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Water-resistant solid Lewis acid catalysts: Meerwein–Ponndorf–Verley and Oppenauer reactions catalyzed by tin-beta zeolite

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Abstract

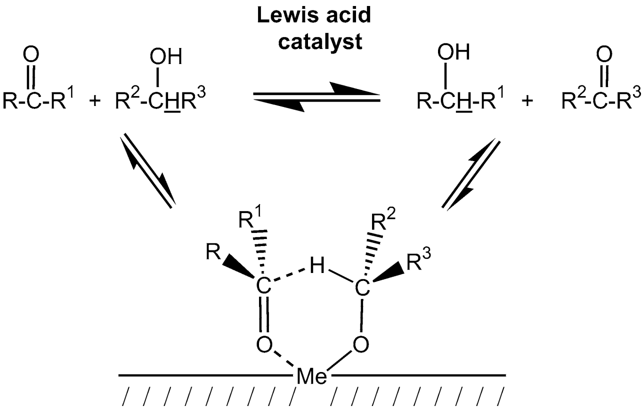
The catalytic activity of Sn-beta zeolite in the Meerwein–Pondorf–Verley (MPV) reduction of carbonyl compounds with secondary alcohols as reductants and Oppenauer oxidation of alcohols were performed with quantitative yields to the corresponding product. This catalyst exhibits a behavior not observed with Ti- and Al-beta zeolites, with excellent activity and selectivity even after four catalytic recycles, and good stereoselectivities to the thermodynamic less favorable *cis*-alcohol isomer when alkyl-cylohexanones were used as substrates. A prochiral ketone has been reduced within an enantiomeric excess close to 50% when using a chiral alcohol as the reducing reactant. Other transition metals incorporated in the beta zeolite framework (V or B) led to poor catalytic activities for this reaction. IR studies using cyclohexanone as probe molecule over beta zeolites demonstrated that the more specific Lewis acid sites in the framework of Sn-beta are responsibles for its better catalytic activity with respect to Ti- or Al-beta. The influence of the structure of the alcohol and ketone shows that reaction transition states that by size can be fitted within the pore of beta may have problems forming on the Lewis acid sites due to the shielding effect of the neighbor framework oxygen atoms. Finally, Sn-beta containing organic groups attached to the structure is able to perform the MPV in the presence of water, offering a real alternative to conventional aluminum *iso*-propoxide catalysts.

Keywords: MPV-O reaction; Tin-beta zeolite; Me-beta catalysts; Solid Lewis acid; Heterogeneous catalysis; Catalysis in aqueous medium

1. Introduction

The Meerwein–Ponndorf–Verley (MPV) reduction of aldehydes and ketones and Oppenauer's (O) oxidation of alcohols, together denoted as MPVO reactions, are considered to be highly selective reactions in which other reducible groups such as C=C double bonds and C–halogen bonds are not reacted [1]. In MPV reduction, a secondary alcohol is the reductant whereas in Oppenauer oxidations a ketone is the oxidant. It is generally accepted that MPVO reactions proceed via a transition-state complex in which the carbonyl group and the alcohol are both coordinated to a Lewis acid metal center and a hydride transfer from the alcohol to the carbonyl group occurs (Scheme 1) [2,3].

Usually, aluminum or titanium alkoxides derived from secondary alcohols are used as homogeneous catalysts in reductions [4] whereas metal *tert*-butoxides are preferred for oxidations [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].



Scheme 1. MPVO reaction pathways. R = alkyl or aryl; R^1 and R^3 = alkyl or hydrogen; Me = metal.

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Recently, Al- and Ti-beta zeolites have been reported as excellent catalysts for MPVO reactions showing that Lewis acid sites are the active centers of the catalyst [9–12]. Following this, it appears that the activity and selectivity of MPVO catalysts 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 [13]. In this sense, Sn in beta zeolite seems to be a good candidate since, on the one hand, it has a higher electronegativity than Ti, and on the other hand, it can be more adequate for coordinating both reactants than extraframework Al species. Furthermore, hydrophobic Sn-beta zeolites could be prepared that should, in principle, increase the water resistance of the catalyst. In a very recent short communication [14] we showed that the Sn-beta is indeed an excellent heterogeneous catalyst for the reduction of aldehydes and ketones to alcohols and the oxidations of alcohols to the corresponding carbonyl group by a MPVO process. The results obtained were compared with those reported with optimized Al- and Ti-beta zeolites [9], and the former shows a higher activity and better selectivity. In this work we have carried out a deep study of this system and will present that the activity of zeolite containing different transition metals for the MPVO reaction correlates well with the Lewis acid strength of the catalyst. By carrying out the reaction with alcohols and ketones of different nature and size, and using basic probe molecules with different degrees of steric hindrance, we demonstrate that in many cases the catalytic activity observed is not controlled by steric hindrance due to pore diameter of the zeolite and the diffusion of reactants or the size of the transition state into the zeolite cavity, but by the shielding effect of the framework oxygen atoms bonded to the Lewis acid. Will also show that high stereoselectivities and reasonable enantioselectivities can be achieved in some cases with this catalyst. Finally, we present modifications in catalyst design and preparation that allow use of Sn-beta in water-containing reaction media with an excellent activity.

2. Experimental

2.1. Synthesis of Sn-beta

In order to achieve hydrophobic Sn-beta samples [15], fluoride medium from gels was prepared with the following molar compositions: SiO_2:$x\,SnO_2$:0.54TEAOH:7.5H_2O:0.54HF where x was $1/120$ and $1/240$. The gel was prepared by hydrolyzing TEOS (98%, Merck) in an aqueous solution of TEAOH (35%, Aldrich), a solution of $SnCl_4 \cdot 5H_2O$ (98%, Aldrich) in water was added, and then the mixture was kept under stirring until the complete evaporation of ethanol formed upon hydrolysis of TEOS. Then HF (48%, Aldrich) was added and finally dealuminated zeolite beta seeds were added. The crystallization was carried out in 60-mL Teflon-lined stainless-steel autoclaves at 140 °C with rotation (60 rpm). After the required heating time, the autoclaves were cooled and the solids were recovered by filtration and extensively washed with distilled water. Finally, the solids were dried at 100 °C and calcined at 580 °C, and the resultant materials were analyzed by XRD showing high crystallinities.

2.2. Synthesis of Al- and Ti-beta zeolites

The Al-beta samples were obtained by hydrothermal synthesis at 140 °C in Teflon-lined stainless-steel autoclaves with rotation (60 rpm), by hydrolyzing TEOS (98%, Merck) in an aqueous solution of TEAOH (35%, Aldrich). Then a solution of metal aluminum (99.95%, Merck) dissolved in aqueous TEAOH was added and the mixture was kept under stirring until the complete evaporation of the ethanol formed upon hydrolysis of TEOS. Finally, HF (48%, Aldrich) and, optionally, dealuminated zeolite beta seeds were added. After the required crystallization time, the autoclaves were cooled and the products were filtered and extensively washed with distilled water. The Si/Al ratios were 50 and 15 as determined from chemical analysis. Finally, the solids were dried at 100 °C and calcined at 580 °C, and the resultant materials were analyzed by XRD showing high crystallinities.

The Al-beta samples containing extraframework aluminum were prepared by a careful postsynthetic treatment with calcinations of the sample in several steps as described in [9]. In the case of Ti-beta catalyst, a hydrophobic Ti-beta sample was prepared following the procedure previously described in [16].

