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Rearrangement of α -pinene oxide to campholenic aldehyde over the trimesate metal–organic frameworks MIL-100, MIL-110 and MIL-96

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ABSTRACT

The catalytic performance of porous metal–benzenetricarboxylates, such as MIL-100(Al, Fe and Cr), MIL-110(Al) and MIL-96(Al), was investigated with a combination of physicochemical and catalytic approaches in the rearrangement of α -pinene oxide to campholenic aldehyde (CA). The investigation of Lewis acidity was done by EPR and IR spectroscopy using 2,2',6,6'-tetramethyl-1-piperidinyoxyl radical and benzonitrile as the probe molecules, respectively. For Al–BTCs, both these methods showed a decrease in the amount of Lewis acid sites as follows: MIL-100 > MIL-110 > MIL-96. The reaction rate and selectivity toward CA also decreased in the same order. A relatively good correlation between selectivity toward CA and the electronegativity of the metal ion was found for isostructural MIL-100(Al, Fe and Cr). The selectivity toward CA decreased in the order: MIL-100(Al) > MIL-100(Fe) > MIL-100(Cr). The high selectivity toward CA in the presence of MIL-100 has been suggested to originate from the unique structure of this material, which favors shape selectivity.

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1. Introduction

During the past two decades, metal–organic frameworks (MOFs) have provoked great interest because of their considerable applications in adsorption and catalysis. Nowadays, catalysis by MOFs is a rapidly expanding field due to the unique textural and physicochemical properties of these materials, including a high specific surface area, the ability to control porosity by the nature of the organic ligands, the high amount and dispersity of metal ions in the framework, and the ability to control acid–base and redox properties by varying both the nature of metals and the organic ligands [1–4]. The presence of coordinatively unsaturated metal sites (CUS) in some of these MOFs allows their application in catalysis as Lewis acids. Recently, metal–benzenetricarboxylates (M–BTCs, M = Fe, Cu and Zr) were shown to be suitable as a heterogeneous catalyst for the isomerization of α -pinene oxide (PO), the

cyclization of (+)-citronellal and Diels–Alder cyclization reactions [1,3–5].

Isomerization of PO is commonly used to produce transcarveol (*trans*-carv) and campholenic aldehyde (CA), which are highly valuable ingredients for the production of flavors (Scheme 1). It is well known that the use of mild Lewis acids favors the formation of CA, while Brönsted acid sites will result in the formation of *trans*-carv and *trans*-sorbrerol (*trans*-sobr) [3,6,7]. ZnCl₂ and ZnBr₂ are the most active and selective homogeneous systems in this reaction. Zeolites, zeotype materials, and MOFs have also been applied as Lewis acids in this reaction [1,3,5,6,8].

Thus, Fe-containing M–BTCs, such as the commercial iron trimesate Basolite F-300 (Fe(BTC)), MIL-100(Fe), MIL-88(Fe) and MIL-127(Fe), have been used as catalysts with Lewis acid sites (LAS) for the rearrangement of PO to CA in the absence of solvent at 70 °C [5]. About 10% conversion of PO with 50% selectivity toward CA was obtained in the presence of these materials. Of note, the TON value for MIL-100(Fe) was comparable with that for Fe–Y zeolite and was higher than that for homogeneous ZnCl₂.

According to De Vos et al. [1], the catalytic performance of MIL-100(Fe) can be significantly changed by acid pretreatment. Acid pretreatment leads to an increase in both Lewis and Brönsted acidity. Prolonged acid pretreatment of the catalyst favors a decrease in



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Scheme 1. Products obtained in the course of PO rearrangement.

the conversion of PO and in the selectivity toward CA. The low selectivity toward CA has been attributed to the presence of the Brönsted acid groups as catalytic sites. Conversely, high selectivity toward CA has been shown in the presence of $Cu_3(BTC)_2$ [9]. The nature of the solvent affects the activity and selectivity of the reaction. Dichloroethane and toluene are the best solvents and have also been found to be the best reaction media for zeolites, Brönsted, and Lewis acids [6,7,10,11].

