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Performance of organic–inorganic hybrid catalysts based on *Ia*-3*d* mesoporous silica

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Abstract

The cubic *Ia*-3*d* mesoporous silica with ordered large pores was synthesized from tetraethoxysilane (TEOS) and a small amount of 3-mercaptopropyltorimetoxysilane (MPTS) as the silica sources under the acidic conditions by using triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$) as a surfactant. After removal of the surfactant by the solvent extraction method, mercaptopropyl (MP) group (–$CH_2CH_2CH_2SH$) remained inside pores with a slight loss. The pore diameter of this mesoporous silica was about 5 nm. After converting the MP group to sulfopropyl (SP) group (–$CH_2CH_2CH_2SO_3H$) by the oxidation with H_2O_2, the amount of organic group was significantly reduced. However, it was possible to introduce additional organic groups by post-synthetic grafting. It was also possible to graft both MP and SP groups at the same time, and cooperative effect was observed in the acid-catalyzed condensation reaction of phenol with acetone. More organics were immobilized to the multi-dimensional cubic *Ia*-3*d* structure than the one-dimensional 2d-hexagonal structure. The catalyst having both SH and SO_3H groups showed much higher selectivity for bisphenol A than Amberlyst 15 and Nafion SAC-13, which could be explained by the SH group-assisted mechanism.

Keywords: Mesoporous silica; Cubic *Ia*-3*d*; Sulfopropyl group; Mercaptopropyl group

1. Introduction

In recent years, new families of ordered mesoporous silica materials have initiated an intensive research effort toward applications in catalysis, adsorption, separation of bulky molecules and environmental pollution control [1,2]. The utilization of mesoporous materials with various new structures is of great interest. So far, the main research efforts have been concentrated on the MCM-41-type structure that possesses a regular hexagonal array of uniform pores with diameters in the range of 2–10 nm [3–6]. A variety of mesoporous silicas with different structures have been obtained using cationic [3], anionic [7,8] and non-ionic [9,10] surfactants with uniform pore diameters and large surface areas.

Recently, a large-pore mesoporous silica with cubic *Ia*-3*d* structure has been synthesized by co-condensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTS) [11]. Since the as-synthesized material already has mercaptopropyl (MP) groups on the pore wall, this material could serve as an acidic catalyst after appropriate modifications [12,13], such as extraction of the surfactant used as a structure-directing agent (SDA), oxidation of MP groups into sulfopropyl (SP) groups, and additional grafting in some case. The aim of this work is to modify this material in order to obtain a highly active and selective catalyst for the synthesis of 4,4′-isopropylidenediphenol (4,4′-IPP; bisphenol A), which is known as a very important raw material of the polycarbonates and epoxy resins.

2. Experimental

2.1. Synthesis of cubic Ia-3d mesostructure

The *Ia*-3*d* cubic mesoporous silica (denoted as MCA) with large pores was synthesized by the co-condensation of TEOS and MPTS using triblock copolymer surfactant P123 ($EO_{20}PO_{70}EO_{20}$, $M_W = 5800$) as SDA. In a typical procedure, a mixture of TEOS (8.19 g, 39.31 mmol) and MPTS (0.69 g,

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3.51 mmol) was added to a mixture of P123 (4.0 g), conc. HCl (7.8 g), and deionized water (100 mL) at 40 °C. After the mixture was stirred at 40 °C for 24 h, it was statically heated at 100 °C for 48 h. The molar gel composition was 1.0 TEOS–0.089 MPTS–0.018 P123–2.0 HCl–148 H_2O. The white precipitate formed was filtered without washing and dried at 60 °C according to the known method [11]. The surfactant was removed by extracting with a mixture of conc. HCl and EtOH or a mixture of conc. HCl and pyridine (the extracted sample is designated as MCAex) at 70 °C for 24 h.