2.3. Synthesis of B- and V-beta zeolites

The B-beta sample was prepared from a silica source (Aerosil 200, Degussa) plus boric acid (H_3BO_3) with TEAOH (35%, Aldrich) as template, by diluting 21.0 g of TEAOH with 7.9 g of water. Then, 0.42 g of boric acid was dissolved in this solution, followed by the addition of 6.0 g of silica. This reaction mixture is heated in a Teflon-lined stainless-steel autoclave at 150 °C rotated at 60 rpm for 6 days. The solid product was filtered, washed, dried at 100 °C, and then calcined at 580 °C. The XRD pattern of this sample showed the beta structure.

In the case of V-beta, 37.8 g of aqueous solution of TEAOH (35%, Aldrich) and 10.0 g silica were mixed. After 30 min a solution of $VOSO_4 \cdot H_2O$ (1.35 g) in water (5.5 g) was added and the mixture was stirred for 30 min. Finally, zeolite beta seeds were added and the gel was introduced in Teflon-lined stainless-steel autoclaves and heated at 140 °C for 12 days. The final zeolite was recovered by centrifugation, washed with distilled water, dried at 100 °C overnight, and finally calcined at 580 °C for 3 h, resulting in a solid sample with the XRD pattern of beta structure.

2.4. *Synthesis of Sn-MCM-41 material*

Sn-MCM-41 sample with approximately 10 wt% of SnO_2 was prepared in the following way. An aqueous solution of hexadecyltrimethylammonium hydroxide/bromide ($C_{16}TAOH/Br$) was mixed with a TMAOH solution (25%, Aldrich) and an aqueous solution of $SnCl_4 \cdot H_2O$ (98%, Aldrich). After homogenization, the silica (Aerosil, Degussa) was added under continuous stirring. The homogeneous gel was sealed in Teflon-lined stainless-steel autoclaves and heated at 135 °C under static conditions for 24 h. The resulting solid was filtered, washed with water, and dried at 60 °C for 24 h. The occluded organic was removed by heating the solid at 540 °C for 1 h in nitrogen flow, followed by 6 h in air. The solid obtained presents the XRD of MCM-41, surface area of 950 $m^2\,g^{-1}$, and 3.5-nm pore diameter (35 Å) and XRD pattern of MCM-41 structure (spectra not shown).

Silylation of calcined samples was carried out following [17,18].

Phase purity of the catalysts was determined by X-ray diffraction (XRD) in a Philips X'Pert MPD diffractometer equipped with a PW3050 goniometer (Cu-K_α radiation, graphite monochromator), provided with a variable divergence slit and working in the fixed irradiated area mode.

^{29}Si MAS NMR and ^{119}Sn MAS NMR were recorded at spinning rate of 5 kHz on a Varian VXR 400S WB spectrometer. Diffuse reflectance UV–visible (DRUV) spectra were recorded in a Cary 5 Varian spectrometer equipped with a "Praying Mantis" cell from Harrick.

Thermogravimetric and differential thermal analysis (TGA-DTA) were performed in a Netzsch STA 409 EP thermal analyzer with about 20 mg of sample and a heating rate of 10 $°C\,min^{-1}$ in air flow (6 $l\,h^{-1}$). Chemical composition was determined by atomic absorption in a Varian SpectrAA-10 Plus and elemental analysis in a Fisons EA1108CHN-S. Scanning electron microscopy in a JEOL 6300 microscope was used in order to know the size and morphology of the crystals. Nitrogen and argon adsorption experiments at 77 and 85 K, respectively, were carried out in a Micromeritics ASAP 2000.

2.5. *IR spectroscopic measurements*

Infrared spectra were obtained in a Nicolet 710 FTIR spectrometer using self-supported wafers of 10 $mg\,cm^{-2}$ outgassed overnight at 653 K and 10^{-3} Pa. The measurements with adsorption of cyclohexanone (and its 2-methyl and 2,6-dimethyl derivatives) at 25 °C and desorption of the organic molecule in vacuum for 1 h were performed at 50, 100, and 200 °C over selected Me-beta zeolites. First, all the water must to be removed from the zeolite. Consequently, the zeolite samples were dehydrated overnight at 400 °C in vacuum, and the first spectrum was recorded. Then the cyclohexanone was adsorbed and again an IR spectrum was taken. Afterward, the organic compound was desorbed successively at 50, 100, and 200 °C, and after each desorption an IR spectrum was recorded. The same procedure was followed for 2,6-dimethylpyridine, 2-ethylpyridine, and pyridine IR adsorption measurements, with the corresponding desorption performed at 25 and 150 °C.

2.6. *Catalytic experiments*

The experiments for the reduction of ketones with secondary alcohols (Meerwein–Ponndorf–Verley reaction) were performed in a 10-ml round-bottom flask immersed in a thermostated bath and equipped with a condenser, a thermometer, and a magnetic stirrer. Typically, 1 mmol of the substrate and 60 mmol of the alcohol were homogenized in the flask under stirring, and the mixture was heated at temperatures between 85 to 100 °C. Then, 75 mg of catalyst was added at once to the reaction mixture (time 0). Small aliquots were withdrawn from the mixture at different time intervals to follow the kinetics of the reaction. For studying the effect of catalyst and alcohol concentrations on the reaction rate, the amount of catalyst was varied between 3 and 75 mg, whereas the concentrations of alcohol were 48, 20, 9, 6, and 3 mmol.

2.7. *Oppenauer oxidations*

The oxidations of *sec*-alcohols to the corresponding ketones were carried out using 2-butanone as oxidating agent. The reactions were performed with the same equipment described above under the following reaction conditions: 1 mmol of the selected alcohol and 80 mmol of 2-butanone were mixed in the reactor at 80 °C. Then the catalyst (75 mg) was added (time 0).

2.8. *Reactions with prochiral substrates*

MPV reduction of different prochiral ketones was made in the same manner as describes above with (*S*)-(+)-2-butanol as reducing agent. The alcohol/ketone molar ratio was 80, with 75 mg of catalyst at 80–100 °C.

The reaction products were analyzed by gas chromatography in a Varian 3400 GC equipped with a capillary column (5% methylphenylsilicone, 25 m length) and a FID. Product identification was performed by GC-MS and compared with available standard compounds. The analysis of chiral products was carried out using a capillary column with chiral stationary phase (BETA-DEX 120, 30 m length).