We can assume that M-BTCs, such as MIL-100(Cr, Fe and Al), MIL-96(Al) and MIL-110(Al), possess high selectivity toward CA, because these materials possess isolated and well-defined Lewis acid sites (LAS). Furthermore, these materials, like zeolites, possess high surface areas and unique well-defined pore openings and, therefore, have potential in heterogeneous catalysis with possible shape selectivity. Noteworthy, MIL-100(Al), MIL-96(Al), and MIL-110(Al) synthesized from identical precursor reactants, and only the pH of the starting mixture and/or the reaction time allow to control structures [12,13]. According to a significant number of studies [12,14], the structure of mesoporous MIL-100(Al), [Al₃O(OH)(H₂O)₂[BTC]·24H₂O], is assembled from trimers of μ_3 -O-bridged Al³⁺ octahedra, which are connected by BTC linkers into a large-pore framework structure. The corresponding three-dimensional framework exhibits two types of cavities. The first type of cavity is delimited by 12 pentagonal windows with a size of 5.5 Å (dodecahedral cage); the second cavity is delimited by 12 pentagonal windows and 4 hexagonal windows with a size of 8.6 Å (hexadodecahedral cage). Therefore, the porosity of MIL-100 originates from both 25 Å and 29 Å mesopores, which are accessible via 5.5 Å and 8.6 Å windows, respectively. MIL-96(Al) and MIL-110(Al) also exhibit a threedimensional framework. MIL-110(Al), with a chemical formula of Al₈(OH)₁₂{(OH)₃(H₂O)₃}[BTC]₃·42H₂O, is also a porous Al-BTC with a honeycomb topology. Its structure is built up from the connection of a new type of octahedrally coordinated aluminum octameric unit through trimesate ligands delimiting one-dimensional large hexagonal channels (16 Å) [13,15,16]. The structure of MIL-96(Al), with a chemical formula of [Al₁₂O(OH)₁₈(H₂O)₃ $(Al_2(OH)_4)[BTC]_6 \cdot 24H_2O]$, contains isolated trinuclear μ_3 -Obridged aluminum clusters and infinite chains of aluminum octahedra forming a honeycomb lattice with 18-membered rings [17]. The structure of MIL-96(Al) has three types of cages. The pore-opening diameters of these cavities are rather small and were estimated to be in the range of 2.5–3.5 Å. Previously [6,10,11,18], it was suggested that microporosity and structure of zeolites and zeotype materials are important for the reaction selectivity. We can assume that structure of Al-BTCs also may allow to control reaction selectivity toward CA. For analysis of main factors which can affect the reaction rate and selectivity for the dominant isomer, we used combination of spectroscopic and catalytic methods. Note that investigations of Lewis acidity of MOFs [19-21] and demonstration of correlations between amount of LAS and catalytic activity of MOFs [1-5,9] are rather limited or nonsystematic. The aims of this study were to developed new spectroscopic approaches for investigation of Lewis acidity of MOFs and to determine correlations between structure/Lewis acidity and catalytic activity of these M–BTCs in the rearrangement of PO to CA.

2. Experimental

2.1. Materials

α-Pinene oxide (98.0%) was purchased from Acros Organics. Octane and FeCl₃·6H₂O were purchased from Merck. Commercial dichloroethane, 2,2',6,6'-tetramethyl-1-piperidinyoxyl radical (TEMPO) (Aldrich), Al(NO₃)₃·9H₂O (98 wt.%, Junsei), 1,3,5-benzenetricarboxylic acid (H₃BTC) and 1,3,5-trimethyl-benzenetricarboxylate (Me₃–BTC, 98%, Aldrich), *ortho*-phosphoric acid (H₃PO₄, 85 wt.%, Merck), sodium hydroxide (NaOH, 4 M), nitric acid (HNO₃, 60 wt.%), iron powder (Fe⁰, 99%, DC Chemical Co.), CrO₃ (98%, Junsei), and hydrofluoric acid (HF, 48%, OCI Company Ltd.) were used without any further purification.

