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Chemoselective synthesis of dithioacetals from bio-aldehydes with zeolites under ambient and solvent-free conditions

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Abstract: Dithioacetals are an important class of versatile compounds extensively applied in pharmaceuticals, separations, electrochemistry and organic synthesis, but few heterogeneous catalytic systems are reported to be generally applicable for their synthesis from a wide range of substrates. Herein, a series of commercial and modified zeolites were demonstrated to be excellent catalysts for thioacetalization of different thiols with carbonyl compounds, including biomass-derived aldehydes, at room temperature under solvent-free conditions. Thus a near quantitative yield of dithioacetal was obtained over H-beta(19) at room temperature with a low catalyst to substrate ratio of 1:19, and a methodology to follow the reaction progress by ex situ UV-Vis absorption analysis was demonstrated. Recycling experiments with H-beta(19) in five consecutive runs resulted in slight loss of activity, but the original activity could be fully restored after calcination at 550 °C. Combined the reaction results and physicochemical properties of the zeolites revealed that relatively large pores and moderate acidity with an appropriate distribution of Brønsted/Lewis acid sites contributed to the pronounced performance in the dithioacetal formation.

Introduction

To alleviate the reliance of industrial production of chemicals and fuels from fossil resources, a great deal of attention has been placed on catalytic valorization of lignocellulosic biomass derivatives to potential replacements ^[1]. 5-Hydroxymethylfurfural (HMF) and furfural are two primary platform molecules, which can be produced from acid-catalyzed dehydration of hexoses and pentoses, respectively ^[2]. Through different upgrading processes such as rehydration, oxidation, etherification and hydrogenation, HMF and furfural can be further converted to a variety of value-added chemicals (e.g., levulinic acid, 2,5furandicarboxylic acid and maleic anhydride) and biofuel additives (e.g., γ -valerolactone, 5-ethoxymethylfurfural and 2,5-

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dimethylfuran) ^[3]. Besides the above transformation routes involving the participation of hydrogen and oxygen atoms, efficient synthesis of nitrogen-containing cyclic compounds from biomass-derived furanics has also been developed in recent years ^[4]. For instance, catalytic reductive amination of furfural or HMF over metal nanoparticles (e.g., Rh, Ru, Ir, Pt and Au) afforded the corresponding furfuryl amines in high selectivities (up to ~90%) ^[4a-c], while acidic catalysts, such as H-ZSM-5(Si/Al = 25) and formic acid, were able to produce indoles and *N*-alkylpyridinium salts from furfural and HMF, respectively ^[4d-e]. However, few studies can be found on the synthesis of biofuranderived sulfur-containing cyclic compounds with zeolites ^[4f].

Among various organic sulfides, dithioacetals are extensively applied in pharmaceutical and pesticidal production ^[5], toxicant separation ^[6], electrochemistry ^[7], and organic syntheses ^[8]. Dithioacetals are formed by either Brønsted or Lewis acidcatalyzed condensation of thiols with ketones and aldehydes in a similar way as acetals are formed with alcohols, but dithiols have also been used to protect carbonyl groups ^[9]. However, unlike alcohols thiols have the possibility to form intermolecular disulfides via oxidative coupling ^[10] and drawbacks such as need of volatile organic solvents (e.g., dichloromethane and acetonitrile), and use of homogeneous and unrecoverable acids or metal salts ^[11] have been entailed in previous studies.

Common heterogeneous acid catalysts such as H₃PW₁₂O₄₀/SiO₂ Montmorillonite K-10 clay, and Amberlyst-15 are easy to separate and reuse, but their applicability is often limited for different substrates ^[12]. In addition, thioacetals are guite sensitive to acidic sources due to the occurrence of reversible reactions, limiting the efficacy of their preparation. Developing alternative and efficient solid catalysts for chemoselective synthesis of dithioacetals through thioacetalization of carbonyl compounds - especially biomass-derived carboxides - is therefore desirable. Zeolites are thermally stable, microporous crystalline aluminosilicates where acidity and regular pore architecture can be controlled by varying the Si/AI ratio ^[13]. Zeolites have been demonstrated to be versatile catalysts for a wide range of organic reactions in both the petrochemical industry and in biomass refinery in the past decades, combining excellent catalytic performance with facile recovery and reuse [14]

In the present study, a variety of commercially available zeolites, including Y, beta, mordenite and ZSM-5, have been explored as catalysts for thioacetalization of biomass-derived carboxides with different alkyl and aromatic thiols to the corresponding dithioacetals under mild reaction conditions. H-beta(19) was further modified by calcination at high temperature, treatment with ammonium hydroxideor co-used with a neutral ionic liquid to investigate the role of acidity and pore size of the zeolite in the reaction.