3. Results and discussion

3.1. *Catalyst characterization*

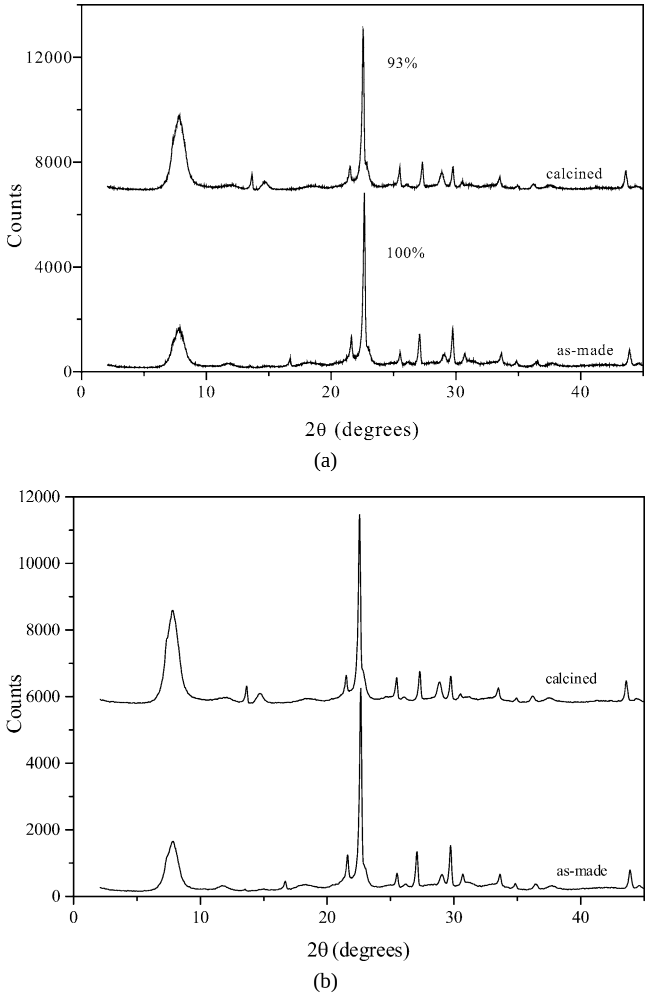
The physical properties of the catalysts are summarized in Table 1. XRD patterns of the Sn-beta (1 and 2 wt% of SnO_2), and Al- (Si/Al = 15 and 50), Ti-, V-, and B-beta samples are shown in Figs. 1 and 2, respectively. Taking as a reference a commercial beta zeolite (Zeolyst Intl) it can be said that the crystallinity of the samples is higher than 90% except for the V-beta sample in which crystallinity ranges between 80 and 90%.

Table 1
Physical properties of the catalyst samples tested in MPVO reactions

Catalyst	Si/Me ratio	BET surface area ($m^2\,g^{-1}$)	Micropore volume ($cm^3\,g^{-1}$)	Crystal size (μm)	Desorbed H_2O (wt%)[a]
Beta (SiO_2)	–	450	0.20	1.0	0.44
Sn-beta	120	475	0.20	0.5	2.93
Sn-beta	240	470	0.20	0.5	–
Ti-beta	65	454	0.19	0.5	1.80
Al-beta	50	484	0.19	0.3	4.87
Al-beta	15	518	0.20	0.3	16.79
Al-beta[b]	12	–	–	2.0	16.83
B-beta	47	460	0.19	1.0–5.0	2.63
V-beta	106	387	0.14	0.2	8.57

[a] Calculated by TG analysis.

[b] Synthetized the same as van Bekkum and colleagues and calcined with the same postsynthesis procedure [9].



(a)

(b)

Fig. 1. XRD pattern of as-made and calcined Sn-beta: (a) with 1 wt% SnO_2, (b) with 2 wt% SnO_2.

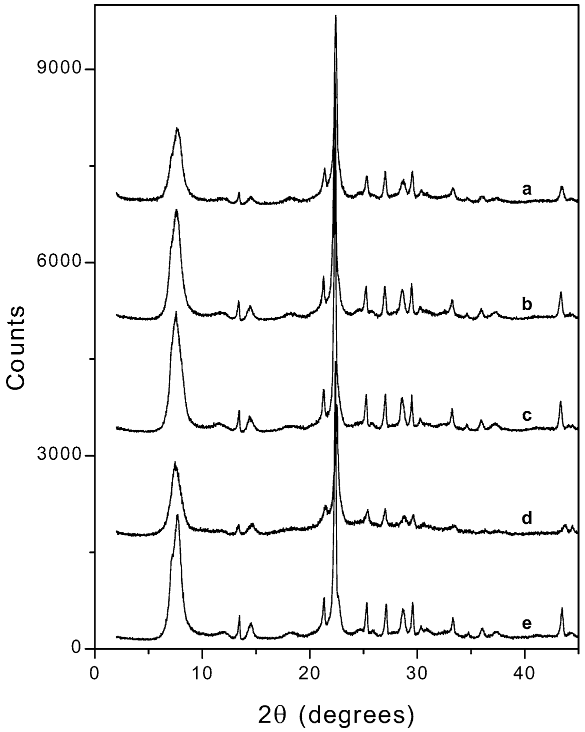


Fig. 2. XRD pattern of calcined: (a) Al-beta (Si/Al = 15), (b) Al-beta (Si/Al = 50), (c) Ti-beta, (d) V-beta, and (e) B-beta zeolites samples.

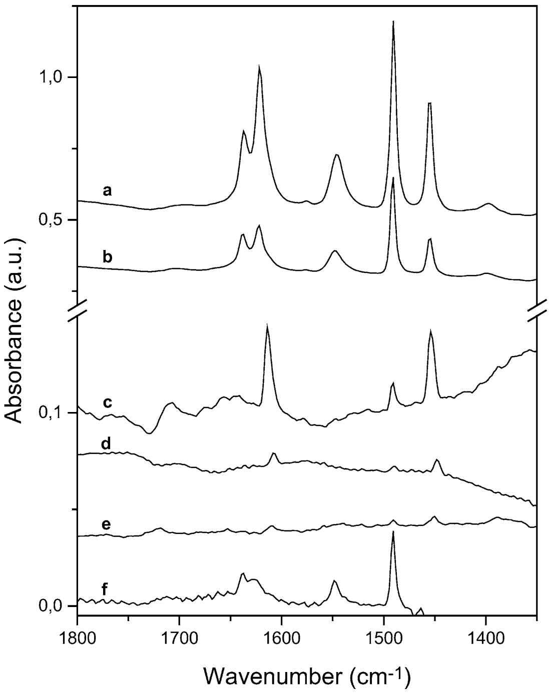


Fig. 3. Infrared spectra of pyridine adsorption (at 25 °C) and desorption at 150 °C over Al-beta (Si/Al = 15) (a), Al-beta (Si/Al = 50) (b), Sn-beta (c), Ti-beta (d), V-beta (e), and B-beta (f).

The amount and strength of Lewis acid sites of the metal-containing zeolites were compared by means of IR spectroscopy of the pyridine adsorbed and desorbed at 150 °C. The IR spectra obtained after pyridine desorption at 150 °C in the 1800–1300 cm^{-1} region are shown in Fig. 3. The appearance of the band corresponding to Lewis acid sites in the IR spectra (1452 cm^{-1}) is clearly observed for the beta samples containing Sn, Ti, and Al. However, the Sn-beta Lewis acidity exhibits a very weak character similar to Ti-beta sample [18], while Al-beta presents a large amount of strong Lewis and Brönsted acidity. When beta zeolites containing V and B were measured, negligible amounts of pyridine coordinated to Lewis acid sites were detected after desorption at 150 °C, showing similar absorbance values than the all-silicon-beta zeolite.

The incorporation of Sn in the framework of beta was checked by means of ^{119}Sn MAS NMR. Thus, a Sn-beta sample enriched with ^{119}Sn isotope was synthesized and the MAS NMR spectrum of the dehydrated Sn-beta gives a peak at -444 ppm, which is related to tetrahedrally coordinated Sn in the framework of zeolites [13]. No peak at -690 and -740 ppm corresponding to octahedrally coordinated Sn in zeolites was found. In an analogous way the UV–visible spectra of Ti- and V-beta samples show the incorporation of these metals by the detection of absorbance bands centered at 220 and 290 nm for titanium- and vanadium-containing samples, respectively.

