Montmorillonite-based heterogeneous catalysts for efficient organic reactions

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Abstract
In this review, we give a brief overview of recently developed montmorillonite-based heterogeneous catalysts used for efficient organic reactions. Cation-exchanged montmorillonite catalysts, metal catalysts supported on montmorillonite, and an interlayer design used for selective catalysis are introduced and discussed. In traditional syntheses, homogeneous acids and metal salts were used as catalysts, but the difficulty in separation of catalysts from products was a bottleneck when considering industrialization. The use of solid heterogeneous catalysts is one of the major solutions to overcome this problem. Montmorillonite can be used as a heterogeneous catalyst and/or catalyst support. This clay material exhibits strong acidity and a stabilizing effect on active species, such as metal nanoparticles, due to its unique layered structure. These advantages have led to the development of montmorillonite-based heterogeneous catalysts. Acidic montmorillonite, such as proton-exchanged montmorillonite, exhibits a high catalytic activity for the activation of electrophiles, such as alcohols, alkenes, and even alkanes. The montmorillonite interlayer/surface also functions as a good support for various metal species used for oxidation and carbon–carbon bond forming reactions. The use of an interlayer structure enables selective reactions and the stabilization of catalytically active species.

1. Introduction

Montmorillonite (mont) is one of the most thoroughly studied clays and is used for the fabrication of catalysts, polymer nanocomposites, and adsorbents. The basic structure of a mont consists of an octahedral alumina layer sandwiched between two tetrahedral silicate layers (figure 1)\textsuperscript{[1]}. The unit crystal layer is anionic because some of the Al\textsuperscript{3+} in the alumina octahedral layer is replaced by 2+ valent cations, such as Mg\textsuperscript{2+} and Fe\textsuperscript{3+}, and thus counter-exchangeable cations are generated in the interlayer. Mont naturally contains adsorbed water on its outer surface and interlayers, which may affect the interlayer distance and catalytic reactions. The effect of water content on the interlayer distance has been well studied. For example, changes in the interlayer distance under different humidity conditions have been reported\textsuperscript{[2, 3]}. Kawamura \textit{et al} reported the relationship between moisture content and interlayer distance by performing XRD measurements of mont under different humidity conditions. The interlayer distance increased with increasing relative humidity for various ion-exchanged mont\textsuperscript{[2]}. The water content and interlayer distance of H-mont after treatment at various temperatures were also reported to be determined from thermal gravimetric analysis and XRD measurement, respectively (table 1)\textsuperscript{[4]}. The decrease in interlayer distance, as well as the decrease in adsorbed water, was observed by increasing the treatment temperature. In this report, it is also reported that varying the water content of H-mont by treatment temperature and water addition has a significant effect on the catalytic activity.

The wide-spread and long-standing interest in mont as a catalyst is because of its low cost, abundance, and tunable acidic properties via cation exchange. Mont naturally contains sodium as an easily exchangeable cation in its interlayer space, and therefore exhibits a variety of properties depending on the type of ions that are exchanged, such as H\textsuperscript{+}, Al\textsuperscript{3+}, Fe\textsuperscript{3+}, Ti\textsuperscript{4+}, Sn\textsuperscript{4+}, and other metals. Because of the delocalized anion charge in its silicate and alumina layers, the incorporated cation exhibits unique catalytic properties, such as acid catalysis,
Figure 1. General structure of montmorillonite.

Figure 2. General preparation method of H-mont [15].

Table 1. Properties of H-monts treated at different temperatures [4].

