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Al-Free Sn-Beta Zeolite as a Catalyst for the Selective Reduction of Carbonyl Compounds (Meerwein−Ponndorf−Verley Reaction)

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The Meerwein−Ponndorf−Verley reduction of aldehydes and ketones and Oppenauer's oxidation of alcohols (MPVO reactions) are highly selective reactions that can be performed under mild conditions.[1] The reaction mechanism involves a complex in which both reactants are coordinated to a Lewis acid metal center and a hydride transfer from the alcohol to the carbonyl group occurs.[2,3] Usually aluminum or titanium alkoxides are used as homogeneous catalysts in reductions and oxidations.[4,5] Other Lewis acid metals such as La or Zr have been used as homogeneous catalysts for MPVO reactions as well as magnesium oxides or phosphates in heterogeneous systems with moderated activity.[6−8] Recently, van Bekkum et al.[9,10] have reported that Al- and Ti-Beta zeolites are excellent catalysts for MPVO reactions showing that Lewis acid sites are the active centers of the catalyst.

The activity and selectivity of MPV catalyst can be improved by introducing the adequate Lewis acidity in the catalyst that can produce the right polarization of the carbonyl group while coordinating both the alcohol and the ketone.[11] Sn has a higher electronegativity than Ti, and may be more adequate for coordinating both reactants than Ti or extraframework Al species. Thus, a zeolite containing Sn in framework positions should be a very good catalyst for carrying out MPV reactions. We have prepared a Sn-Beta zeolite and we report here its use as new heterogeneous catalyst in the carbonyl to alcohol groups reduction by MPV process. The results obtained are compared with those reported with optimized Al- and Ti-Beta zeolites following the work by van Bekkum et al.[9] Sn-Beta shows a much higher activity with a better selectivity than any of the solid catalysts reported before.

Synthesis of Sn-Beta (93% crystallinity) was performed in fluoride medium as described previously.[11−13] ^{29}Si MAS NMR, UV−Vis, and IR spectroscopic measurements[12] (spectra not shown) and elemental and chemical analysis were performed. The physical properties of the catalysts are summarized in Table 1.

The MPV experiments were performed in a 10 mL round-bottom flask at 85−100 °C with 75 mg of catalyst and alcohol/ketone molar ratios of 60, 20, or 6, analyzing the reaction mixtures by GC-MS (5% methylphenylsilicone, 25 m length). Sn-Beta gives good activities and selectivities with secondary alcohols using cyclohexanone as the probe molecule (Figure 1). The results given in Table 2 show that Sn-Beta is more active than either Ti- or Al-Beta. Its activity and selectivity to cyclohexanol is higher than that of the most active Al-Beta catalyst, even working at low alcohol/ketone ratio.

Table 1. Physical Properties of the Catalyst Samples Tested in MPV Reduction of Ketones

catalyst	Si/Me ratio	BET surface area (m^2/g)	micropore vol (cm^3/g)	crystal size (μm)
Beta (SiO_2)		450	0.20	1.0
Sn-Beta	120	475	0.20	0.5
Sn-Beta	240	470	0.20	0.5
Ti-Beta	65	454	0.19	0.5
Al-Beta	50	484	0.19	0.3
Al-Beta	15	518	0.20	0.3
Al-Beta[a]	12			2.0

[a] Synthesized and calcined the same as van Bekkum et al.[9]

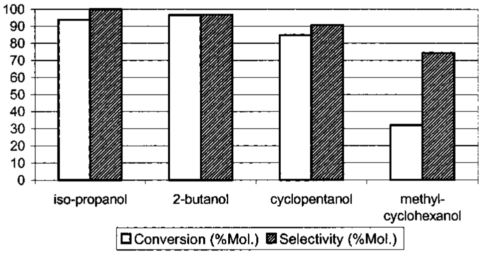

Figure 1. Selective reduction of cyclohexanone over Sn-Beta (2 wt % of SnO_2) with different alcohols (MPV reaction) (reaction conditions: 6 h of reaction, 1 mmol of substrate, 60 mmol of the alcohol, 75 mg of catalyst at 100 °C, 85 °C for 2-propanol).