3.2. *Catalytic activity*

The selection of the beta structure for catalyst preparation was based on the fact that this is a large-pore tridimensional zeolite that allows the incorporation of transition metals in framework positions [19], achieving in this way single isolated Lewis acid sites that can, in principle, be active for MPVO reactions. Thus, when Sn-, V-, Ti-, B-, and Al-beta zeolites were tested in the MPV reduction of cyclohexanone using 2-butanol as reductant, the results given in Fig. 4 show that yields of cyclohexanol obtained with vanadium and boron beta zeolites were much lower than the analogous Sn-, Al-, and Ti-beta catalysts. The results obtained for V- and B-beta materials are not surprising taking into account the poor Lewis acid character shown by these materials as measured by pyridine adsorption. This is probably due to the fact that boron and vanadium have a high tendency to come out from the framework during the calcinations of the samples [20,21].

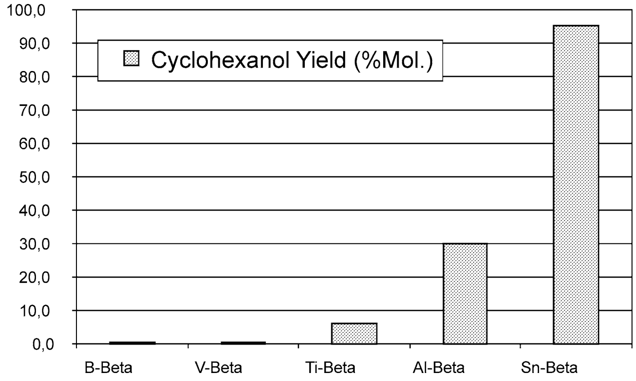


Fig. 4. Selective reduction of cyclohexanone with 2-butanol as reductant over different Me-beta catalysts (MPV reaction) (reaction conditions: 1 h of reaction, 1 mmol of substrate, 60 mmol of the alcohol, 75 mg of catalyst at 100 °C).

Table 2

Selective reduction of cyclohexanone with 2-propanol over Sn-beta and other materials (MPV reaction) (reaction conditions: 85 °C, 1 h of reaction, 1 mmol. of substrate, 60 mmol of 2-propanol and 75 mg of catalyst)

Catalyst (wt% MeO_2 or Si/Me ratio) type	Conversion (% mol) 1 h	Selectivity (% mol)		
		Cyclohexanol	Alquene	Others
–	0	0	0	0
Al(*iso*-propoxide)$_3$	100	100	0	0
Ti(*iso*-propoxide)$_3$	0	0	0	0
2% SnO_2/SiO_2	0	0	0	0
$SnCl_4 \cdot 5H_2O$[a]	0	0	0	0
Si-beta	0	0	0	0
2% SnO_2/Si-beta	0	0	0	0
Sn-beta (1 wt% SnO_2)	56.8	100.0	0	0
Sn-beta (2 wt% SnO_2)	91.0	100.0	0	0
Ti-beta (2 wt% TiO_2)	3.9	100.0	0	0
Al-beta (Si/Al = 50)	15.0	100.0	0	0
Al-beta (Si/Al = 15)	44.6	94.6	0	5.4
Al-beta (Si/Al = 12)[b]	53.5	97.6	0.7	3.7

[a] With 100 mg of the salt.

[b] Synthetized and calcined the same as van Bekkum and colleagues [9].

Table 3

Selective reduction of cyclohexanone with 2-butanol over Sn-beta and other materials (MPV reaction) (reaction conditions: 100 °C, 1 h of reaction, 1 mmol of substrate, 60 mmol of 2-butanol, and 75 mg of catalyst)

Catalyst (wt% MeO_2 or Si/Me ratio) type	Conversion (% mol) 1 h	Selectivity (% mol)		
		Cyclohexanol	Alquene	Others
–	0	0	0	0
Al(*iso*-propoxide)$_3$	100	100	0	0
Ti(*iso*-propoxide)$_3$	0	0	0	0
$TiCl_4$[a]	9.9	78.5	3.9	17.6
2% SnO_2/SiO_2	0	0	0	0
$SnCl_4 \cdot 5H_2O$[a]	0	0	0	0
Si-beta	0	0	0	0
2% SnO_2/Si-beta	0	0	0	0
Sn-beta (1% SnO_2)	64.5	100.0	0	0
Sn-beta (2% SnO_2)	95.4	100.0	0	0
^{119}Sn-beta (2% SnO_2)	95.8	100.0	0	0
Sn-beta (2% SnO_2)[b]	91.0	99.5	0.1	0.4
Sn-beta (2% SnO_2)[c]	63.2	98.8	0.2	1.0
Sn-beta (2% SnO_2)[d]	94.5	99.2	0	0.8
Ti-beta (2% TiO_2)	6.1	100.0	0	0
Al-beta (Si/Al = 50)	31.5	95.2	0	4.8
Al-beta (Si/Al = 15)	57.5	95.5	1.4	3.1
Al-beta (Si/Al = 15)[b]	23.7	97.0	0.7	2.3
Al-beta (Si/Al = 12)[e]	80.3	98.4	0.3	1.3

[a] With 100 mg of the salt.

[b] Alcohol/ketone ratio = 20/1 (mmol).

[c] Alcohol/ketone ratio = 6/1 (mmol).

[d] Zeolite after 4 recycles.

[e] Synthetised and calcined the same as van Bekkum and collegues [9].

Comparative catalytic tests between Sn-beta and other homogeneous and heterogeneous catalysts were carried out using cyclohexanone as substrate and 2-propanol and 2-butanol as reducing agents. The results given in Tables 2 and 3 clearly show that Sn-beta is a more active catalyst than either Ti-, Al-beta, $TiCl_4$, $SnCl_4$, or SnO_2, and almost as active as Al-(*iso*-propoxide)$_3$. These results indicate not