| Temperature/°C | Adsorbed water/wt%a | Interlayer distance/Åb |
|----------------|----------------------|------------------------|
| 25             | 5.6                  | 3.4                    |
| 100            | 2.1                  | 2.6                    |
| 120            | 1.3                  | 2.4                    |
compared with homogeneous cationic catalysts, such as HCl and AlCl₃. In addition, the size of the interlayer space of mont is tunable, which affects selective catalysis owing to steric hindrance. Homogenous catalysts, such as metal complex, are mainly nanostructured, precisely designed catalysts. However, a significant drawback is difficulty to recover and recycle as well as their stability. Heterogeneous catalysts, such as metal oxides, are recyclable, while their random surface structure results low product selectivity. Zeolites are heterogeneous and have crystalline structure, however, fine chemicals synthesis using zeolites is limited due to their small pore size. On the other hand, the mont catalyst has the potential to overcome these problems because it is solid, highly stable, expandable layered clay, and with uniformed crystalline, nanostructured surface. It is possible to adjust the acidity and introduce a single metal species by cation exchange of mont. The ability of mont to stabilize metal cations make it useful for the synthesis of fine chemicals with large molecular sizes where pore size does not need to be considered. The nanospace of mont interlayer can also contribute to stabilize metal nanoparticles, and control the reaction product selectivity. These abilities of mont will enable precise catalyst design at nanoscale to realize challenging reactions.

Several comprehensive reviews and accounts of mont-based catalysts have been published [5–16]. In contrast, in this short review, we focus on more recent and/or representative examples, including recent studies by our group.

2. Catalysis of cation-exchanged montmorillonite

Cation exchange is the most common procedure for preparing mont catalysts. The exchangeable cations between the mont layers can be readily replaced under mild conditions in various precursor solutions. For
Table 2. Akylation of benzene with \textit{n}-heptane using the solid acid and supported Pd combined systems [34].

| Solid acid | Supported Pd | Benzene conv/% | Ph-C7 | Biphenyl | Ph-Cn b |
|------------|--------------|----------------|-------|---------|--------|
| Al-mont    | Pd/HT        | 6.8            | 82    | 10      | 4      |
| Al-mont    | —            | 1.8            | 58    | <1      | 42     |
| —          | Pd/HT        | 0.4            | <1    | >99     | <1     |

- Reaction conditions: solid acid (0.10 g), supported metal (0.10 g, metal: 0.05 mmol), \textit{n}-heptane (1.0 mL; 6.8 mmol), benzene (1.2 mmol), 150 °C, 16 h.
- Alkylbenzenes other than Ph-C7.
example, proton-exchanged mont (H-mont) is easily ion-exchanged by heating and stirring Na-mont at 90 °C in HCl aqueous solution (figure 2) [17]. For Al-mont, representative conditions are at 50 °C in AlCl₃ aqueous solution. After the heating, the resulting solids are filtered, washed, and dried to obtain H-mont and Al-mont. Prepared mons are often used as solid acids because of their high acidic qualities.

H-mont is a typical example of a cation-exchanged mont [4, 18–31]. H-mont can promote various liquid-phase organic synthesis reactions at low temperatures by effectively activating unreactive electrophiles, such as polyethers and simple alkenes. Maeno et al reported efficient depolymerization of polyethers with carboxylic acid derivatives to give glycol diesters [20]. Using H-mont as a catalyst, 99% yield was achieved in the reaction of polyether with benzoic anhydride at 100 °C for 5 h (figure 3). H-mont showed excellent catalytic performances for depolymerization of various polyethers including high molecular weight polymers (Mn∼2,000,000). In addition, the use of acid and acid anhydride mixture system enables production of unsymmetric glycol diesters. In the allylsilylation of alkenes using allylsilanes, the amount of water in the reaction system is the key factor [28]. For example, in the allyl silylation of p-chlorostyrene with allyltrimethylsilane the addition of a small amount of water increased the reaction rate by 60-fold compared to that without water. The water improves the reaction rate by stabilizing the active cationic di-Si species on the mont surface (figure 4).

Chen et al reported that H-mont was the most suitable catalyst for the highly efficient synthesis of heterocyclic diarylmethane under mild conditions by the alkylation of arenes with heterobenzyl acetates [29]. Furthermore, they demonstrated that this reaction could be used to synthesize zafirlukast, which is used to treat bronchial asthma (figure 5). In addition, H-mont can be applied to other nucleophilic substitution reactions of heterobenzyl acetates with various alcohols and 1, 3-dicarbonyl compounds, indicating its utility as a catalyst for the synthesis of a wide range of fine chemicals.