Results and Discussion

In a sustainable transformation approach, furfural was predominantly used as a crucial platform chemicalfor producing C4 and C5 compounds [15]. In this context, the selective thioacetalization of furfural with ethyl-2-mercaptoacetate to furfuryl dithioacetal was conducted at room temperature (23 °C) under solvent-free conditions. The results obtained with various zeolites for the reaction are shown in Table 1. It can be seen that no significant amount of furfural was converted and dithioacetal formed in the absence of a catalyst (entry 1). Intriguingly, Y type zeolites effectively catalyzed the transformation of furfural to dithioacetal with moderate to excellent yields up to 95% (entries 2-4). It is worth mentioning that H-Y(2.6) despite possessing a higher acidity (2.1 mmol/g, Table S1) exhibited a lower catalytic performancethan the other Y zeolites, yielding 51% of dithioacetal with a TOF of 0.8 h⁻¹, which can be ascribed to its lower Brønsted to Lewis (B/L) acid ratio of 1.4 and the relatively high crystal size (ca. 162 nm; Table S2). A very poor activity was found with H-ZSM-5(15) for

thioacetalization of furfural (8% yield, TOF of 0.2 h⁻¹; entry 5), indicating occurrence of mass transfer hindrance due to its relatively narrower pore size (~5.5 Å) than furfural (ca. 5.6 Å) and ethyl-2-mercaptoacetate (ca. 5.8 Å) [16]. Compared to H-Y(30), H-mordenite(10) possessed more acidity but gave a relatively lower dithioacetal yield of 69% and TOF of 1.2 h⁻¹ (entry 6), indicating that a higher molar ratio of B/L acid sites and smaller crystal size (Table S2) were more favorable for dithioacetal formation. Likewise, the catalytic results of beta zeolites H-beta(12.5), H-beta(19) and H-beta (150)demonstrated a concerted role of pore/crystal size, total acidity, and B/L acid ratio for the thioacetalization (entries 7-9; Figures S1-S3), wherein H-beta(19) having superior activity with respect to product yield (98%) and selectivity (99%) seems to be a better candidate for further experimental optimization. It should be noted that the mass balance of carbon and sulfur is close to 100%, with hemiacetals (1-12%) and disulfides (1-9%) via oxidative coupling of thiols as major byproducts in all reactions performed with zeolites (Table 1).

 Table 1. Catalytic thioacetalization of furfural with ethyl
 2-mercaptoacetate over different zeolites^[a]



Entry	Catalyst	Total acidity (mmol/g) ^[b]	B/L ratio ^[c]	Furfural conv. (%)	Dithioacetal yield/[selec.] (%)	TOF (h ⁻¹) ^[d]	Disulfide yield / [selec.](%) ^[e]
1	-	-	· · · ·	3	1/[33]	-	<0.1/[>99]
2	H-Y(2.6)	2.1	1.4	63	51/[81]	0.8	1.3/[97]
3	H-USY(6)	1.4	2.3	99	95/[96]	2.3	0.8/[99]
4	H-USY(30)	0.9	2.9	90	83/[92]	3.1	1.0/[99]
5	H-ZSM-5(15)	1.2	0.2	18	8/[44]	0.2	8.9/[95]
6	H-mordenite (10)	1.9	0.3	77	69/[90]	1.2	5.6/[97]
7	H-beta(12.5)	1.3	2.7	97	95/[98]	2.4	1.6/[>99]
8	H-beta(19)	1.5	2.1	99	98/[99]	2.2	1.3/[>99]
9	H-beta(150)	0.5	0.2	48	40/[83]	1.9	4.8/[98]
10 ^[f]	H-beta(19)-700	0.8	1.0	74	68/[92]	2.8	5.9/[>99]
11 ^[g]	H-beta(19)-NH₃		-	93	87/[94]	-	2.1/[>99]
12 ^[h]	H-beta(19)			86	80[93]	-	0.6/[99]
13	Amberlyst-15 👗	4.7		97	89/[92]	0.6	0.3/[98]