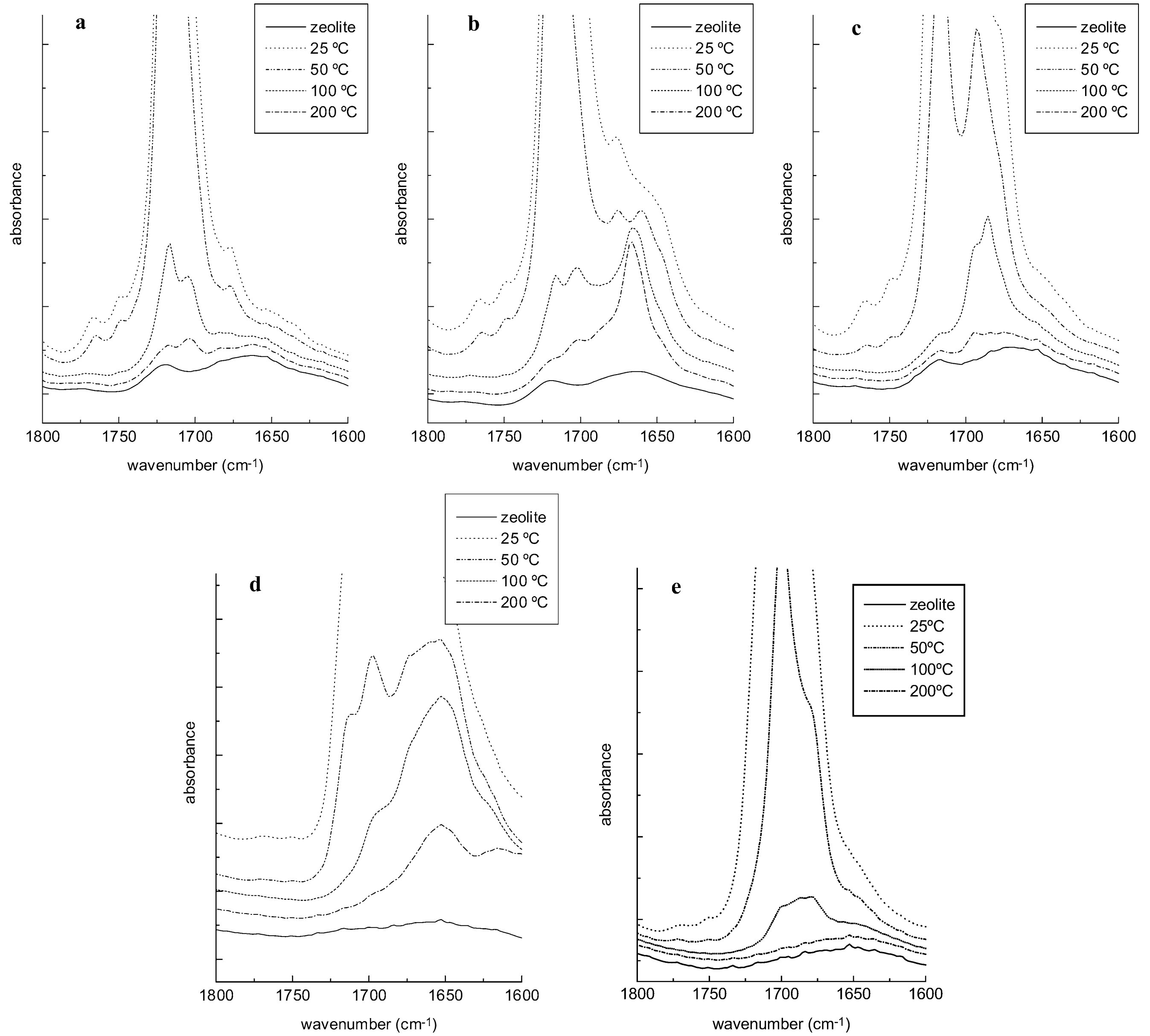


Fig. 5. Infrared spectra of cyclohexanone adsorption (at 25 °C) and desorption at 50, 100, and 200 °C over Si-beta (a), Sn-beta (b), Ti-beta (c), Al-beta (d), and V-beta (e).

only the relative good catalytic performance of Sn-beta, but also that the catalytic active sites in this catalyst are very probably the Sn atoms in framework positions. If this is so, these sites should be able to coordinate the ketone and polarize the carbonyl group. To check this, cyclohexanone has been adsorbed on the Sn-beta in the IR cell at 25 °C and then desorbed at 50, 100, and 200 °C for 1 h, while the IR spectra were recorded. The results are compared with those obtained with the other zeolite catalysts in Fig. 5. It can be seen there that the band associated to the carbonyl group at 1713 cm^{-1} is clearly visible on the pure silicon beta zeolite at 25 °C. However, in this zeolite almost all cyclohexanone has been desorbed at 100 °C (Fig. 5a), and no carbonyl bands below 1700 cm^{-1} can be detected. Identical IR spectra as for the pure silicon beta were obtained when SnO_2 was dispersed on the surface of this zeolite sample. For Sn-beta (Fig. 5b) a shift of 48 cm^{-1} of the carbonyl band towards lower wavenumbers after desorption at 100 °C occurred, indicating the formation of an adduct between the carbonyl oxygen and the tetrahedral Sn in the beta framework. This band persists even after desorption at 200 °C. When Sn is replaced by Ti a smaller shift of the carbonyl band (32 cm^{-1}) was observed (Fig. 5c) and elimination of the band occurred after desorption at 200 °C. Both observations, i.e., the smaller shift and the earlier desorption with Ti-beta, let us to conclude that the interaction of the carbonyl oxygen and the titanium was weaker than the observed for the tin. Incorporation of Al into the zeolite framework involves various types of interactions with cyclohexanone since besides Lewis acidity also Brönsted acidity is present in this sample [22] (Fig. 5d), and the presence of various broad carbonyl bands in the IR spectra could be observed. For the V-beta sample (Fig. 5e) a lower shift (< 25 cm^{-1}) of the band associated to the carbonyl group occurs and the shift disappears when temperature was increased to 100 °C.

These observations suggest that the interaction of the carbonyl group with the Sn center is stronger than with Ti and V, and more selective than with Al centers in Al-beta zeolite. These interactions are a measure of the Lewis acidity of the sites of the catalyst and would indicate that Lewis acidity in V-beta is not strong enough, and/or the amount of framework V is too small to carry out efficiently the reaction. In the case of Al-beta, even if it is catalytically active, the presence of residual Brönsted acidity catalyzes undesired reactions and decreases the selectivity to the desired products.

3.3. *Effects of the molecular structure of the alcohol*

A series of *sec*-alcohols were tested for the MPV reduction of cyclohexanone using Sn-beta as heterogeneous catalyst. As shown in Fig. 6, all the alcohols studied are reactive, though the smaller 2-propanol and 2-butanol give the best activities and selectivities for the MPV reaction. The lower activity achieved with bulkier alcohols such as cyclopentanol and 2-methylcyclohexanol cannot be due to pore diameter limitations of the zeolite since the pore diameters of beta are large enough to compile with the size of the transition state formed between cyclohexanone and the above alcohols. Therefore, steric limitations should not occur in the pore but probably occur near the Sn active site when increasing the diameter of the secondary alcohol molecule or, more precisely, when bulk substituted are present near the alcohol function owing to the shielding effect of the oxygens bonded to the Sn atom. To investigate this hypothesis, the reduction of cyclohexanone with cyclopentanol was carried out with Sn-MCM-41, which is also active for this reaction. It is clear that in the case of mesoporous molecular sieves no limitation due to pore dimensions should exist for the reaction between cyclohexanone and cyclopentanol. Thus, since Sn-MCM-41 is active for the reduction of cyclohexanone with 2-butanol but not with cyclopentanol (Table 4), we could certainly conclude that the reaction is not limited by pore dimensions. Therefore, we propose that the observations made can be due to geometrical limitations for the formation of the transition state on the Lewis acid, probably due to the presence of the framework oxygen atoms bonded to the Lewis acid site. Note that the activity of the aluminum *iso*-propoxide also decreases when the bulkier alcohols are reacted.

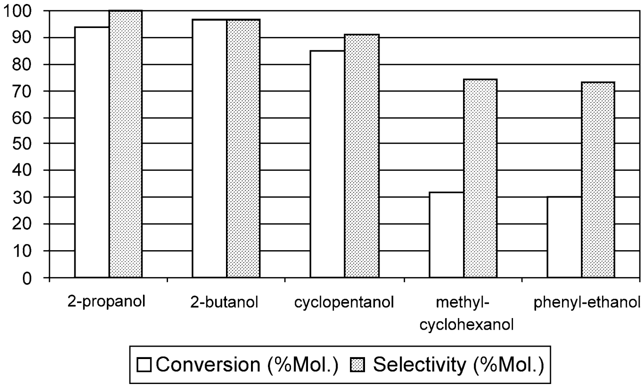


Fig. 6. Selective reduction of cyclohexanone over Sn-beta (2% SnO_2) with different alcohols (MPV reaction) (reaction conditions: 6 h of reaction, 1 mmol of substrate, 60 mmol of the alcohol, 75 mg of catalyst at 100–85 °C for 2-propanol).