2.2. Synthesis of M-BTCs (M = Al, Fe and Cr)

Al-BTCs were synthesized from Al(NO₃)₃·9H₂O, 1,3,5-benzenetricarboxylic acid (H₃BTC) or trimethyl 1,3,5-benzenetricarboxylate (Me₃-BTC), sodium hydroxide (NaOH, 4M), nitric acid (HNO₃, 60%), and deionized water similar to the reported methods for MIL-100 [12,14], MIL-110 [12,15], and MIL-96 [17] under autogenous pressure at 210 °C. The reactant compositions for the desired phases are shown in Table 1. For conventional electric crystallization, the reaction mixture of 20 g was loaded in a Teflonlined autoclave and put in a preheated electric oven. The crystallization times for MIL-100(Al) and MIL-110(Al) were 2 h, while for MIL-96(Al) this was 2 days. MIL-100(Fe) was synthesized according to a reported procedure [22]. In this case, iron powder, H₃BTC, hydrofluoric acid (HF, 48%), HNO₃ and water were mixed, then the mixture was transferred to a Teflon-lined autoclave and heated in an electric oven at 160 °C for 12 h. MIL-100(Cr) was synthesized similar to a reported method [23]. For the preparation of MIL-100(Cr), chromium (VI) oxide, HF, H₃BTC, and H₂O were mixed and then the reactant mixture was transferred to a Teflon-lined autoclave and heated in a conventional electric oven for 4 days at

Table 1
The reaction conditions of synthesis of M–BTC materials.

	Reaction conditions Reaction mixture (mol.%)	
MIL-100(Cr)	CrO ₃ :HF:H ₃ BTC:H ₂ O 1.0:1.0:0.67:265	220 °C, 4 days
MIL-100(Fe)	Fe ⁰ :H ₃ BTC:HF:HNO ₃ :H ₂ O 1.0:0.67:2.0:0.6:277	160 °C, 12 h
MIL-100(Al)	Al(NO ₃) ₃ ·9H ₂ O/Me ₃ -BTC/H ₂ O/HNO ₃ 1.0:0.67:255:1.26	210 °C, 2.5 h
MIL-110(Al)	Al(NO ₃) ₃ .9H ₂ O/Me ₃ -BTC/NaOH/H ₂ O 1.0:0.5:2.3:310	210 °C, 2.5 h
MIL-96(Al)	Al(NO ₃) ₃ ·9H ₂ O/H ₃ BTC/H ₂ O 1.0:0.67:400	210 °C, 2 days

a temperature of 220 °C. After crystallization for a fixed period of time, the autoclaves were cooled to room temperature and the solid products were recovered by filtration. The solid products were washed with a water/ethanol mixture (1:1 v/v) and stirred in ethanol at 60 °C for 5 h to remove the unreacted H₃BTC or Me₃–BTC. After filtration, the purified solids were dried overnight at 100 °C. The designation of the samples, chemical composition, and textural data of the M–BTC samples are presented in Table 2.

2.3. Instrumental measurements

The porous structure of the materials was determined from the adsorption isotherm of N₂ at -196 °C using Micromeritics ASAP 2400 equipment. The specific surface area (S_{BET}) was calculated from the adsorption data over the relative pressure range between 0.05 and 0.20. The total pore volume (V_{Σ}) was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The X-ray diffraction patterns were measured on a X-ray diffractometer (ThermoARL) with Cu K α (λ = 1.5418 Å) radiation.

To study Lewis surface acidity by benzonitrile (PhCN), Al–BTC samples were pretreated within the IR cell at 200 °C for 2 h, then samples were exposed to saturated PhCN vapors at room temperature. The FT-IR spectra of PhCN adsorbed on the catalysts were recorded every 10 min up to saturation by PhCN. FT-IR spectra were recorded on a Shimadzu FTIR-8300S spectrometer in the range of 400–6000 cm⁻¹ with a resolution of 4 cm⁻¹.