[a] Reaction conditions: 1 mmol furfural, 2.2 mmol ethyl 2-mercaptoacetate, 50 mg catalyst, 6 h, 23 °C. [b] Total content of acid sites was determined by NH₃-TPD. [c] The molar ratio of Brønsted/Lewis acid sites was determined by pyridine-adsorbed FT-IR. [d] Turnover frequency TOF = (mole of dithioacetal) / [(catalyst amount × total acidity) × time]. [e] Disulfide yield and selectivity were obtained by excluding the mole of ethyl-2-mercaptoacetate reacted with furfural [f] Prepared by calcination of H-beta(19) at 700 °C for 3 h with a heating rate of 5 °C/min. [g]Treated by aq. NH₃ (0.02 M, 200 mL/g) for 1 h, washed with water, and calcined at 350 °C for 0.5 h. [h] 50 µL water was added prior to the reaction.

In order to examine the influence of acid type on product formation, H-beta(19) was modified by calcination at a high temperature of 700 °C and by treatment with aq. NH_3 , respectively. The calcination greatly increased the amount of Lewis acid sites at the expense of Brønsted acid sites in the catalyst, and the aq. NH_3 treatment enlarged the pore diameter but had little effect on the acid site distribution. In addition, both

catalysts obtained a reduced total acid contentby the treatments (entries 10-11; Figure 1). For H-beta(19)-700 a slight increase in disulfide formation and a lower dithioacetal yield compared to the parent zeolite H-beta(19) under identical conditions can be correlated with the content of Lewis acid sites, indicating the dominant role of an appropriate ratio of B/L acid sites in enhancing the selectivity toward dithioacetal. H-beta(19) treated

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with aq. NH₃ further substantiated the predominant role of Lewis acid sites on the yield of dithioacetal, as also previously reported ^[17]. In addition, dithioacetal yield (80%) decreased when adding water prior to the reaction over H-beta(19), suggesting that Lewis acid sites were inhibited by water (entry 12). When Amberlyst-15 (entry 13) - containing only Brønsted acid sites - was applied as catalyst, a slightly lower yield of dithioacetal (89%) compared to H-beta-19 (98%) was observed ^[18], demonstrating that the thioacetalization seems to take place more smoothly with the assistance of Lewis acid sites, which is consistent with the results reported for the acetalization of aldehydes with methanol ^[19].

The influence of reaction time on the thioacetalization of furfural with ethyl 2-mercaptoacetate with H-beta(19) was further studied at room temperature under solvent-free conditions, and the results are presented in Figure 2. The yield of dithioacetal significantly increased as the reaction proceeded from 0.5 to 4 h, and reached near quantitative furfural conversion after 6 h. However, when the reaction time was extending to 10 h, a small decline in dithioacetal yield was observed, and more of the byproduct disulfide (4.2%) was formed at this elevated time period. These results clearly demonstrate that dithioacetal can be synthesized in excellent yields with H-beta(19).



Figure 1. NH_3 -TPD profile (A) and pyridine-adsorbed FT-IR spectra (B) of different treated and parent H-beta(19) zeolites.



Figure 2. Influenceof reaction time on thioacetalization of furfural with ethyl-2mercaptoacetate over H-beta(19). Reaction conditions: 1 mmol furfural, 2.2 mmol ethyl-2-mercaptoacetate, 50 mg H-beta(19), 23°C.