Table 4
Comparative MPV reduction of cyclohexanone with selected *sec*-alcohols over Sn-beta, Sn-MCM-41, and Al(*iso*-propoxide)$_3$ (reaction conditions: 100 °C, 6 h of reaction, 1 mmol of substrate, 60 mmol of *sec*-alcohol and 75 mg of catalyst)

Catalyst (wt% SnO_2)[a]	Alcohol	Conversion (% mol)	Selectivity (% mol)	
			Cyclohexanol	Others
Sn-beta (2)	2-Butanol	98.6	100.00	0.00
	Cyclopentanol	95.5	99.08	0.72
	Me-cyclohexanol	32.0	74.40	25.60
	Phenyl-ethanol	30.0	73.22	26.78
Sn-MCM-41 (10)	2-Butanol	54.2	98.64	1.36
	Cyclopentanol	16.0	94.19	5.81
	Me-cyclohexanol	10.5	85.68	14.32
	Phenyl-ethanol	21.1	69.23	30.77
Al(*iso*-propoxide)$_3$[b]	2-Butanol	100.0	100.00	0.00
	Cyclopentanol	66.1	99.69	0.31
	Me-cyclohexanol	39.0	96.99	3.01
	Phenyl-ethanol	77.4	99.58	0.42

[a] (% SnO_2) present in the zeolite.
[b] With 100 mg of the salt (11.67 wt% of Al).

Besides the geometrical effect described above it should be noted that the presence of an aromatic ring in the phenylethanol reduces cyclohexanol yields. A similar behavior was found with others secondary aromatics alcohols as reductants when the alcoholic function is separated by one or two carbon bonds with respect to the aromatic ring. All these experimental observations let to us to conclude that presence of the electron π cloud in the aromatic alcohol competes with the OH group of the alcohol for the coordination on the Lewis center resulting in a decrease of the yield of the desired product. A similar effect is observed when using Al-(*iso*-propoxide)$_3$ as catalyst (Table 4).

3.4. *Effects of the molecular structure of the ketones*

By reacting a series of alkyl-cyclohexanones, with methyl or *tert*-butyl substituents in different positions of the ring and using 2-butanol and 2-propanol as the reducing agents, shape selectivity effects of the Sn-beta catalyst are seen. As it was found with Ti-beta [12], Sn-beta inhibits the formation of 4-alkyl-*trans*-cyclohexanol isomers but not that of the *cis*-

Table 5
Selective reduction of alkyl-cyclohexanones over Sn-beta (2 wt% SnO_2) with secondary alcohols (MPVO reaction) (reaction conditions: 100 °C, 6 h of reaction, 1 mmol of substrate, 60 mmol of alcohol[a], and 75 mg of catalyst)

Substrate	Alcohol	Conversion ketone (% mol)	Selectivity (% mol)		
			Alcohol (cis/trans)[b]	C.P.[c]	Others
Cyclohexanone	2-Propanol	96.8	100.0	0.0	0.0
	2-Butanol	98.6	100.0	0.0	0.0
	2-Butanol[d]	54.2	98.6	0.0	1.4
4-Me-cyclohexanone	2-Propanol	95.8	100/0	0.0	0.0
	2-Butanol	96.5	100/0	0.0	0.0
	2-Butanol[d]	72.4	100/0	0.0	0.0
4-*t*-Butyl-cyclohexanone	2-Propanol	97.3	99/0.5	0.0	0.5
	2-Butanol	97.2	96/1.5	0.6	1.9
	2-Butanol[d]	82.2	60/38.0	2.0	0.0
3-Me-cyclohexanone	2-Butanol	9.3	100.0	0.0	0.0
	2-Butanol[d]	33.6	99.1	0.0	0.9
2-Me-cyclohexanone	2-Butanol	74.0	50/45.4	0.0	4.6
	2-Butanol[d]	19.0	72.7/22.0	0.0	5.3
2-*t*-Butyl-cyclohexanone	2-Butanol	0.0	0.0	0.0	0.0
	2-Butanol[d]	0.0	0.0	0.0	0.0

[a] With 2-propanol the reaction temperature was 85 °C.

[b] Ratio of *cis*/*trans* alcohols evaluated by GC and GC-MS vs standard compounds.

[c] Condensation products.

[d] With Sn-MCM-41 (10 wt% SnO_2) mesoporous material as catalysts.

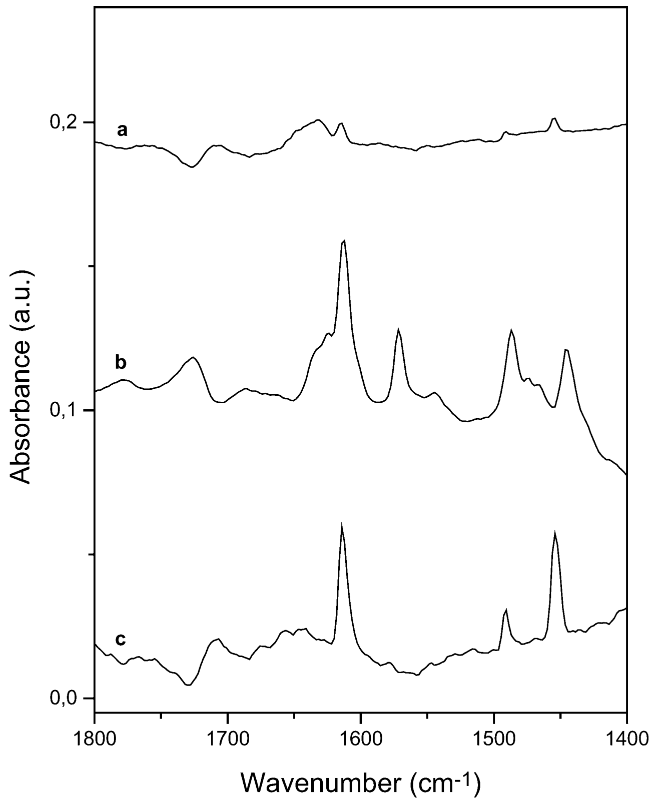


Fig. 7. Infrared spectra of aromatic amines adsorption (at 25 °C) and desorption at 150 °C over Sn-beta zeolite: (a) 2,6-dimethylpyridine, (b) 2-ethylpyridine, and (c) pyridine.

isomers (Table 5). Thus, the less favorable *cis*-isomers, *cis*-4-*tert*-butylcyclohexanol and *cis*-4-methylcyclohexanol, are obtained in very high yield with respect to the *trans*-alcohol isomers.

In the case of 2-alkyl-cyclohexanones, the proximity of the alkyl substituent to the carbonyl group induces steric hindrance near the tin active site in the transition state of the reaction. Thus, activity decreases when 2-methylcyclohexanone is reacted instead of cyclohexanone, and it is totally suppressed when the methyl is changed by the bulkier *t*-butyl substituent in the 2 position. For the 3-methylcyclohexanone, the distance between the methyl group and the carbonyl group is not as determinant as the spatial configuration (equatorial or axial) that can introduce steric effects with respect to the walls of the zeolite pore. This results in poor levels of 3-methylcyclohexanone conversion compared with 2- and 4-methyl-substitued cyclohexanones.

The importance of hindrance at the framework Lewis acid sites for alkyl-substituted rings in the vicinity of the electron donating group of the reactant molecule has been proven by adsorbing pyridine, 2-ethylpyridine, and 2,6-dimethylpyridine on the Sn-beta sample. The results presented in Fig. 7 show that while pyridine and 2-ethylpyridine are coordinated to the Lewis acids after desorption at 150 °C; 2,6-dimethylpyridine does not owing to the negative steric effect of the two methyl groups vicinal to the nitrogen atom that coordinates to the Lewis center. This hindering effect of the methyl group has been the basis for using 2,6-dimethylpyridine as probe molecule that absorbs on Brönsted but not on Lewis acid sites [23].