The ESR spectra were measured with an ERS-221 EPR spectrometer working in the X-band ($\nu = 9.3$ GHz). The EPR spectra were recorded at 20 dB attenuation with a typical microwave power of 3 mW. All samples for EPR measurements were prepared using "break seal" techniques. For this, 0.015–0.025 g of Al–BTC was added into a quartz cell and evacuated at 200 °C until an absolute pressure of 20 mTorr was reached and maintained for 3 h. After cooling to room temperature under vacuum conditions, 1 ml of 3.2×10^{-5} – 3.2×10^{-4} M TEMPO solution in toluene was added to the sample. The EPR spectra were recorded at room temperature. The concentration of TEMPO was calculated after the calibration procedure (error ± 10%).

2.4. Catalytic tests

The isomerization of PO was carried out at 30 °C in a glass reactor equipped with a magnetic stirrer. Dichloroethane was used as the solvent. Before the reaction, all catalysts were activated at 200 °C for 4 h in order to remove the adsorbed water. Then, 25 or 75 mmol of PO, 2 ml of dichloroethane, 10 mmol of octane (internal standard), and 5 mg of the catalyst were added to the reactor. At different time intervals, aliquots were taken from the reaction mixture and analyzed. A mass spectrometer (Shimadzu GCMS QP-2010 Ultra with a GsBP1-MS column, 30 m × 0.32 mm, thickness 0.25 µm) was used to identify the reaction products. A gas chromatograph (Agilent 7820) with a flame ionization detector on an HP-5 capillary column was used to analyze the products quantitatively.

Table 2

Chemical composition and textural data of M-BTC materials.

	Al content (wt.%)	Textural data			
		$S_{BET}(m^2/g)$	$V_{\Sigma} (\mathrm{cm}^3/\mathrm{g})$	V_{μ} (cm ³ /g)	
MIL-100(Cr)	-	1462	0.77	0.31	
MIL-100(Fe)	-	1296	0.81	0.34	
MIL-100(Al)	15.9	1486	0.70	0.38	
MIL-110(Al)	17.3	679	0.58	0.27	
MIL-96(Al)	17.6	315	0.14	0.13	

3. Results and discussion

3.1. Investigation of Lewis acidity

3.1.1. Analysis of Lewis acidity by IR spectroscopy

The Lewis acidity of Al–BTCs with different structures, such as MIL-110(Al), MIL-110(Al) and MIL-96(Al), was studied by the adsorption of PhCN as a probe molecule in combination with FT-IR spectroscopy. PhCN as a soft base is usually used as a probe molecule for the identification of the LAS of oxides and zeolites [24,25]. Fig. 1A shows the spectra of PhCN adsorbed on Al–BTCs. The band at 2178 cm⁻¹ was observed in the IR spectra of all samples. This band can be assigned to the interaction between the non-bonding electrons of PhCN and electron-deficient Al ions (LAS), which exist in the structure of Al–BTCs dehydrated at 200 °C. The results show that the intensity (absorbance/ ρ) and integral intensity (S_q) of the band at 2178 cm⁻¹ depend on the structure of the Al–BTC. Integral intensity (S_q) decreased as follows:

MIL - 100(Al) > MIL - 110(Al) > MIL - 96(Al)

Therefore, the amount of LAS decreased in this order.

3.1.2. Analysis of Lewis acidity by EPR spectroscopy

Information on the nature and concentration of LAS (for example, Al_{CUS}^{3+}) on the surface of solids can be obtained with the spin probe method, which is a powerful tool to investigate coordinatively unsaturated sites in zeolites and oxides [26,27]. Using this method, we tried to determine the concentration of surface LAS (Al_{CUS}^{3+}) by sample titration with TEMPO radicals. It is well known [26–28] that the TEMPO molecule reacts with only one acid site; therefore, the concentration of acid sites can be calculated by the maximum amount of radicals adsorbed (until the EPR spectrum of the TEMPO radical appears in the solution).

The EPR spectra of TEMPO complex adsorbed on MIL-100(Al) are shown in Fig. 2. An anisotropic EPR signal (A) appeared when TEMPO adsorbed and interacted with the LAS (Fig. 2). On MIL-100(Al) sample, an EPR spectrum with g = 2.006 was observed. For TEMPO complexes with Lewis acids, the superfine splitting constant was equal to 35 G. These values and the shape of the EPR signal show that the distribution of TEMPO molecules was random in MIL-100(Al). The same values of g and the superfine splitting constant were obtained for MIL-110(Al) and MIL-96(Al).