Table 2. Selective Reduction of Cyclohexanone with 2-Butanol (or 2-Propanol)[a] over Sn-Beta and Other Materials (MPV Reaction)[f]

catalyst (wt % of MeO$_2$ or Si/Me ratio) type	conversion[a] (% mol) 1 h	selectivity[a] (% mol)		
		cyclohexanol	alkene	others
2% SnO_2/SiO_2	0 (0)	0 (0)	0 (0)	0 (0)
$SnCl_4 \cdot 5H_2O$[b]	0 (0)	0 (0)	0 (0)	0 (0)
Si-Beta	0 (0)	0 (0)	0 (0)	0 (0)
Sn-Beta (1% SnO_2)	64.5 (56.8)	100.0 (100.0)	0 (0)	0 (0)
Sn-Beta (2% SnO_2)	95.4 (91.0)	100.0 (100.0)	0 (0)	0 (0)
Sn-Beta (2% SnO_2)[c]	91.0	99.5	0.1	0.4
Sn-Beta (2% SnO_2)[d]	63.2	98.8	0.2	1.0
Ti-Beta (2% TiO_2)	6.1 (3.9)	100.0 (100.0)	0 (0)	0 (0)
Al-Beta (Si/Al = 50)	31.5 (15.0)	95.2 (100.0)	0 (0)	4.8 (0)
Al-Beta (Si/Al = 15)	57.5 (44.6)	95.5 (94.6)	1.4 (0)	3.1 (5.4)
Al-Beta (Si/Al = 15)[c]	23.7	97.0	0.7	2.3
Al-Beta (Si/Al = 12)[e]	80.3 (53.5)	98.4 (97.6)	0.3 (0.7)	1.3 (3.7)

[a] Values between parentheses were obtained with 2-propanol at 85 °C. [b] With 100 mg of the salt. [c] Alcohol/ketone ratio = 20/1 (mmol). [d] Alcohol/ketone ratio = 6/1 (mmol). [e] Synthesized and calcined as van Bekkum et al.[9] [f] Reaction conditions: 100 °C, 1 h of reaction, 1 mmol of substrate, 60 mmol of 2-butanol, and 75 mg of catalyst.

For this reaction the Sn atoms isolated within the framework of the Beta zeolite must be the active sites since neither SnO_2 supported on SiO_2 nor $SnCl_4 \cdot 5H_2O$ is active (see Table 2). It appears then that the reaction with Sn-Beta occurs over the tetrahedral tin in the framework of the zeolite but not on extraframework Sn in the

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Table 3. Sn-Beta Zeolite before and after MPV Reduction of Cyclohexanone: Differences between Fresh and Reused Catalysts[e]

catalyst[a]	wt % of SnO_2[b] before	after	conversion (% mol)	selectivity (% mol) alcohol	others
Sn-Beta (1% SnO_2)	1.19	1.18	64.5	100.00	0.00
Sn-Beta (2% SnO_2)	2.15	2.14	95.7	100.00	0.00
Sn-Beta (2% SnO_2)[c]	2.14	2.18	95.4	100.00	0.00
Sn-Beta (2% SnO_2)[d]	2.15	2.16	94.5	99.20	0.80

[a] Wt % of SnO_2 present in the zeolite. [b] Wt % of SnO_2 before and after reaction. [c] Zeolite used and then regenerated by calcination at 580 °C. [d] Zeolite used and then regenerated by calcination at 580 °C four times. [e] Reaction conditions: 100 °C, 1 h of reaction, 1 mmol of substrate, 60 mmol of 2-butanol, and 75 mg of catalyst.

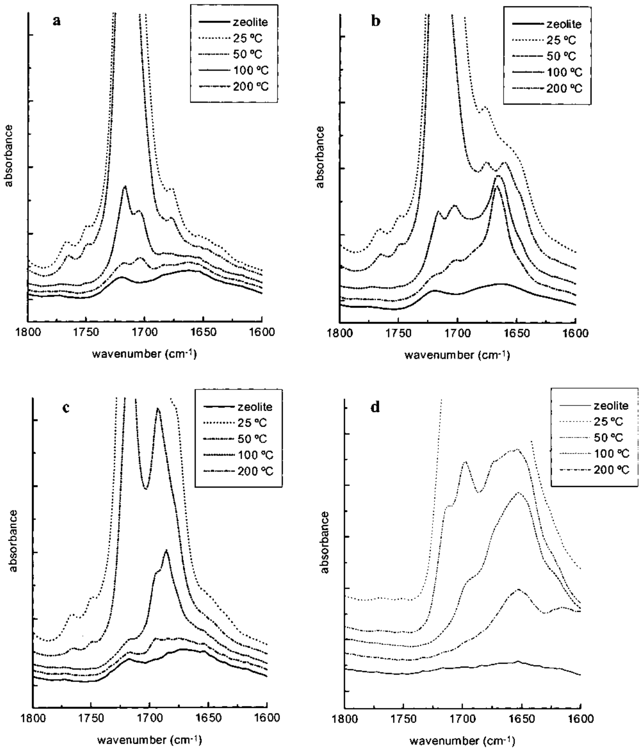

Figure 2. Infrared spectra of cyclohexanone adsorption (at 25 °C) and desorption at 50, 100, and 200 °C over Si-Beta (a), Sn-Beta (b), Ti-Beta (c), and Al-Beta (d).