The reaction catalyzed by aluminum-exchanged mont (Al-mont), which has a stronger acid sites than H-mont, has also been studied extensively. In 1984, Thomas et al reported that Al-mont facilitates various organic synthetic reactions, including intermolecular and intramolecular dehydration of alcohols, ether synthesis by addition of alcohols to alkenes, and synthesis of thioethers from alkenes and thiols [32, 33]. In particular, in the dehydration reaction of primary alcohols, the intermolecular dehydration proceeded smoothly and the corresponding ethers were obtained, unlike homogeneous systems.

In addition, the strong acidic characteristic of Al-mont has been used to catalyze the dehydrogenative coupling reaction between alkanes and benzene via the C-H bond activation of alkanes [34]. In this reaction, the successful synthesis of alkylbenzene from simple alkanes and benzene was accomplished with high selectivity and conversion using Al-mont in comparison with zeolites and homogeneous acids, which are commonly used as acid catalysts. In addition, the combination of Al-mont and hydrotalcite-supported Pd nanoparticles enabled a significant increase in benzene conversion, while maintaining alkylbenzene selectivity (Ph-C7) (table 2) [34]. Interparticle hydrogen transfer is a key step in promoting the dehydrogenative coupling of benzene and alkanes (figure 6).

Many reactions catalyzed by ion-exchanged mont of other metal ions have been reported. Fe-mont, in which the interlayer mont cations are exchanged with iron ions, functions as a catalyst for the benzylation of arenes and the acylation of sulfonamides [35, 36]. The structure of Fe-mont was revealed by Kaneda and co-workers: chain-like Fe³⁺ species, including Fe–O–Fe, were observed in Fe-mont with FeCl₃ as a precursor [37]. This Fe-mont exhibited very high activity in the oxidation of alkanes by hydrogen peroxide, achieving a TON of more than 20,000. Regarding epoxidation and alkane oxidation, vanadium cation-exchanged mont (V-mont) was reported as a highly active catalyst [38].
Ti-mont is also known to adopt a chain-like structure similar to that of Fe-mont and has been widely utilized as a solid acid catalyst in many catalytic reactions, such as the Beckmann rearrangement, acetalization of carbonyl compounds, deprotection of acetics, esterification, synthesis of ethers from two alcohols, and aromatic alkylation for the synthesis of 9,9-bis-(2-hydroxyethoxy)phenylfluorene (BHEPF). In these catalytic reactions, Ti-mont exhibited significantly higher activity than other homogeneous and heterogeneous acid catalysts and a broad substrate adaptability. Ti-mont can also facilitate one-pot synthesis. In the presence of Ti-mont and hydrotalcite-supported palladium, 2-carbomethoxy-2-benzylglutaronitrile was obtained from methanol, cyanoacetic acid, and acrylonitrile via four acid/base reactions, namely esterification, deacetalization, reduction by hydrogen, and Michael addition.

Sn-exchanged mont (Sn-mont) is another type of mont prepared by ion exchange that is known to have a unique structure and high catalytic performance. The Sn-mont, prepared by the ion exchange of Na-mont and a SnCl₄ aqueous solution, does not exhibit the typical stacking structure but instead demonstrate a disordered layer arrangement, resulting in a high surface area and pore volume. While the surface area of H-mont is about 27 m² g⁻¹, the surface area of Sn-mont is reported to be 280 m² g⁻¹. Furthermore, Sn-mont possesses both mesopores and micropores because of the formation of Sn(OH)₄ nanoparticles, which are surrounded by a unit layer of mont. Because of its high surface area resulting from its unique structure, Sn-mont has been applied to various catalytic reactions since 1993, when Onaka and co-workers reported that Sn-mont facilitates the reaction of benzaldehyde dimethyl acetal with Et₃SiH. Recently, it has been reported that Sn-mont can catalyze reactions such as cyanosilylation of various hindered ketones, deoxygenation of benzylic alcohols into alkanes, Mukaiyama aldol reactions, conversion of triose sugars to alkyl lactates, synthesis of α-amino nitriles, and so on. Various other cation-exchanged monts have also been reported. For example, Sun et al. showed that Nb-mont catalyzes the synthesis of 5-hydroxymethylfurfural from glucose. Other monts, such as Cu-mont and Sc-mont, have also been reported, indicative of its broad ion-exchange adaptability. For Sc and Cu, an aqua complex was formed in the interlayer of mont. These unique metal complexes showed excellent catalytic activity.
activity for the Michael reactions of 1,3-dicarbonyl compounds \[60, 61]\), Sakurai-Hosomi allylation of allylsilanes \[61]\, and Diels–Alder reaction \[61]\.