The experimental data on the estimation of the amount of LAS in MIL-100(Al), determined by the EPR method, are given in Table 3. According to the experimental data, the amount of LAS (Al_{CUS}^{3+}) was 0.98 mmol/g for MIL-100(Al) calcined at 200 °C. This value is lower than that determined by IR spectroscopy using CO (2180–2220 cm⁻¹) as the probe molecule (about 1.7 ± 0.2 mmol/g) [21]. This difference is probably related to the difference in the size of the probe molecule, which affects the accessibility of LAS. Of note, to explain the correlation between the acid–base properties and catalytic activity of the catalyst, it is preferable if the size of the probe molecule is comparable with the size of the reagents and reaction products.

The results of the EPR investigation of the Lewis acidity of Al–BTCs with different structures are presented in Table 3. The amount of Lewis acid sites decreased in the order: MIL-100(Al) > MIL-110(Al) > MIL-96(Al). These data are in agreement with those obtained by IR spectroscopy using PhCN as the probe molecule. TEMPO adsorption resulted in changes in the EPR spectra as well as in the IR spectra of coordinatively bonded PhCN (band at 2178 cm⁻¹). The quite good linear correlation between the EPR and IR spectroscopy data shown in Fig. 1B indicates that EPR spectroscopy can be used to analyze the Lewis acidity on the surfaces of M–BTCs.



Fig. 1. (A) IR spectra of PhCN adsorbed on MIL(Al) samples and (B) correlation between the amount of LAS (integral intensity of band at 2178 cm⁻¹) and the amount of TEMPO adsorbed on MILs.



Fig. 2. EPR spectra of TEMP in toluene $(3.2\times10^{-5}\,mol/l)$ and TEMPO complex adsorbed on MIL-100(Al) (0.98 mmol/g and 0.05 mmol/g).

 Table 3

 Amount of LAS in Al-BTC materials determined by EPR spectroscopy using TEMPO as probe molecule.

	Al _{total} (mmol/g)	Al ³⁺ _{CUS} (mmol/g)	Al_{CUS}^{3+}/Al_{total} (mol/mol)
MIL-100(Al) MIL-110(Al)	5.89 6.40	0.98 0.62	0.17 0.10
MIL-96(Al)	6.52	0.14	0.02

The correlation between the Al–BTC type and the amount of Lewis sites could be explained by the difference in the textural properties, i.e. the specific surface area (S_{BET}) and porosity (V_{Σ}) (Table 2). Another explanation may be related to differences in the structures of Al–BTCs. Thus, these structural features of the Al–BTCs are known to affect their adsorption properties; thus, the amount of CO₂ adsorbed on MIL-100(Al), MIL-110(Al) and MIL-96(Al) was 20 mmol/g, 16 mmol/g and 6.5–9.3 mmol/g [29,30], respectively. Based on these data, we also can expect that the structure, i.e. the size of the cavities and channels, affects the

adsorption values of the probe molecules (TEMPO and PhCN). The effect of the Al–BTC structure on the adsorption values of the probe molecules can be estimated from the effective density of Al_{CUS}^{3+} , i.e. the amount of LAS based on the surface area and the micropore volume. These values for MIL-100(Al) and MIL-110(Al) are larger compared to MIL-96(Al), which is in good agreement with the differences in their structures. Therefore, the experimental data clearly show that the amount of LAS in these three Al–BTCs depends on their structure and textural properties.

3.2. Catalytic performance of metal-benzenetricarboxylates

Particular interest was given to a study on the catalytic properties of isostructural M–BTCs [31], such as MIL-100(Al), MIL-100(Fe), and MIL-100(Cr). The empirical formula of MIL-100 is $3D-{M_3O(X)(H_2O)_2[BTC]_2} \cdot nH_2O$, where M = Cr, Fe and Al; and X = OH, F; BTC = benzene-1,3,5-tricarboxylate (BTC). The textural properties of the MIL-100 samples are shown in Table 2. Note that the textural properties of the MIL-100(Al, Cr, Fe) materials are not much different from one another and similar to previously reported results [32].