2.2. *Oxidation and/or post-synthetic grafting*

The MCAex tethering MP group was oxidized with 30% H_2O_2 aqueous solution (10 g of the solution per 3.0 g of the MCAex was used) at room temperature for 24 h to give the MCAox sample. Part of this sample (1.0 g) was heated with MPTS (0.27 g, 1.4 mmol) in refluxing toluene (50 mL) for 3 h to give MP-[MCAox], which has both MP and SP groups. The MP-[MCAox] was further oxidized to SP-[MCAox] with 30% H_2O_2 in a similar manner. For comparison, the MPTS grafting was applied to MCAex and MCAcal (in which the SDA was removed by calcination at 550 °C for 10 h) to give MP-[MCAex] and MP-[MCAcal], respectively. Successively, the MP-[MCAex] and the MP-[MCAcal] were oxidized to SP-[MCAex] and SP-[MCAcal], respectively. For better understanding, the relationship between the samples and abbreviations is shown in Fig. 1.

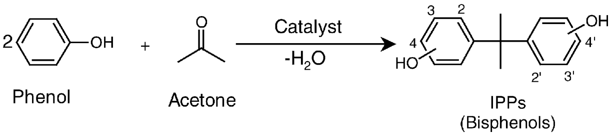
The similar procedure was applied to the typical SBA-15 [9,10] to prepare SBA-15ex and SP-[SBA-15ex] for comparison.

2.3. *Characterization*

The powder X-ray diffraction (XRD) patterns of prepared materials were collected on an MX Labo powder diffractometer using Cu Kα (λ = 1.5418 Å) radiation over the range of $2\theta = 1.5–8°$. Nitrogen adsorption and desorption isotherms at −196 °C were measured for the samples pre-treated at 200 °C for 2 h on a BELSORP 28SA gas adsorption instrument. The specific surface area was calculated using the BET method. The pore size distributions were obtained from the adsorption branch of isotherms using the BJH method. FE-SEM and STEM images were recorded on a Hitachi S5200 microscope. The ^{29}Si MAS NMR and ^{13}C CP MAS NMR spectra were recorded on a JEOL JNM-CMXP-400 system equipped with a magic-angle spin probe in a 4 mm ZrO_2 rotor. A Shimadzu DTG-60 thermogravimetric analyzer was used to carry out the thermogravimetric analysis (TGA). The acid amount was determined by acid–base titration. The amount of the MP group was determined by iodometry method.

2.4. *Catalytic reaction*

The prepared catalysts were used as the catalyst for the reaction of phenol with acetone to give bisphenols (Eq. (1)). In a typical procedure, phenol (25.0 mmol), acetone (5.0 mmol), and catalyst (100 mg) were charged into a pressure bottle. Then the mixture was stirred at 100 °C for 24 h. The products were analyzed on gas chromatography (GC-14A, Shimadzu) equipped with an OV-1 capillary column.



(1)

3. Results and discussion

3.1. *Properties of the mesoporous silica with cubic Ia-3d mesostructure synthesized under acidic conditions (MCA)*

The XRD patterns of each step of the catalyst preparation are shown in Fig. 2. The as-synthesized, extracted, and oxidized

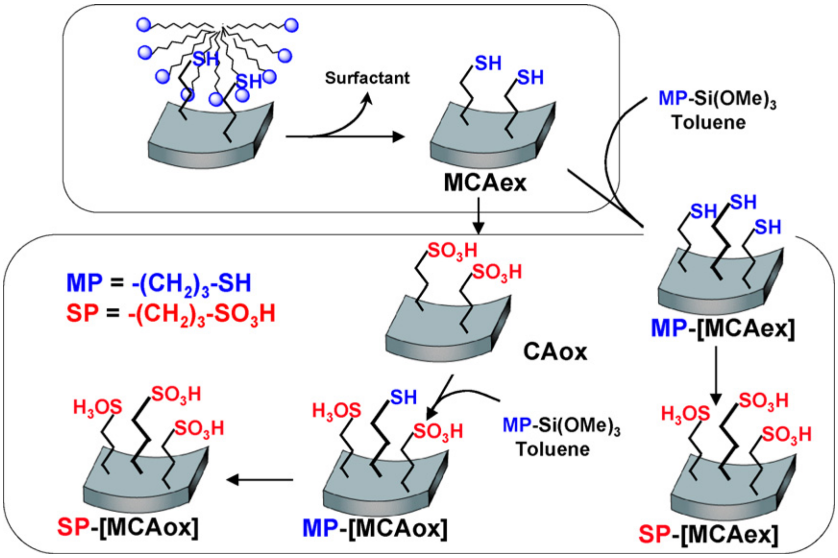


Fig. 1. Schematic illustration of post-synthetic modification of MCA.