Table 2 illustrates the effect of H-beta(19) dosage on the thioacetalization of furfural with ethyl-2-mercaptoacetate. Full conversion of furfural was achieved with a relatively large amount of H-beta(19) zeolite (70 mg) with slightly lower selectivity towards dithioacetal (entry 1) compared to when lower

amount of H-beta(19) (50 mg) was used (entry 2). Trace amounts of furfural condensation products and disulfide were observed by subjecting the sample to GC-MS analysis. In addition, partial adsorption of the product into the pore channel of the zeolite with relatively high dosage could also lead to a slight decrease in selectivity. When further reducing the catalyst amount to 30, 15 or 5 mg, no significant decrease in the selectivity towards dithioacetal was observed, although the corresponding yields were significantly descended (entries 3-5). Interestingly, comparable product yields (89-91%) could be achieved by prolonging the reaction time to 12 or 24 h with lower catalyst amounts. An experiment with a high concentration of furfural (10 mmol) was also performed (entry 6), and here an excellent yield of dithioacetal (88%) with high selectivity (91%) was also achieved.

Table	2.	Thioacetalization	of	furfural	with	ethyl	2-mercaptoacetate	using
differei	nt a	mounts of H-beta(*	(9) [[]	a]				

Entry	H-beta(19) (mg)	Time (h)	Furfural conv. (%)	Dithioacetal yield (%)	Dithioacetal selec. (%)
1	70	6	100	94	94
2	50	6	99	98	99
3	30	6	92	90	98
4	15	6/[12]	80/[96]	78/[91]	98/[95]
5	5	12/[24]	54/[97]	52/[89]	96/[92]
6 ^[b]	50	2 0	97	88	91

 [[]a] Reaction conditions: 1 mmol furfural, 2.2 mmol ethyl-2-mercaptoacetate, 23°C.
 [b] Reaction conditions: 10 mmol furfural, 22 mmol ethyl-2mercaptoacetate, 23°C.

Recyclability is an important parameter in heterogeneous catalysis to evaluate long term catalyst activity. Hence, the reusability of H-beta(19) was examined for the thioacetalization of furfural as well. After each reaction cycle, the H-beta(19) zeolite was separated by centrifugation, washed with dichloromethane and methanol, and dried at 80 °C overnight. The amount of substrates (furfural and ethyl 2-mercaptoacetate) was scaled with respect to the amount of recovered catalyst in subsequent reaction cycles, and the obtained results are compiled in Figure 3. During five consecutive reaction runs, the yield of dithioacetal gradually decreased to 85% with an almost constant selectivity of >97%. N2 adsorption-desorption isotherms and pyridine-adsorbed FT-IR spectra of fresh and recovered Hbeta(19) zeolites demonstrated a small decrease in specific surface area from 685 to 593 m²/g (Figure S4) and acidity from 1.5 to 1.2 mmol/g, which could be partially responsible for the activity loss (Figure 4). TG analysis further substantiated deactivation of active sites located in the H-beta(19) zeolite by adsorption of organic species during the reaction by comparing the weight loss of fresh and used catalyst (Figure S5). Importantly, the catalyst activity was re-established after calcination at 550 °C for 3 h after the fifth run, and the dithioacetal yield attained to 96% (Figure 3) which was almost the same as for the fresh zeolite (98%).

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Figure 3. Catalytic recycling study of H-beta(19) in thioacetalization of furfural with ethyl 2-mercaptoacetate. Reaction conditions: furfural to ethyl-2-mercaptoacetate = 1:2.2 mmol, mass ratio of furfural to H-beta(19) = 1.92:1, 6 h, 23 °C.



Figure 4. Pyridine-adsorbed FT-IR spectra of fresh and recovered H-beta(19).

Table 3. Catalytic thioacetalization of furfural with different thiols over H-beta(19)[a]



[a] Reaction conditions: 1 mmol furfural, 2.2 mmol thiol, 50 mg H-beta(19), and 23 °C. [b] Kinetic diameter σ was estimated from 0.84 × $(V_c)^{1/3}$ or 2.44 × $(T_c/p_c)^{1/3}$, V_c (cm³/mol) = critical volume, T_c (K) = critical temperature, and p_c (bar) = critical pressure.^{1fel} [c] H-beta(19) treated with aq. NH₃(0.02 M, 200 mL/g) for 1 h, followed by washing with water and calcination at 350 °C for 0.5 h. [d] 1-Butyl-3methylimidazolium chloride (100 mg) was added.

of the H-beta(19) The reaction progress catalvzed thioacetalization was followed by monitoring a reaction solution diluted with methanol by ex-situ UV-Vis in the wavelength range of 190-350 nm (Figure 5). Apparently it is seen that the substrate peaks centered at ~275 nm (furfural) and ~210 nm (ethyl 2mercaptoacetate) (Figure S6) gradually disappeared with the progression of reaction time from 0.5 to 6 h. Concurrently, the dithioacetal product peak at ~225 nm gradually increased in intensity over the reaction time, as expected. This clearly indicates that UV-Vis is a simple and effective technique to monitor the reaction progress, and the approach could likely be extended to analogues thioacetalization reactions of aldehydes.