In summary, cation-exchange monts were active in a variety of reactions. In particular, mont is often used as a solid acid catalyst (H-mont and Al-mont), and is effective in the synthetic reactions of organic molecules with large molecular sizes. Introduction of various metal cations, such as Ti\(^{4+}\), Sn\(^{4+}\) and Fe\(^{3+}\), enables important organic reactions, such as carbon-carbon bond-forming reactions and redox reactions. Cation-exchanged monts have also been reported as a part of mixed catalyst system with other solid catalysts, and the concerted effect of these catalysts lead to one-pot synthesis and challenging reactions.

3. Catalysis of metals supported on montmorillonite

The utility of mont as a support for metal nanoparticles has also attracted attention for the design of high-performance catalysts. Mont-supported metal catalysts exhibit properties different from those of other catalyst supports, such as the combined effect of the solid acidity of mont and the supported metal \[62, 63]\ and the stabilizing effect of metal particles in the interlayer \[64–66]\.

Bhanage et al reported the synthesis of 2, 5-diformylfuran (DFF) from fructose catalyzed by Ru nanoparticles supported on mont \[62]\. The synthesis of DFF from fructose involves two steps, namely, dehydration and oxidation (figure 8). With the previous catalyst, the first dehydration step did not proceed under an oxygen atmosphere; consequently, two steps were required in which oxygen was introduced after the dehydration reaction completed. However, in the case of Ru/mont, both dehydration, by the solid acidic material, and oxidation reaction, by the Ru nanoparticles, proceeded smoothly under an oxygen atmosphere, and therefore a one-step synthesis with a two-step reaction was realized. In addition, Ru/mont showed a wide range of substrate adaptability and could be reused multiple times, maintaining a yield of over 90% until the fifth time.

The stabilization of metal particles by the interlayer of mont is another advantage of using mont as a support. Mitsudome et al demonstrated the use of mont-entrapped subnano-ordered Pd clusters for allylic substitution reactions \[64]\. In general, this type of substitution reaction does not proceed on a Pd-nanoparticle catalyst. The subnano Pd cluster stabilized in the mont interlayer enables a coordinatively unsaturated Pd site, resulting in the formation of a \(\pi\)-allylpalladium intermediate. Dutta et al reported the activity of Pd/mont in the Heck-Sonogashira coupling reaction \[65]\. Pd/mont showed no significant loss of catalytic activity after multiple reuses and no change in the catalytic structure. For example, in the reaction of iodobenzene with methyl acrylate, the target product was obtained in more than 90% yield, and the yield was maintained above 85% even when the catalyst was reused. These results indicate the stability of mont as a support and its stabilizing effect on the supported active metal species.

Other bifunctional catalysts consisting of an organic group and palladium immobilized on mont have also been reported by Varadwaj et al \[67]\. Pd(II)NH\(_2\), Ph@MMT, prepared by immobilizing amine and phenyl groups on mont via silane coupling and reacting with an amine using PdCl\(_2\) as a precursor, was reduced with NaBH\(_4\) to yield Pd(0)NH\(_2\), Ph@MMT. Pd(0)NH\(_2\), Ph@MMT showed good activity, especially in Suzuki-
Miyaura coupling, where up to 98% yield was achieved. In particular, a significant increase in catalytic activity was observed for the reaction in an aqueous solution, owing to the improved hydrophobicity around the active site by the immobilization of organic groups.

As described above, the use of mont as a carrier can be applied to a variety of reactions by utilizing its unique acidic quality and layered structure that are not found in other carriers. In addition, the fact that the supported metal has two active sites, one for the acid and the other for the metal, means that there are many possibilities for application in other reactions.