form of SnO_2 (as least as large particles). This was tested by characterizing the Sn-Beta sample by ^{119}Sn MAS NMR. The spectrum of the dehydrated Sn-Beta gives a peak at −444 ppm, which is related to tetrahedrally coordinated Sn in the framework of zeolites.[11] No peak at −690 and −740 ppm corresponding to octahedrally coordinated Sn in zeolites was found. Besides, the poor activity of $SnCl_4 \cdot 5H_2O$ in homogeneous system is very good evidence that the activity in Sn-Beta should be associated to "framework" Sn and not to any leached Sn. In any case, neither leaching of Sn nor activity loss were detected, even after four reuses of Sn-Beta catalyst (Table 3).

Table 4. Selective Reduction of Alkylcyclohexanones over Sn-Beta (2 wt % of SnO_2) with Secondary Alcohols (MPVO Reaction)[a]

substrate	alcohol	conversion (% mol) ketone	selectivity (% mol) alcohol (cis/trans)[b]	CP[c]	others
4-methylcyclohexanone	2-propanol	95.8	100/0	0.0	0.0
	2-butanol	96.5	100/0	0.0	0.0
4-*tert*-butylcyclohexanone	2-propanol	97.3	99/0.5	0.0	0.5
	2-butanol	97.2	96/1.5	0.6	1.9
2-methylcyclohexanone	2-butanol	74.0	50/45.4	0.0	4.6
2-*tert*-butylcyclohexanone	2-butanol	0.0	0.0	0.0	0.0

[a] Reaction conditions: 100 °C, 6 h of reaction, 1 mmol of substrate, 60 mmol of alcohol (with 2-propanol the reaction temperature was 85 °C), and 75 mg of catalyst. [b] Ratio of cis/trans alcohols evaluated by GC and GC-MS vs standard compounds. [c] Condensation products.

IR spectra of adsorbed cyclohexanone at 25 °C and desorbed in a vacuum for 1 h at 50, 100, and 200 °C were performed over Sn-, Al-, Ti, and Si-Beta. The band associated to the carbonyl group at 1713 cm^{-1} is clearly visible on the all Si-Beta zeolite at 25 °C, but almost all adsorbed cyclohexanone is desorbed at 100 °C (Figure 2a). For the Sn-Beta (Figure 2b) a 48 cm^{-1} shift of the carbonyl band toward lower wavenumbers after desorption at 100 and 200 °C indicates the interaction between Sn^{IV} and the carbonyl oxygen. When Sn is replaced by Ti a smaller shift of the carbonyl band (32 cm^{-1}) was observed (Figure 2c) and elimination of the band occurred after desorption at 200 °C. Incorporation of Al into the zeolite involved various types of interactions with cyclohexanone since besides Lewis acidity also Brönsted acidity is present in this sample (Figure 2d).

Thus, the interaction of the carbonyl group with the Sn center is stronger than with Ti and more selective than with Al centers in Al-Beta zeolite, this being a possible reason for the higher activity and selectivity of Sn-Beta.

Shape selectivity effects of the Sn-Beta catalyst are shown with a series of alkylcyclohexanones as substrates. As was found with Ti-Beta,[10] Sn-Beta inhibits the formation of 4-alkyl-*trans*-cyclohexanols isomers instead of the cis isomers (Table 4). This is clear proof that the reaction occurs within the pores of the zeolite, and also that the tin active centers are not at the external surface of the zeolite or in solution.

In conclusion, Sn-Beta is an efficient catalyst for the MPV reduction of carbonyl groups. Its particular Lewis acidic properties as well as pore dimensions allow excellent conversion and selectivity to the corresponding alcohol, showing high stereoselectivity with alkylcyclohexanones when the transition states can be controlled by shape selectivity effects within the zeolite pores.

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Supporting Information Available: Synthesis details, XRD patterns, and ^{119}Sn-MAS NMR spectrum of Sn-β (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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