

EXPERIMENTAL EVIDENCE FOR A DUAL SITE MECHANISM IN Sn-BETA AND Sn-MCM-41 CATALYSTS FOR THE BAEYER-VILLIGER OXIDATION

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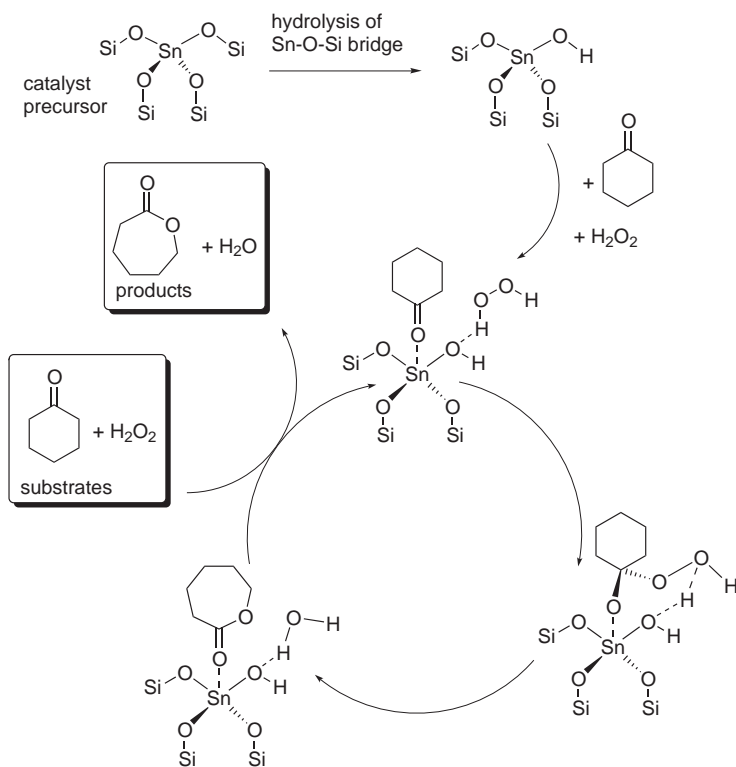
It is postulated that the catalytic active centre in Sn-Beta and Sn-MCM-41 zeolites for Baeyer–Villiger oxidations involves not only the framework Sn sites but also an associated “basic” oxygen that stabilises the reaction transition state through hydrogen bonding. The presence of these “basic” sites has been studied by cross-polarization MAS NMR $H \rightarrow Sn$, and by carrying out the condensation of ketones with malononitrile. The reaction proceeds highly selectively and the reactivity of the substrates corresponds to that of the ketones in the Baeyer–Villiger oxidation with hydrogen peroxide, catalysed with tin-containing molecular sieves.

Keywords: Heterogeneous catalysis; Knoevenagel-type condensation; Malononitrile; Ketones; Sn-Beta; Sn-MCM-41; Zeolites; MAS NMR spectroscopy.

Isolated tin sites incorporated into a siliceous matrix have been introduced as heterogeneous Lewis-acid sites capable of catalysing organic reactions such as the Baeyer–Villiger reaction^{1,2}, the intramolecular carbonyl-ene cyclisation of citronellal to isopulegol³ or the Meerwein–Ponndorf–Verley and Oppenauer redox reactions^{4,5}. In all these reactions, the reactant is activated through the coordination and polarization of a carbonyl group. On the other hand, since materials where Sn is coordinated by four Sn–O–Si bonds show Lewis acidity and are able to adsorb the ketone but have little activity for catalyzing the Baeyer–Villiger reaction, we can postulate that this reaction requires a pair of sites, i.e., the Sn to activate the ketone and an adjacent weakly basic site (an oxygen associated to a Sn–OH bond) to adsorb and activate H_2O_2 by a hydrogen bond. If we take this into account, then the reaction mechanism may be described as in Scheme 1. There, in the first step, cyclohexanone is coordinated to the Lewis-acid tin centre, as established before^{1,2}, and the second centre should bind to a hydrogen peroxide molecule building up the “loaded complex” (Scheme 1). In the corre-

sponding spatial arrangement the oxygen atom to be inserted is placed on the line of approach for the nucleophilic attack of the activated carbonyl group. Oxygen transfer and rearrangement are the next steps, followed by product desorption.