4. Interlayer design for selective and efficient catalysis

The unique layered structure of mont allows for a variety of catalyst designs by controlling the distance between the layers and creating active sites on the layers. Our group has reported that the product selectivity can be controlled by the interlayer distance of H-mont, which can be altered by sonication during ion exchange or by preheating and drying [31]. The interlayer distances of H-mont with sonication treatment (H-mont(ui)) and after pretreatment at 150 °C (H-mont(150)) were calculated from the (001) peak of the x-ray diffraction (XRD) patterns (figure 9) and found to be 5.0, 3.0, and 2.5 Å, respectively. The reaction of \( n \)-heptane with benzene at 150 °C was performed using H-mont with different interlayer distances. The initial selectivities at low benzene conversion to alkylated products without cracking (Ph-\( \text{C7} \)) and tertiary butylbenzene (Ph-\( \text{t-C4} \)) were as follows:

\[
\text{Ph-\( \text{C7} \)} : \text{Ph-\( \text{t-C4} \)} = \begin{cases} 80 & \text{H-mont} \text{(ui)} \\ 60 : 20 & \text{H-mont} \text{(150)} \end{cases}
\]

For untreated H-mont with a certain interlayer distance, the alkane substrate penetrated the interlayer, and monomolecular cracking proceeded, resulting in stable tertiary butyl cation formation (figure 10(B)). However, when the interlayer distance was not sufficiently large, a rapid bimolecular reaction occurred at the acid sites on the surface/edge of the H-mont. (figure 10(A)). For the ultrasonically irradiated and heat-dried H-mont, the interlayer distance was
too narrow for the substrate to penetrate the interlayer; therefore, bimolecular reactions at the surface and edge of the H-mont occurred, resulting in the formation of heptylbenzene as the main product (figure 10(A)).

A bifunctional acid-base catalyst based on the immobilization of primary amines on the interlayer of H-mont (H-mont-NH₂) has also been reported (figure 11) [68]. Primary amines were introduced into the interlayer of H-mont by widening the interlayer distance from 2.6 to 7.7 Å, as determined from XRD patterns. The loading, interlayer distance, and acid-base interactions were determined by the solvent used during immobilization. The clustering of amine precursors in nonpolar solvents, such as heptane, may prevent strong interactions with the acid sites on the H-mont surface. The acid-base bifunctional catalyst prepared in the n-heptane solvent, H-mont-NH₂, was highly active toward tandem deacetalization-Knoevenagel condensation, especially for maximum yields of 95%, whereas the catalyst prepared in acetonitrile resulted in a negligible yield of the final product.