According to the experimental data in Fig. 3, the conversion of PO was 96–98% after 30 min of reaction in the presence of the MIL-100 samples. The heterogeneous character of the reaction was confirmed in special experiments for the most active sample, MIL-100(Al). The MIL-100(Al) sample was filtered off after 15 min of reaction in dichloroethane at 30 °C, where the conversion of PO was about 75%. Then, the filtrate without the catalyst was stirred at 30 °C for 30 min. After removing the catalyst, further conversion of PO (76%) was negligible, providing evidence of heterogeneous catalysis.

One can see from Table 4 that selectivity toward CA also depends on the type of metals used to form the MIL-100 structure; the selectivity decreased in the following order:

 $MIL - 100(Al) > MIL - 100(Fe) > MIL - 100(Cr) \label{eq:mill}$

At the same time, the yield of *trans*-carv changed as follows:

 $MIL-100(Cr) > MIL-100(Al) \sim MIL-100(Fe)$

Rustad et al. [33] estimated the intrinsic acidity of Al(III), Cr(III), and Fe(III) μ_3 -hydroxo functional groups from *ab initio* electronic structure calculations. It was found that =Fe₃OH and =Al₃OH groups have nearly the same intrinsic acidity, while ~Cr₃OH groups are significantly more acidic. The order of selectivity



Fig. 3. Kinetic curves of isomerization of PO over MIL-100(Al), MIL-110(Al), and MIL-96(Al) (reaction conditions: 25 mmol PO in 2 ml dichloroethane, 5 mg catalyst, 30 $^{\circ}$ C).

toward *trans*-carv is in agreement with the order of intrinsic acidity of Al(III), Fe(III), and Cr(III) (Table 4). It is well known that the electronegativity of ions (X_i) is proportional to Lewis acidity, which is a parameter of the electron-withdrawing ability of the metal ion [34,35]. The value of X_i was calculated from the oxidation state of the ion (Z) and the Pauling electronegativity (X_o) using the following equation [36]:

$$X_i = X_0 (1 + 2Z) \tag{1}$$

The relatively good correlation between the parameter X_i and the yield of CA is shown in Fig. 4. The yield of CA decreased steadily with the parameter X_i . This interdependency can be explained by the inductive effect of the metal ions on Lewis acidity in the solids. Note that X_i has been used very often to characterize the acidity and catalytic activity of solids [37,38].

The high yield of CA shows that the MIL-100 samples possess LAS accessible to reactant molecules. The effect of LAS on the selectivity toward CA was demonstrated by De Vos et al. [1] in the isomerization of PO over MIL-100(Fe). Both the conversion and selectivity toward CA decreased after acid pretreatment of MIL-100(Fe), which was explained by the formation of Brönsted acid sites in the structure of MIL-100(Fe). Dhakshinamoorthy et al. [5] investigated the isomerization of PO in the absence of a solvent over a series of Fe–BTCs, including MIL-100(Fe). About 22% conversion of PO with 45% selectivity toward CA was obtained in the presence of MIL-100(Fe) at 70 °C for 6 h. MIL-100(Fe) was found to exhibit about two times greater conversion compared to Fe(BTC). Note that the catalytic properties of Fe(BTC) are similar to those of Al(OH)(BTC).

Table 4				
Isomerization	of PO	over	M-BTC	mat



^a Reaction conditions: 25 mmol PO in 2 ml dichloroethane, 5 mg catalyst, 30 °C, 30 min.



Fig. 4. The relationship between electronegativity of the metal ions (X_i) and yield of CA in the isomerization of PO over isostructural M–BTCs (the yield of CA was determined by GLH; reaction conditions: 25 mmol PO in 2 ml dichloroethane, 5 mg catalyst, 30 °C, 30 min).