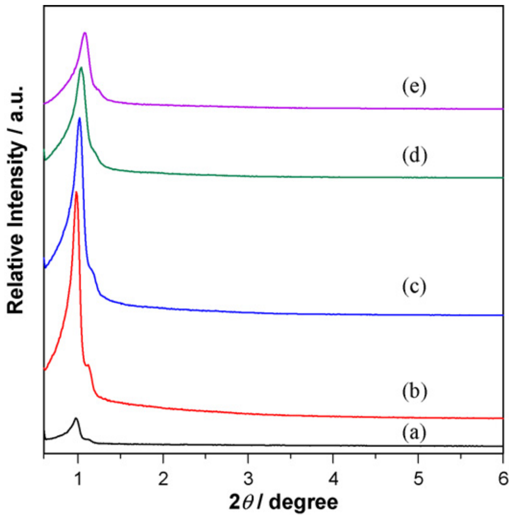


Fig. 2. Powder XRD patterns of (a) as-synthesized MCA, (b) MCAex, (c) MCAox, (d) MP-[MCAox], and (e) SP-[MCAox].

samples all exhibited two well-resolved diffraction peaks corresponding to 2 1 1 and 2 2 0 reflections in the 2θ range of 0.9–1.2° (Cu Kα), showing that the extracting, grafting and oxidizing procedures have no severe effect on the cubic structure. The STEM images indicated the regular arrangement of mesochannels (Fig. 3). N_2 adsorption/desorption measurements gave type-IV isotherms (not shown), which indicated that the obtained materials possess a large surface area (400–700 m^2/g) with a pore size of around 5 nm as listed in Table 1.

Fig. 4 shows ^{13}C CP MAS NMR spectra of as-synthesized and modified MCA samples. The oxidation from the SH to the SO_3H group was confirmed by ^{13}C CP MAS NMR. In the spectrum of MCAas, the signals assignable to three carbons of MP group appeared at 11.5, 27.7 and 27.7 ppm besides the large signals of the surfactant (Fig. 4a). After extracting the surfactant, the signals of the surfactant greatly decreased and those of MP group became major peaks (Fig. 4b). Signals assignable to ethanol were remaining due to imperfect drying of the material in Fig. 4b. These peaks are not due to the formation of surface ethoxy groups, judging from the chemical shift of the carbon next to oxygen (59 ppm). Oxidation made the peaks at

Table 1
Textural properties of modified MCA and SBA-15 samples

Entry	Sample	S_{BET}[a] ($m^2\ g^{-1}$)	Pore volume[b] ($cm^3\ g^{-1}$)	Pore diameter[b] (nm)
1	MCAex	508	0.76	6.2
2	MCAcal	547	0.71	5.4
3	MCAox	294	0.31	4.2
4	MP-[MCAox]	284	0.31	4.2
5	SP-[MCAox]	267	0.28	3.7
6	SP-[MCAex]	402	0.36	3.6
7	SBA-15ex	690	0.65	6.2
8	SP-[SBA-15ex]	440	0.54	6.1

[a] BET specific surface area.
[b] Calculated by using the BJH method.