### Table 3. Summary of various montmorillonite catalysts and catalytic reactions.

| Catalyst | Catalytic reaction | References |
|----------|--------------------|------------|
| H-mont   | Allylsilylation of alkenes | [4] |
|          | Poly(oxybutyleneoxymaleyl) synthesis | [19] |
|          | Ring opening polymerization of e-caprolactone | [20] |
|          | Ethanol dehydration | [21] |
|          | Depolymerization of polyethers to glycol diesters | [22] |
|          | Addition of 1,3-dicarbonyl to alkenes and alcohols | [23] |
|          | C—N bond formations of alkenes and alcohols with amides and anilines | [24, 25] |
|          | Nucleophilic substitution reactions of alcohols | [25] |
|          | Ring-opening alylation of cyclic acetals with allylsilanes | [26] |
|          | Allylsilylation of aromatic and aliphatic alkenes | [27] |
|          | Intermolecular allylsilylation, arylsilylation, and silylation of alkenes | [28] |
|          | Cyanation of alkenes using nitromethane | [29] |
|          | Alkylation of (hetero)arenes by heterobenzyl acetates | [30] |
|          | Dehydrogenative coupling of alkanes and benzene | [31] |
| Al-mont  | Ether formation by dehydration of alcohols and addition of alcohols to alkenes | [32] |
|          | Dehydrogenative coupling of alkanes and benzene | [18, 34] |
| Fe-mont  | Benzylation of arenes | [35] |
|          | Acylation of sulfonamides with carboxylic acid anhydrides | [36] |
|          | Oxidation of alkanes with H₂O₂ | [37] |
| V-mont   | Beckmann rearrangement | [38] |
|          | Acetolysis of carbonyl compounds | [39] |
| Ti-mont  | Deacetylation of acetals | [40] |
|          | Esterification of carboxylic acids with alcohols | [41] |
|          | Synthesis of ethers from two alcohols | [42] |
|          | Aromatic alkylation for the synthesis of BHEPF | [43] |
| Sn-mont  | Synthesis of nitriles from alcohols with trialkylsilyl cyanide | [44] |
|          | Cyanotrimesilylation of benzophenone with cyanotrimethylsilane | [45] |
|          | Reduction of carbonyl compounds with hydrosilanes | [46] |
|          | Silylation of Alcohol | [47] |
|          | Cyanosilylation of carbonyl compounds | [48] |
|          | Deoxygenation of benzylic alcohols into alkanes with trialkylsilyl cyanide | [49] |
|          | Mukaiyama Aldol Reactions | [50] |
|          | Alkylation of α-aryl alcohols with allylsilanes | [51] |
|          | Ring-opening polymerization of lactones | [52] |
|          | Conversion of triose sugars with alcohols to alkyl lactates | [53] |
|          | Synthesis of α-amino nitriles from carbonyl compounds, amines, and trimethylsilyl cyanide | [54] |
| Nb-mont  | Synthesis of 5-hydroxymethylfurfural from glucose | [55] |
| Sc-mont  | Michael reaction | [56, 57] |
| Cu-mont  | Michael reaction, Alkylation of carbonyl compounds, Diels-Alder reaction | [58] |
| Ru/mont  | Direct conversion of glucose to DFF | [59] |
| Pt/mont  | Glycerol hydrogenolysis | [60] |
| Pd/mont  | Allylic substitution reaction | [61] |
| Pd/mont  | Heck-Sonogashira coupling reaction | [62] |
| Au/mont/ CeO₂ | Nitrophenol reduction | [63] |
| Pd(0) NH₂ Ph@MMT | Suzuki-Miyaura coupling reaction | [64] |
| H-mont-NH₂ | Deacetalization-Knoevenagel condensation | [65] |
In summary, designing the mont interlayer is useful to control product selectivity. Introduction of organic functional groups into the interlayer is also possible. Interestingly, introduction of basic amines into the interlayer enables acid-base bifunctional catalysis for one-pot synthesis.

5. Conclusion

Mont-based catalysts for liquid-phase organic reactions were reviewed. The unique catalysts fabricated based on the cation-exchange ability and layered structure of mont can be applied to various reactions, including acid-, metal-, and base-catalyzed reactions. The montmorillonite catalysts and their catalytic reactions introduced are summarized in table 3.

As an acid catalyst, it could be used for dehydration, addition with alcohols and alkenes, and even direct addition of alkanes. Furthermore, an interesting feature of mont catalyst is its dual functionality. By supporting metal particles or organic groups, a concerted catalysis with acidity of mont can be achieved. Consequently, mont clay will be continuously used as a unique support material to integrate catalysis for highly efficient organic synthetic reactions. One of the further research directions is expected to include the utilization of bifunctionality of mont: for example, introduced metal cation/metal complex/organic cation and acidity may exhibit concerted catalysis in the mont interlayer space which enables highly selective catalysis.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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References