Figure 5. Reaction progress study of thioacetalization of furfural with ethyl-2mercaptoacetate over H-beta(19) with UV-Vis spectrophotometry. Reaction conditions: 1 mmol furfural, 2.2 mmol ethyl 2-mercaptoacetate, 50 mg H-beta(19), 23 °C.

То examine the applicability of H-beta(19) zeolite thioacetalization, the substrate scope was expanded to other thiolating agents (Table 3) and aldehydes including biomassderived carboxides (Table 4). Facile transformation of both aliphatic thiols and aldehydes to the corresponding dithioacetals took place in high yields (>90%) in 2-6 h of reaction time (Table 3, entries 1-4; Table 4, entries 1-2), while disulfides was only formed in small amount (6-10%) via Lewis acid-catalyzed oxidative coupling of the thiols ^[10]. Conversely, the aromatic counterparts, especially mercaptobenzene (kinetic diameter: 6.2 Å), veratraldehyde (6.9 Å) and vanillin (6.2 Å) were more reluctant to dithioacetal formation (Table 3, entries 5-8; Table 4, entries 3-8). However, use of longer reaction time (e.g. 9-12 h) and enlargement of the pores in H-beta(19) by treatment with aq ammonia ^[17] was demonstrated to increase the dithioacetal yields (Table 3, entries 7-8), most likely as a result of more easy access and availability of the relatively steric hindered substrates to the acidic sites in the zeolite. Alternatively, coaddition of the ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM][CI]) substantially increased the yields of dithioacetals (>71%) formed by phenyl thiols and aldehydes (Table 3, entries 7-8; Table 4, entries 5-8), possibly by facilitating release of protons inside the H-beta(19) zeolite [20]. Combined, these results confirmed the necessity of having large pore size and moderate acidity with an appropriate distribution of Brønsted and Lewis acidic sites to achieve a pronounced yield of dithioacetal.

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[a] Reaction conditions: 1 mmol aldehyde, 2.2 mmol ethyl-2-mercaptoacetate, 50 mg H-beta(19), and 23 °C. [b] Kinetic diameter σ was estimated from 2.44 × $(T_d/p_c)^{1/3}$; T_c (K) = critical temperature, and p_c (bar) = critical pressure.^[16] [c]1-Butyl-3-methylimidazolium chloride (100 mg) was added.

Aldehyde acetalization is normally reversible when catalysed with strong Brønsted acids, and a great excess of alcohol relative to aldehyde is thus used to promote the formation of the corresponding acetal [14a]. For thioacetalization, the reaction pathway with Brønsted acid sites alone might involve the activation of carbonyl groups as shown in Scheme 1A. On the other hand, Lewis acid sites could simultaneously activate both aldehvde and thiol groups of the substrates ^[18b]. With respect to the present zeolite system operated by both Brønsted and Lewis acid sites, it is speculated that the reaction most likely proceed through formation of a thiocarbenium ion, followed by external addition of R-SH to give the dithioacetal (Scheme 1B). Therefore it is proposed that the dissociation of the Lewis acid centre (i.e. Al species) from the anion by a proton (Brønsted acid) could thiocarbenium ion, thus stabilize the facilitating the thioacetalization reaction in an efficient way.