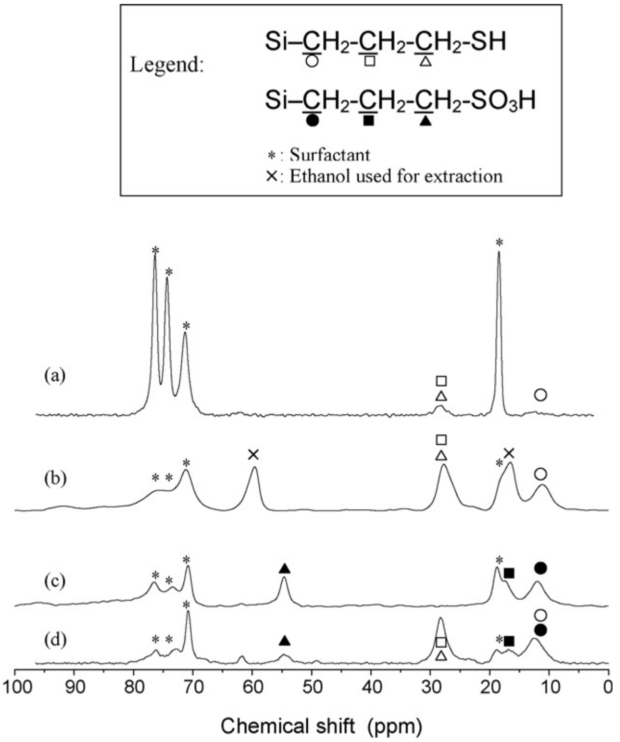


Fig. 4. ^{13}C CP MAS NMR spectra of (a) as-synthesized MCA, (b) MCAex, (c) MCAox, and (d) MP-[MSAox]. Co-existence of MP and SP groups is obvious in the spectrum (d).

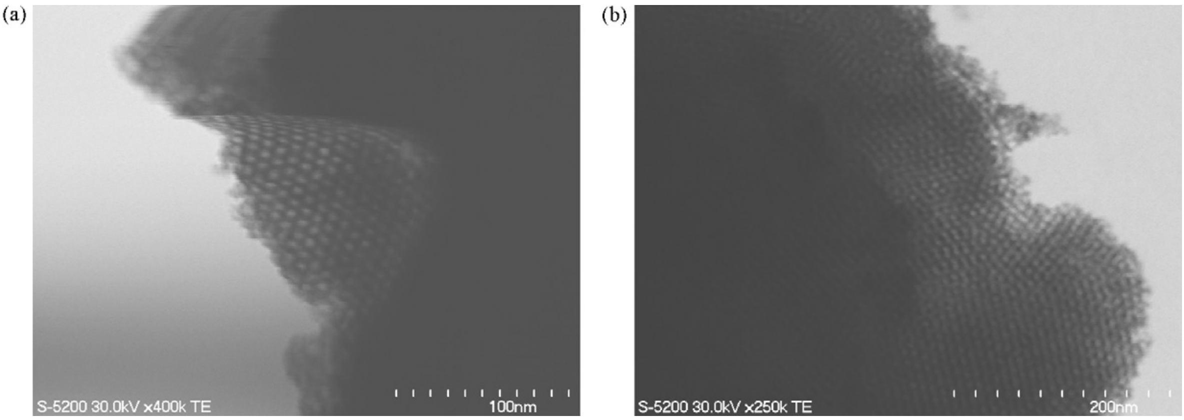


Fig. 3. STEM images of (a) MCAex and (b) MCAcal showing the ordered arrangement of the mesopores.

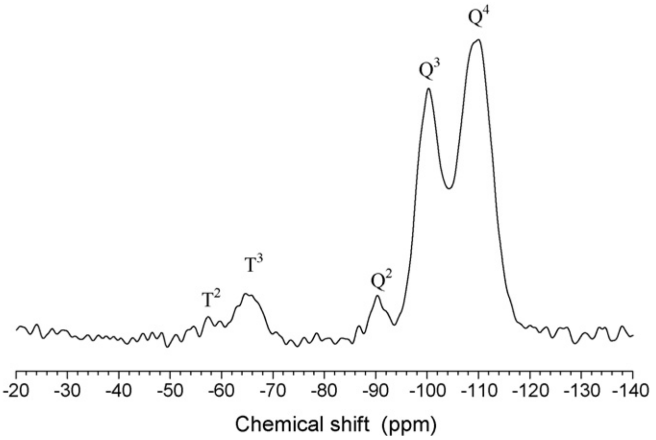


Fig. 5. ^{29}Si MAS NMR spectrum of MCAex.

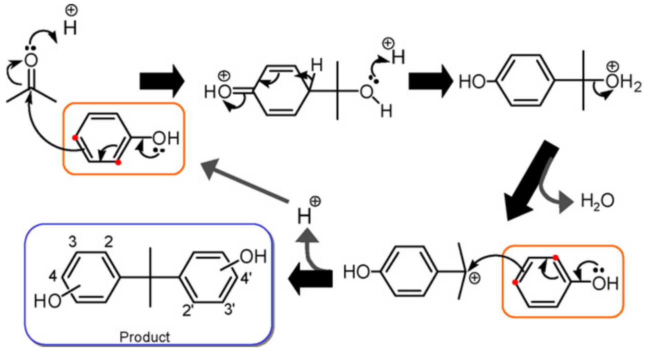


Fig. 6. Common mechanism of acid-catalyzed reaction of phenol with acetone.