More specifically, when cyclohexanone, 2-methylcyclohexanone and 2,6-dimethylcyclohexanone have been adsorbed on Sn-beta in the IR cell, the results presented in Fig. 8 show that after desorption at 100 °C, only the two first reactants remain adsorbed.

From the above discussion and the results given in Table 6 we concluded that transition-state limitation is a key factor for explaining activities and selectivities found with certain carbonyl compounds. Consequently, not only the size or position of the substituent at the ring is important, but also the type of substituent (alkyl or aryl) can play a very important role in the coordination of the carbonyl group to the active site. If we compare all the substrates in Table 6 and their corresponding conversions, we can correlate the data of the cyclic or bicyclic ketones containing different substitutes with the level of transition-state limitations that those can originate. For instance, the fact that the diffusion of cyclododecanone is restricted within the pores of zeolite beta can justify the low level of conversion obtained with this compound. In the case of the norcamphor–camphor couple, the steric hindrance presented by the latest ketone due to the methyl substituents absolutely inhibits the MPV-O process.

Nevertheless, the negative resonance or conjugation effect between the carbonyl band and C=C double bond be-

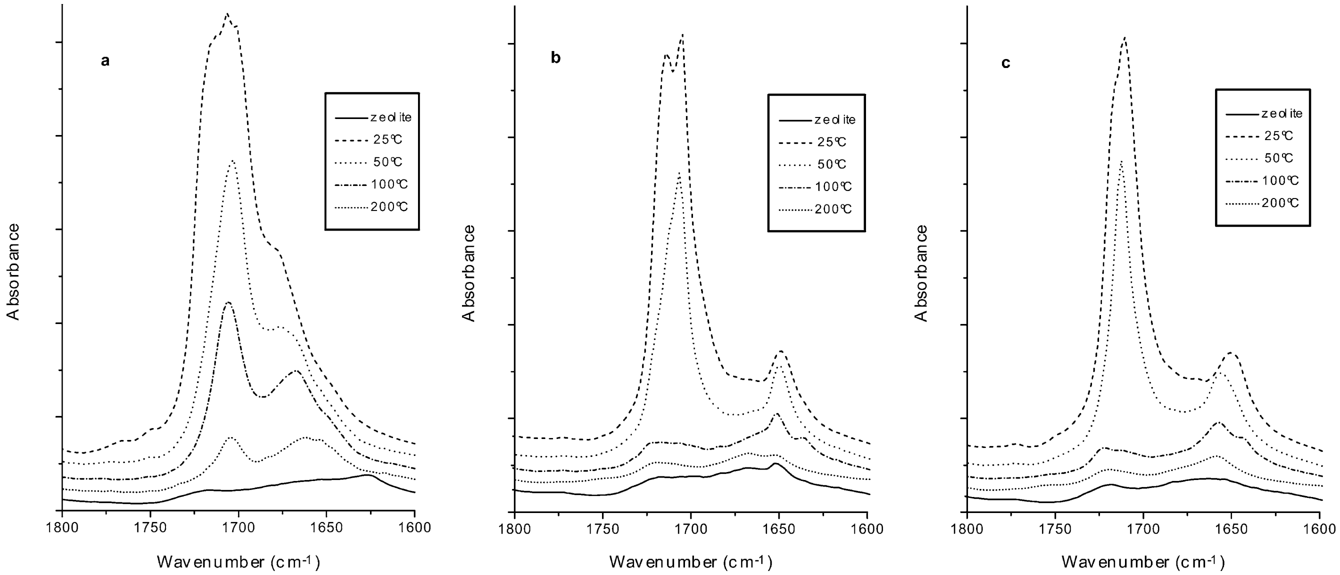


Fig. 8. Infrared spectra of alkyl-cyclohexanone derivatives adsorption (at 25 °C) and desorption at 50, 100, and 200 °C over Sn-beta zeolite: (a) cyclohexanone, (b) 2-methylcyclohexanone, and (c) 2,6-dimethylcyclohexanone.

comes very clear using cyclohexenone as substrate, taking into account the low level of alcohol yield achieved with this substrate compared with those of the above-noted cyclic ketones (Table 6).

In the case of ketones with aryl groups as substituents, the evident increase in the conversion values in the order: propiophenone < acetophenone < phenylacetone indicates that the closer the aromatic ring is to the carbonyl group, the bigger the steric effect produced. However, besides the above-noted steric impediments, the activities achieved with ketones containing aromatic groups can be influenced by other effects, such as resonance and inductive effects of the aromatic ring. Thus, the differences in conversion levels observed for the last three substrates detailed in Table 6 cannot be explained following only the steric hindrance hypothesis, suggesting that the electronic effects become more important in this case.

It must be taken into account that the interaction of the carbonyl group with the metal center leads to polarization of the carbonyl double bound enhancing the positive charge on the carbon atom and the negative charge density on the oxygen. When the aryl substituent group has an electron donor effect (positive induction effect) stabilization of the right polarization of the carbonyl double bond occurs, increasing the effect of the catalyst and increasing the conversion to the corresponding alcohol product. On the other hand, a negative inductive effect as in a *p*-metoxiphenyl substituent leads to a poor polarization of the carbonyl group and then the ketone conversion decreases. We conclude that for a given metal, zeolite catalyst steric effects at the Lewis site owing to the size of the transition state, together with factors derived from the electronic structure of the reactants, are responsible for the final conversion observed.

3.5. Stereoselectivity and chirality: Oppenauer reaction

As it can be seen in Table 7, when using a 1:1 reactant mixture of *cis*- and *trans*-4-alkyl-cyclohexanols, Sn-beta catalysts show excellent selectivities for reacting the *cis*-alcohol, with respect to the *trans* isomer owing to geometrical constraints for the transition state of the second. This is in agreement with what occurs when reducing the 4-alkyl-cyclohexanone and proves that both alcohol and ketone are coordinated to the zeolite metal site in the transition state.

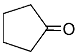
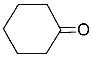
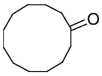
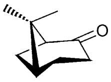
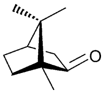
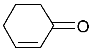
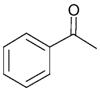
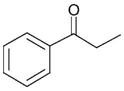
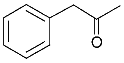
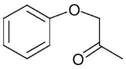
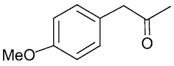
With respect to the enantioselective reduction of prochiral ketones, it was found [12] that Ti-beta can produce 34% of enatiomeric excess at 77% conversion after 20 days of reaction time when phenyl-acetone is used as prochiral ketone with (*S*)-2-butanol as reductant. We performed similar experiments with Sn-beta catalysts and we achieved 43.0% e.e. of the (*S*)-phenyl-2-propanol, at $\sim$ 70% conversion in only 4 h. At complete conversion of the phenyl-acetone (24 h) the e.e. decreases to 38.9%.

In conclusion, the combination of pore dimensions and Lewis acidity in Sn-beta zeolites affords a highly active, stereoselective and moderately enantioselective catalyst for MPVO reactions.