Strong differences were observed in PO isomerization in the presence of Al–BTCs with different structures (MIL-110(Al), MIL-110(Al), and MIL-96(Al)). Conversion of PO and selectivity toward CA decreased in the order MIL-100(Al) > MIL-110(Al) > MIL-96(Al) (Fig. 3 and Table 4). It is well known that LAS favor the formation of CA [3,7]; therefore, it is reasonable to suggest that the catalytic properties of Al–BTCs are determined by Lewis acidity. Fig. 5 shows the effect of the concentration of LAS determined by EPR and IR spectroscopy (see Section 3.1) on the reaction rate and selectivity toward CA are proportional to the total amount of LAS.

We can suggest that distribution of LAS in structure of Al–BTCs can be also important for activity and selectivity of the reaction. This effect was revealed from the change of TON calculated using the following equation:

$$TON = moles of PO consumed/moles of LAS_{CUS}$$
(2)

TON decreased in the order: MIL-96(Al) > MIL-110(Al) > MIL-100(Al). This order may point that surface density of LAS_{CUS} in structure of MIL-96(Al) is higher than that in MIL-110(Al) and MIL-100(Al). Interestingly, high surface density of LAS_{CUS} does not favor the high selectivity toward CA.

Another explanation for the correlation between the Al–BTC type and the catalytic properties may be the difference in the structure of these three Al–BTCs, which can affect the reagents accessibility to active sites (see Section 1). For optimal catalytic activity, the active sites should be freely accessible to reagent



Fig. 5. Dependence of the reaction rate and selectivity toward CA on the integral intensity of the band at 2178 cm⁻¹ (\bigcirc) and the amount of TEMPO adsorbed on MILs (\blacksquare) (reaction conditions: 25 mmol PO in 2 ml dichloroethane, 5 mg catalyst, 30 °C).

molecules, preferably via large channels or cavities. The effect of the structure on selectivity toward CA was observed in the presence of Al-MSU-S_{FAII} (Si/Al 70) [10] and Ti-BEA zeolites [11]. It was suggested that the rearrangement of PO to CA occurs within the micropores of the zeolites. The high selectivity toward CA was a result of (i) LAS, (ii) the transition state shape selectivity induced by the pore structure of the zeolite and (iii) the impact of the solvent, which should favor low intraporous concentrations of PO. Thus, dichloroethane as a non-polar solvent yielded a low intraporous PO concentration due to the hydrophobic nature of Ti-Beta and led to high selectivity toward CA. Based on this approach, the high selectivity, in the presence of mesoporous MIL-100, very likely arose from the unique structure, i.e. the 29 Å supercages that are tetrahedrally connected via \sim 9 Å windows, which are large enough to allow the free passage of PO and the reaction products. Threedimensional connectivity of the supercages will greatly increase the ease of molecular transport through the crystals.

4. Summary

The effect of Lewis acid sites on the catalytic properties of M–BTCs, such as MIL-100(Al, Fe, and Cr), MIL-110(Al) and MIL-96(Al), were studied in the isomerization of PO. The investigation of Lewis acidity was done by EPR and IR spectroscopy using TEMPO and PhCN as the probe molecules, respectively. Both these methods showed a decrease in the amount of LAS in the order MIL-100(Al) > MIL-110(Al) > MIL-96(Al).

It was shown that the rearrangement of PO to CA in the presence of all materials proceeded in dichloroethane at 30 °C. The catalytic activity and selectivity of the Al–BTCs significantly depend on the structure of the Al–BTCs and the amount of LAS, and decreased as follows: MIL-100(Al) > MIL-110(Al) > MIL-96(Al). The investigation into the catalytic properties of isostructural M–BTCs based on the structure of MIL-100 showed that the selectivity toward CA depends on the type of metal that forms the MIL-100 structure and decreased in the order: MIL-100(Al) > MIL-100(Fe) > MIL-100(Cr). This order is in agreement with the electronegativity of the metal ion. It was suggested that the high selectivity toward CA in the presence of MIL-100s arises from the unique structures that allow free passage of PO and the reaction products into 29 Å supercages via 9 Å windows, which favors shape selectivity.

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