Cs2.5SiW and Cs2.5PW. Similarly as H4SiW/SiO$_2$, three peaks were observed at 470, 600, and 720 K. The three peaks should come from physically adsorbed BN, BN adsorbed on the HPAs, and BN adsorbed on decomposed HPAs, respectively. Sum of peak areas at 600 and 720 K peaks of Cs2.5PW was about 2 times larger than that of Cs2.5SiW. Table 1 presents the catalytic performances on 2 wt.% Pt loaded catalysts. Both conversions were adjusted to ca. 60% by changing W/F: 4.1 and 20.3 g h mol^{-1} for Pt–Cs2.5PW and Pt–Cs2.5SiW, respectively. Smaller W/F of Pt–Cs2.5PW than that of Pt–Cs2.5SiW was caused by higher catalytic activity of Pt–Cs2.5PW than that of Pt–Cs2.5SiW. It appears that a correlation exists between peak area in BN-TPD and catalytic activity in *n*-heptane isomerization. It is noteworthy that Pt–Cs2.5PW produced branched heptane with similar selectivity and with similar formation rate of branched heptanes to Pd-20% H4SiW.

4. Conclusion

High yield of branched heptanes were realized on acid strength-attenuated catalysts in the skeletal isomerization of *n*-heptane. The activity and the selectivity to cracking products in the *n*-heptane isomerization are nicely correlated with peak areas at higher temperature than 600 K in BN-TPD spectra.

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References

[1] Y. Ono, J.M. in, K.I. Zamaraev Thomas (Eds.), Perspectives in Catalysis, Blackwell, London, 1992, p. 431.
[2] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113.
[3] Y. Izumi, J. Hisano, T. Hida, Appl. Catal. A 181 (1999) 277.
[4] J. Mao, T. Nakajo, T. Okuhara, Chem. Lett. 31 (2002) 1104.
[5] A. Miyaji, T. Echizen, K. Nagata, Y. Yoshinaga, T. Okuhara, J. Mol. Catal. A 201 (2003) 145.
[6] K. Sano, H. Uchida, S. Wakabayashi, Catal. Surv. Jpn. 3 (1999) 55.
[7] V.M. Mastihkin, S.M. Kulikov, A.V. Nosov, I.V. Kozhevnikov, I.L. Mudrakovsky, M.V. Timofeeva, J. Mol. Catal. 60 (1990) 65.
[8] F. Lefebvre, J. Chem. Soc., Chem. Commun. (1992) 756.
[9] R. Thoubenot, C.R. Delcheff, M. Fournier, J. Chem. Soc., Chem. Commun. (1991) 1252.
[10] R. Thoubenot, M. Fournier, C.R. Delcheff, J. Chem. Soc., Faraday Trans. 87 (1991) 2829.
[11] T. Okuhara, Catal. Today 73 (2002) 167.
[12] Y. Izumi, K. Urabe, A. Onaka, Zeolite, Clay and Heteropolyacids in Organic Reactions, Kodansha, Tokyo-VCH, Weinheim, 1992.
[13] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.
[14] G.J. Meuzelaar, L. Maat, R.A. Sheldon, Catal. Lett. 45 (1997) 249.
[15] E.F. Kozhevnikov, E.G. Derouane, I.V. Kozhevnikov, Chem. Commun. (2002) 1178.
[16] C. Castro, A. Corma, J. Primo, J. Mol. Catal. A 177 (2002) 273.
[17] C. Castro, J. Primo, A. Corma, J. Mol. Catal. A 134 (1998) 215.
[18] A. Miyaji, R. Ohnishi, T. Okuhara, Appl. Catal. A 262 (2004) 143.
[19] E.P.L. Hunter, S.G. Lias, J. Phy. Chem. Ref. Data 27 (1998) 413.
[20] V. Gutmann, Coordination Chemistry in Non-Aqueous Solutions, Springer-Verlag, Wien-New York, 1968, p19.
[21] M. Hino, K. Arata, Catal. Lett. 30 (1995) 25.
[22] P. Gallezot, Catal. Sci. Eng. 20 (1979) 121.
[23] M. Yoshimune, Y. Yoshinaga, T. Okuhara, Microporous Mesoporous Mater. 51 (2002) 165.
[24] T. Okuhara, T. Yamada, K. Seki, K. Johkan, T. Nakato, Microporous Mesoporous Mater. 21 (1998) 637.
[25] A. Saito, H.C. Foley, AIChE J. 37 (1991) 429.
[26] T. Yamada, K. Johkan, T. Okuhara, Microporous Mesoporous Mater. 26 (1998) 109.