27.7 ppm shift to 17.3 and 54.5 ppm (MCAox; Fig. 4c). The large downfield shift from 27.7 to 54.5 ppm is consistent with the chemical transformation from SH to SO_3H group. The ethanol peaks disappeared at this stage. Co-existence of MP and SP groups was confirmed on the spectrum of MP-[MCAox] (Fig. 4d). Although the complete removal of the surfactant by repeated extraction process was not successful, the amount of the remaining surfactant was slight and it was not harmful for the utilization as the catalyst. Control experiment revealed that more organics were immobilized by post-synthetic grafting to the multi-dimensional cubic *Ia*-3*d* structure than the one-dimensional 2d-hexagonal structure such as SBA-15. This is consistent with relatively large Q^3 and Q^2 peaks on the ^{29}Si MAS NMR spectrum of the MCA sample (Fig. 5).

3.2. Catalytic performances of the modified MCA materials

Table 2 summarizes the catalytic results of three series of catalysts for the reaction of phenol with acetone (Eq. (1)). MP-[MCAex] free of SO_3H groups is nearly inactive (Entry 1). In contrast, the use of MCAox without SH groups gave a 14.5% conversion (Entry 2). Clearly, MCAox as a catalyst led to a selectivity of about 80% because of the formation of a considerable amount of 2,4′-IPP. Despite of this, a further grafting with MPTS resulted in a remarkable increase in both activity and selectivity (Entry 3). This suggests that mercapto (SH) and sulfo (SO_3H) groups collaborate to promote the conversion of phenol. Judging from the results of the Entries 1 and 2, SO_3H groups are the active sites while SH group is a promoter. The relative amounts of SH to SO_3H significantly influence the catalytic performance, as revealed by the catalytic results for MP-[MCAox], SP-[MCAox] and SP-[MCAex] (Entries 3–5). The optimum ratio of SH to SO_3H was found to be about 2.2–2.4. Considering this value, specific surface area, and the organic content, ca. one SO_3H group and two SH groups may exist on the surface of 1 nm^2, where approximately one bisphenol A molecule could exist. The low activity of SP-[MCAcal] results from the presence of a small number of active sites and the absence of SH groups (Entry 6). Although commercial catalysts such as Amberlyst-15 and Nafion SAC-13 resulted in comparable phenol conversion, the comparison of turnover number (TON) values revealed a much stronger ability of SO_3H groups present in the MP-[MCAox] catalyst. It is noteworthy that MP-[MCAox] showed much higher 4,4′-IPP/2,4′-IPP ratio (91.4/4.0) than Amberlyst-15 (81.2/12.0) and

Table 2
Condensation reaction of phenol with acetone over various catalysts[a]

Entry	Catalyst	S content (mmol g^{-1})		Conversion of phenol (%)	Selectivity[b] (%)				TON[c]
		SH[d]	SO_3H[e]		4,4′-IPP	2,4′-IPP	2,2′-IPP	Others	
1	MP-[MCAex]	1.7	0.0	0.3	>99.9	0.0	0.0	0.0	0
2	MCAox	0.0	1.3	14.5	83.8	14.9	0.6	0.7	28
3	MP-[MCAox]	1.1	0.5	21.2	91.4	4.0	0.8	3.8	110
4	SP-[MCAox]	0.0	1.0	10.3	86.1	11.2	2.3	0.4	27
5	SP-[MCAex]	0.0	1.2	13.7	77.5	20.5	0.8	1.2	29
6	SP-[MCAcal]	0.0	0.2	1.1	64.9	29.3	5.8	0.0	13
7	Amberlyst-15	0.0	4.0	19.9	81.2	12.0	0.7	6.1	12
8	Nafion SAC-13	0.0	1.0	22.6	88.3	10.9	0.5	0.2	57
9	SP-[SBA-15ex]	0.0	0.5	3.0	85.8	4.2	9.1	0.9	15

[a] Reaction conditions: phenol, 25 mmol; acetone, 5 mmol; catalyst, 100 mg; temperature, 100 °C; time, 24 h.
[b] IPP = isopropylidenediphenol (bisphenols).
[c] Turnover number.
[d] Determined by iodometry method.
[e] Determined by acid–base titration.