Scheme 1. Plausible reaction mechanisms for catalytic thioacetalization of furfural with zeolites containing Brønsted and Lewis acid sites

Conclusions

A series of aliphatic and aromatic dithioacetals were synthesized in moderate to quantitative yields over commercial and modified zeolites at room temperature (23 °C) under solvent-free conditions. It was demonstrated that H-beta(19) showed superior catalytic performance to other employed zeolites in thioacetalization of different carbonyl compounds, including biomass-derived carboxides, to give corresponding dithioacetals in near quantitative yields (>99%). A relatively large average pore size and moderate total acidity with an appropriate Brønsted/Lewis acid site ratio of the zeolite evidently played a promotional effect for the dithioacetal formation. During recyclability the H-beta(19) exhibited a small loss of activity towards dithioacetal formation after five consecutive runs. However, the parent catalytic performance of H-beta(19) to achieve near quantitative yield of dithioacetal could be regained by a simple calcination at 550 °C, thus revealing the structural integrity of the used zeolite. In summary, commercially available zeolites are established as attractive and versatile catalysts for synthesizing dithioacetals of interest for the chemical industry.

Experimental Section

Catalyst preparation

All the commercially available zeolites in NH₄-form used throughout the study were supplied by Zeolyst International. The acidic zeolites were prepared by calcination at 550 °C in air for 6 h with a ramp of 1.2 °C/min, while the dealuminated zeolite H-beta(19)-700 was obtained by calcination at 700 °C in air for additional 6 h. To increase the pore size of the zeolite, H-beta(19) was treated with aq. NH₃ (0.02 M, 200 mL/g) for 1 h, followed by washing with water and calcination at 350 °C for 0.5 h ^[17].

Catalyst characterization

The number of acid sites present in the zeolites was measured by NH₃ temperature-programmed desorption (TPD) using an AutoChem II 2920 pore analyzer, wherein the ammonia desorption was determined every second from 100-600 °C with a heating ramp of 10 °C/min. Thermogravimetric (TG) analysis was conducted by use of a NETZSCHSTA 429 instrument under N₂ atmosphere (30 mL/L) in the temperature range of 25-600 °C with a constant heating rate of 10 °C/min. Nitrogen sorption measurements were performed at liquid nitrogen temperature on a Micromeritics ASAP 2020 instrument. FT-IR spectra of pyridine adsorbed to zeolites were measured with TPD 250 °C for 30 min with a heating ramp of 5 °C/min using a Bruker VERTEX V70v system. Before desorption of pyridine in the sample cell, the degassed mixture was heated at 100 °C to remove physisorbed pyridine.

Reaction procedure

All catalytic batch experiments were performed in an Ace pressure tube at room temperature under vigorously stirring. All reagents were obtained from J&K Scientific Ltd. (Beijing) in analytical gradeand used as received. In a general procedure, 50 mg H-beta(19), 1 mmol furfural and 2.2 mmol ethyl 2-mercaptoacetate were added into the tube and mixed. After a specific reaction time, the mixture was quenched and extracted with dichloromethane. ¹H and ¹³C NMR (nuclear magnetic resonance) spectra of the isolated furfural dithioacetal are shown in Figure S7, which were recorded on a JEOL-ECX 500 NMR spectrometer at room temperature. Liquid products were identified by GC-MS (Agilent 6850 GC system coupled with an Agilent 5975C mass detector; Figure S8), and quantitatively analyzed by GC (Agilent 6890N instrument, HP-5 capillary column 30.0 m × 320 µm × 0.25 µm).

To monitor the reaction process, a certain amount of the reaction solution was directly taken out, diluted with methanol, and subjected to UV-Vis analysis. From the first to fifth run, the H-beta(19) catalyst was separated by centrifugation, washed with dichloromethane and methanol three times, and dried at 80 °C overnight. The recovered catalyst was directly used for the next cycle under identical reaction conditions. After reuse in five consecutive reaction cycles, the H-beta(19) catalyst was regenerated by calcination at 550 °C for 3 h to remove deposited carbon residues.

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Keywords: zeolites • biomass • dithioacetal • value-added chemicals • heterogeneous catalysis

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Benign biorefinery route: Various value-added dithioacetals are catalytically synthesized in near quantitative yields from solvent-free thioacetalization of biomass-derived aldehydes at room temperature. The pronounced performance is obtained with large pore zeolites having moderate acidity with an appropriate distribution of Brønsted/Lewis acid sites. The robust and controllable catalytic system shows great potential for large-scale production of dithioacetals.



H. Li, T. Yang, A. Riisager, S.Saravanamurugan,* S. Yang*

Page No. – Page No.

Chemoselective synthesis of dithioacetals from bio-aldehydes with zeolites under ambient and solventfree conditions