[1] Nguana W B F and Kalinichev A G 2014 J. Phys. Chem. C 118 12758–73
[2] Morodome S and Kawamura K 2011 Clays Clay Miner. 59 165–75
[3] Watanabe T and Sato T 1988 Clay Sci. 7 129–38
[4] Motokura K, Matsunaga S, Noda H, Miyaji A and Baba T 2012 ACS Catal. 2 1942–6
[5] Kaneda K, Ebintani K, Mizugaki T and Mori K 2006 Bull. Chem. Soc. Jpn. 79 981–1016
[6] Chellapandi T and Madhumitha G 2021 Mol. Divers. In Press
[7] Kaur N and Kishore D 2012 J. Chem. Pharm. Res. 4 991–1015
[8] Kaneda K 2007 Synlett 7 999–1013
[9] Kumar B S, Dhakshinamoorthy A and Pitchumani K 2014 Catal. Sci. Technol. 4 2378–96
[10] Varadwaj G B B and Parida K M 2013 RSC Adv. 3 13583–93
[11] De Stefanis A and Tomlinson A A G 2006 Catal. Today 114 126–41
[12] Izumi Y, Urabe K and Onaka M 1998 Micropor. Mesopor. Mater. 21 227–33
[13] Motokura K and Baba T 2012 Green Chem. 14 565–79
[14] Hecheldi M, Ghinet A, Louvel B, Dufénoy P, Rigo B, Daich A and Waterlot C 2008 Chem. Sus. Chem 11 1249–77
[15] Izumi Y, Urabe K and Onaka M 1997 Catal. Surv. Ips. 1 17023
[16] Dutta D K, Borah B J and Sarma P P 2015 Catal. Rev. 57 257–305
[17] Rode C V, Garade A C and Chikate R C 2009 Catal. Surv. Asia 12 205–20
[18] Takabatake M, Nambo M, Manaka Y and Motokura K 2020 ChemPlusChem 85 450–3
[19] Ferrahi M I and Belbachir M 2004 Molecules 9 968–77
[20] Harrane A, Meghabar R and Belbachir M 2006 React. Funct. Polym. 66 1696–702
[21] Krupiti C and Jongsomjit B 2016 J. Oleo Sci. 65 347–53
[22] Maeno Z, Yamada S, Mitsudome T, Mizugaki T and Jitsukawa K 2017 Green Chem. 19 2612–9
[23] Motokura K, Fujita N, Morii K, Mizugaki T, Ebintani K and Kameda K 2006 Angew. Chemie-Int. Ed. 45 2605–9
[24] Motokura K, Nakagiri N, Morii K, Mizugaki T, Ebintani K, Jitsukawa K and Kameda K 2006 Org. Lett. 8 4617–20
[25] Motokura K, Nakagiri N, Mizugaki T, Ebintani K and Kameda K 2007 J. Org. Chem. 72 6006–11
[26] Motokura K, Yoneda H, Miyaji A, Sakamoto Y and Baba T 2011 Catal. Sci. Technol. 1 470–9
[27] Motokura K, Matsunaga S, Miyaji A, Sakamoto Y and Baba T 2010 Org. Lett. 12 1508–11
[28] Motokura K, Matsunaga S, Miyaji A, Yashima T and Baba T 2011 Tetrahedron Lett. 52 6687–92
[29] Motokura K, Matsunaga K, Miyaji A, Yamaguchi S and Baba T 2014 Tetrahedron Lett. 55 7034–8
[30] Yang L, Chen X, Ni K, Li Y, Wu J, Chen W, Ji Y, Feng L, Li F and Chen D 2020 Tetrahedron Lett. 61 152123
[31] Takabatake M, Nambo M, Manaka Y and Motokura K 2020 J. Jpn. Petrol. Inst. 63 289–96
[32] Ballantine J A, Davies M, O’Neil R M, Patel I, Purnell J H, Rayanakorn M, Williams K J and Thomas J M 1984 J. Mol. Catal. 26 57–77
[33] Ballantine J A, Davies M, Patel I, Purnell J H, Rayanakorn M, Williams K J and Thomas J M 1984 J. Mol. Catal. 26 57–56
[34] Takabatake M, Hashimoto A, Chum W, Nambo M, Manaka Y and Motokura K 2021 JACS Au 1 124–9