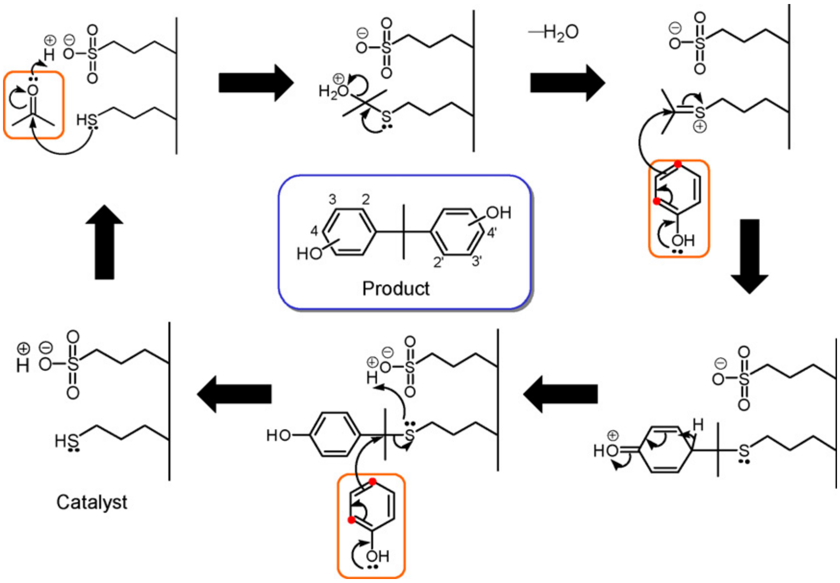


Fig. 7. Possible mechanism of SH group-assisted, acid-catalyzed reaction of phenol with acetone.

Nafion SAC-13 (88.3/10.9), which could be explained by the SH group-assisted mechanism (*vide infra*). The cubic *Ia*-3*d* mesoporous silica exhibited better TON than similarly modified 2d-hexagonal mesoporous silica (Table 2, Entries 5 and 9), suggesting that the *Ia*-3*d* pore structure has some advantage over 2d-hexagonal structure.

3.3. Mechanistic consideration

Widely accepted common mechanism of acid-catalyzed reaction of phenol with acetone is shown in Fig. 6. Carbonyl group of acetone is activated by acid and aromatic carbon of phenol makes a nucleophilic attack on the carbonyl carbon. Carbocation forms via the elimination of water. The second phenol makes a nucleophilic attack again on the carbocation to form the product. Mainly, 2- or 4-position of aromatic carbon would work as an electrophile. Fig. 7 shows the possible mechanism of SH group-assisted, acid-catalyzed reaction of phenol with acetone. Carbonyl group of acetone is activated by a sulfonic acid and adjacent SH group makes a nucleophilic attack, forming a strongly electrophilic carbon. To this carbon, the aromatic carbon at 2- or 4-position attacks as an electrophile with the effect of hydroxy group. Unlike the case in Fig. 6, the electrophilic carbon is regarded as very bulky moiety because it is tethered on the pore wall. Thus the aromatic carbon at 4-position would approach the electrophilic carbon much more easily than the carbon at 2-position. The second phenol would also approach a very bulky intermediate, forcing the aromatic carbon at 4-position to make a nucleophilic attack. This explains the high selectivity of 4,4′-IPP isomer.

4. Conclusions

The cubic *Ia*-3*d* mesoporous silica with ordered large pores was synthesized from TEOS and MPTS as the silica sources under the acidic conditions, which was named MCA. After the surfactant was removed by extraction, the remaining MP group was converted to SP group by oxidation with H_2O_2. It was possible to introduce additional organic groups by post-synthetic grafting. It was also possible to graft both MP and SP groups at the same time. Co-operative effect of MP and SP groups was observed in the acid-catalyzed condensation reaction of phenol with acetone, giving bisphenol A in high conversion and selectivity. MP-[MCAox] having both SH and SO_3H groups showed much higher selectivity for bisphenol A than Amberlyst 15 and Nafion SAC-13, which could be explained by the SH group-assisted mechanism. Although the Amberlyst type resins are mainly used as industrial solid acid catalysts for the present reaction, the heat- and chemical-resistances of resins are limited. In this sense also, the silica-based organic–inorganic hybrid catalyst has a great advantage.

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