3.6. Stability and activity of the catalyst with water in the reaction media

One of the limitations of using aluminum *iso*-propoxide is its fast and irreversible deactivation by water. Moreover, aluminum alkoxides dispersed on siliceous MCM-41-type materials were demonstrated to be nonresistant to the presence of water traces in the MPVO reaction system [24]. In the case of zeolites, it is known that highly hydrophobic samples can be prepared. Thus, hydrophobic zeolites containing Lewis acids can be quite suited for the MPVO re-

Table 6
Selective reduction of different ketones over Sn-beta (2 wt% SnO_2) with 2-butanol (MPVO reaction) (reaction conditions: 100 °C, 6 h of reaction, 1 mmol of substrate, 60 mmol of alcohol, and 75 mg of catalyst)

Substrate	Structure	Conversion ketone (% mol)	Selectivity (% mol)		
			Alcohol	C.P.[a]	Others
Cyclopentanone		40.9	96.1	0.0	3.9
Cyclohexanone		98.6	100.0	0.0	0.0
Cyclododecanone		1.2	100.0	0.0	0.0
4-*t*-Butyl-cyclohexanone		97.2	97.5	0.6	1.9
Nopinone		12.4	80.9	0.0	19.1
Norcamphor		10.1	100.0	0.0	0.0
Camphor		0.0	0.0	0.0	0.0
Cyclohexenone		25.8	32.4	37.0	30.6
Acetophenone[b]		18.9	93.9	6.1	0.0
Propiophenone[b]		7.6	87.4	12.6	0.0
Phenyl-acetone[b]		65.2	93.2	6.8	0.0
Phenoxy-acetone[b]		82.9	96.8	3.2	0.0
p-Methoxy-phenyl-acetone[b]		2.9	0.0	0.0	100.0

[a] Condensation products.

[b] At 20 h of reaction.

Table 7
Oppenauer oxidation of 1/1 mixtures of *cis*- and *trans*-4-alkyl-cyclohexanols over Sn-beta (2 wt% SnO_2) with 2-butanone as oxidant (reaction conditions: 80 °C, 6 h of reaction, 1 mmol of substrate, 80 mmol of ketone, and 75 mg of catalyst)

Substrate	Time (h)	Conversion Alcohol (*cis*/*trans*)[a] (% mol)	Selectivity (% mol)		
			Ketone	C.P.[b]	Others
4-Methylcyclohexanol	1	8.6/1.6	100.0	0.0	0.0
	6	29.1/6.9	99.7	0.3	0.0
4-*t*-Butylcyclohexanol	1	25.0/1.0	99.5	0.5	0.0
	6	53.7/1.3	97.3	2.3	1.5

[a] Ratio of *cis*/*trans* alcohols evaluated by GC and GC-MS vs standard compounds.

[b] Condensation products.

Table 8
Effect of the H_2O addition to the MPVO activity of Me-zeolites (reaction conditions: 100 °C, 1 h of reaction, 1 mmol of cyclohexanone, 60 mmol of 2-butanol and 75 mg of catalyst)

Catalyst	TON ($\mathrm{mol\,mol^{-1}\,h^{-1}}$) water added		
	0	0.2 g	0.5 g
Ti-beta	1.2	0.7	0.7
Al-beta	7.0	0.1	0.1
Al-beta[a]	9.8	0.5	0.2
Sn-beta	109.0	17.8	3.8
Sn-beta–Sil.[b]	108.0	56.7	48.0

[a] Synthetized the same as van Bekkum and collegues and calcined with the same postsynthesis procedure [9].

[b] Silylated sample.

action when water is present, since its low water adsorption will have a lower effect on catalyst deactivation. Higher zeolite hydrophobicities should be achieved when no framework charges or defects (silanols) are present. Taking this into account, one could expect the order of hydrophobicity of our samples to be Ti-beta > Sn-beta > Al-beta. The results of adsorption–desorption of water on these samples (Table 1) show that indeed this order of hydrophobicity is the one presented above. This order of hydrophobicity corresponds well with the resistance of the catalysts to deactivation by water (Table 8).

Indeed, Ti-beta and Sn-beta retain a higher percentage of catalytic activity when water is present in the reaction media. It is noticeable that even with ~ 4 wt% of H_2O (0.2 g) in the media Sn-beta gives a higher turnover number than Ti- or Al-beta when working in absence of water (Fig. 9). Moreover the sample still retains a reasonable activity when ~ 10 wt% of H_2O (0.5 g) was present. It appears then that preparing hydrophobic metal-containing zeolites offers a possibility for preparing solid Lewis acids that can work in the presence of water.

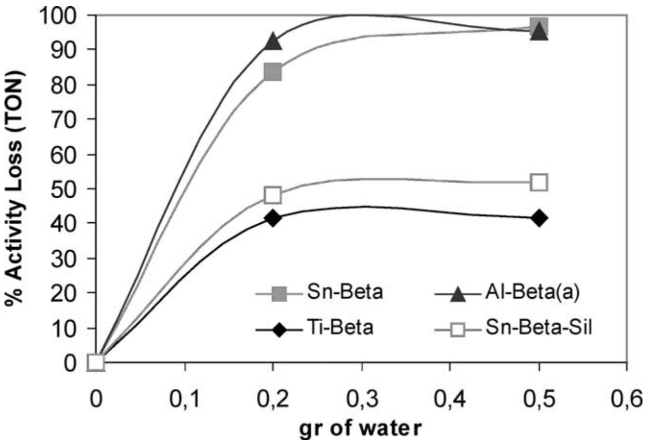


Fig. 9. Loss of activity (as % of TON loss) for different Me-beta catalysts by addition of water as poisoning agent (MPVO reaction) (reaction conditions: 1 h of reaction, 1 mmol of cyclohexanone, 60 mmol of 2-butanol, 75 mg of catalyst at 100 °C). (a) Synthetized and calcined the same as van Bekkum and collegues [9].

Thus, if catalyst hydrophobicity is an important issue in this case, we can improve such a hydrophobicity by a zeolite postsynthesis treatment that involves surface silylation [17]. When we did this using hexamethyl-di-silazane as silylating agent, a Sn-beta-Sil sample was produced that contains 1.63 wt% of organic and shows a very high catalytic activity even when ~ 10 wt% of H_2O was present in the reaction media (Table 8).

4. Conclusions

Sn-beta is an efficient catalyst for the MPV reductions of carbonyl groups and Oppenauer's oxidations of alcohols. The structure as well as pore dimensions added to its particular Lewis acid properties allows excellent conversion and selectivity to the corresponding alcohol product. Thus, the catalyst can be recycled several times and alcohol/ketone ratios as low as 6 or 3 can be used without important loss in the activities, this being of clear interest for a potential industrial application of the catalyst.

This MPVO catalyst shows good stereoselectivity an reasonable enantioselectivity for reducing a prochiral ketone with a chiral alcohol.

By studying the reactivity of alcohols and ketones with different molecular structures, it has been shown that the reaction transition states that by size can be fitted within the pore of Beta zeolite may have problems forming on the framework Lewis acid sites due to the shielding effect of the neighbor framework oxygen atoms.

The better activity shown by Sn-beta catalysts compared with the analogous Ti- and Al-beta zeolites might be attached to the adequate Lewis acidity of the tin active sites in the zeolite framework. It is possible to prepare water-resistant MPVO catalysts, by synthesizing hydrophobic zeolites. The water resistance can be further improved by postsynthesis sylilation of the zeolite. These catalysts are highly active and selective for MPVO process even in the presence of ~ 10 wt% of H_2O.

Acknowledgments

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