[35] Pai S G, Baipai A R, Deshpande A B and Samant S D 2000 J. Mol. Catal. A: Chem. 156 233–43
[36] Singh D U, Singh P R and Samant S D 2004 Tetrahedron Lett. 45 4805–7
[37] Ebitani K, Ide M, Mitsudome T, Mizugaki T and Kaneda K 2002 Chem. Commun. 2690–1
[38] Mitsudome T, Mori K, Mizugaki T, Ebitani K and Kaneda K 2005 Chem. Lett. 34 1626–7
[39] Mitsudome T, Matsuno T, Sueoka S, Mizugaki T, Jitsukawa K and Kaneda K 2012 Tetrahedron Lett. 53 5211–4
[40] Kawabata T, Mizugaki T, Ebitani K and Kaneda K 2001 Tetrahedron Lett. 42 8329–32
[41] Kawabata T, Kato M, Mizugaki T, Ebitani K and Kaneda K 2003 Chem. Lett. 32 648–9
[42] Kawabata T, Mizugaki T, Ebitani K and Kaneda K 2005 Tetrahedron Lett. 44 9205–8
[43] Mitsudome T, Matsuno T, Sueoka S, Mizugaki T, Jitsukawa K and Kaneda K 2012 Green Chem. 14 610–3
[44] Ebitani K, Kawabata T, Nagashima K, Mizugaki T and Kaneda K 2000 K. Green Chem. 2157–60
[45] Motokura K, Fujita N, Mori K, Mizugaki T, Ebitani K and Kaneda K 2005 J. Am. Chem. Soc. 127 9674–5
[46] Wang J, Masui Y and Onaka M 2011 ACS Catal. 1 446–54
[47] Masui Y, Wang J, Teramura K, Kogure T, Tanaka T and Onaka M 2014 Microporous Mesoporous Mater. 198 129–38
[48] Onaka M, Higuchi K, Nanami H and Izumi Y 1993 Bull. Chem. Soc. Jpn. 66 2638–45
[49] Onaka M, Hosokawa Y, Higuchi K and Izumi Y 1993 Tetrahedron Lett. 34 1171–2
[50] Wang J, Masui Y, Hattori T and Onaka M 2012 Tetrahedron Lett. 53 1978–81
[51] Tandiary M A, Masui Y and Onaka M 2014 Tetrahedron Lett. 55 4160–2
[52] Takehira S, Masui Y and Onaka M 2014 Chem. Lett. 43 498–500
[53] Wang J, Masui Y and Onaka M 2010 Tetrahedron Lett. 51 3300–3
[54] Hazemornou A and Belbakhir M 2005 Mater. Lett. 59 3904–8
[55] Wang J, Masui Y and Onaka M 2011 App. Catal. B Environ. 107 135–9
[56] Wang J, Masui Y, Watanabe K and Onaka M 2009 Adv. Synth. Catal. 351 553–7
[57] Higuchi K, Onaka M and Izumi Y 1993 Bull. Chem. Soc. Jpn. 66 2016–32
[58] Wang J, Masui Y and Onaka M 2010 Eur. J. Org. Chem. 1763–71
[59] Qiu G, Huang C, Su S and Chen B 2019 Green Chem. 21 3930–9
[60] Kawabata T, Mizugaki T, Ebitani K and Kaneda K 2003 J. Am. Chem. Soc. 125 10486–7
[61] Kawabata T, Kato M, Mizugaki T, Ebitani K and Kaneda K 2005 Chem. Eur. J. 11 288–97
[62] Raut A B, Shende V S and Bhanage B M 2020 New J. Chem. 44 13659–68
[63] Samudrala S P, Kundasana S and Bhattacharya S 2018 Sci Rep. 8 7484
[64] Mitsudome T, Nose K, Mori K, Mizugaki T, Ebitani K, Jitsukawa K and Kaneda K 2007 Angew. Chem. Int. Ed. 46 3288–90
[65] Borah B J and Dutta D K 2013 J. Mol. Catal. A: Chem. 366 202–9
[66] Chenouf M, Megias-sayago C, Ammari F, Ivanova S and Angell M 2019 Comptes Rendus Chim. 22 621–7
[67] Varadwaj G B, Rana S and Parida K 2014 J. Phys. Chem. C 118 1640–51
[68] Motokura K, Tada M and Iwasawa Y 2009 J. Am. Chem. Soc. 131 7944–5