We have tried to get direct spectroscopic evidence for the $(\text{SiO})_3\text{Sn-OH}$ centre, by cross-polarization $\text{H} \rightarrow {}^{119}\text{Sn}$ MAS NMR spectroscopy. The associated problem is the small number of Sn-OH groups that makes it difficult to distinguish the signal from the background noise. Nevertheless, the NMR results indicate the possibility of the existence of Sn-OH groups, and, there-



SCHEME 1

Mechanism of the Baeyer-Villiger oxidation of cyclohexanone with hydrogen peroxide catalysed by Sn-Beta. In the catalyst precursor one Sn-O-Si bridge has to be hydrolysed to form the active species. Cyclohexanone coordinates to the Sn centre and hydrogen peroxide is hydrogen-bonded to the adjacent oxygen atom. Both molecules form a perhydrate or Criegee intermediate that rearranges to the lactone and water products. Both products have to be substituted by new substrate molecules to regenerate the initial "loaded complex"

fore, of the presence of the "basic" and more flexible oxygen associated to the Sn-OH hydroxyl. Thus, and in order to get more evidence of the presence of this "basic" coordination site, we decided to carry out a typical base-catalysed reaction, i.e., the condensation of ketones with malononitrile which requires only weak basicities. This type of reaction has been often used to characterise basic sites of solid materials⁶, and has been successfully performed with ordered aminoalkylated silicas⁷, tetraalkylammonium hydroxide immobilized on MCM-41⁸, ammonia-grafted FSM-16⁹, hydrotalcites¹⁰ and many others. Certainly, all these materials involve stronger basic sites than Sn-containing molecular sieves with the $(\text{SiO}_2)_3\text{Sn-OH}$ centres. However, a combination of the Lewis-acid tin sites with an adjacent weak basic site with good hydrogen bonding ability may be a valuable catalytic system for these Knoevenagel reactions. Indeed, it has been reported that the product of interaction of acid and basic sites of aluminium oxide is able to catalyse the reaction, although with a high amount of catalyst (350 wt.%)¹¹. Only half of the amount of catalyst was needed when $\text{AlPO}_4\text{-Al}_2\text{O}_3$, a material with similar characteristics, was used¹². Herein we report on the application of Sn-Beta and Sn-MCM-41 molecular sieve in the condensation of ketones with malononitrile and, thereby, add further experimental evidence of a hydrogen bonding site near the tin-Lewis acid centre.

EXPERIMENTAL

All reagents were purchased from Aldrich or Acros and used without further purification. GC analyses were carried out with a HP 5890 gas chromatograph equipped with a 25 m HP-5 column. GC-MS analyses for the identification of products were carried out with an Agilent Technologies 6890N apparatus coupled with a mass selective detector network. ¹H NMR spectra were recorded with a Bruker spectrometer at a frequency of 300 MHz and ¹³C NMR spectra at a frequency of 75 MHz.

Synthesis of Molecular Sieves

Sn-Beta zeolite was synthesized according to a literature procedure^{2,13}. The Sn content (2.0 wt.% as SnO_2) was determined by AAS. After calcination at 580 °C for 3 h, the zeolite was highly crystalline, and no peaks of SnO_2 were found by XRD. Nitrogen adsorption experiments on the calcined Beta samples gave an isotherm very similar to that of pure silica Beta with a micropore volume of $0.21 \text{ cm}^3 \text{ g}^{-1}$ and BET surface areas of $450\text{--}475 \text{ m}^2 \text{ g}^{-1}$.

The Sn-MCM-41 sample was synthesized by the following procedure¹⁴. An aqueous solution of hexadecyltrimethylammonium hydroxide (C_{16}TAOH) was mixed with a tetramethylammonium hydroxide solution (25%, Aldrich) and an aqueous solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (98%, Aldrich). After homogenisation, the silica (Aerosil, Degussa) was added under continuous stirring. The final composition was the following: 1 SiO_2 :0.16 C_{16}TAOH :0.26 TMAOH:

0.040 SnCl₄:24.3 H₂O. 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 recovered by filtration, washed and dried at 60 °C for 24 h. The occluded organics were removed by heating the solid at 540 °C for 1 h in a flow of N₂, followed by 6 h in air. The solid obtained presents a typical XRD pattern of the MCM-41 structure. The tin content was 10 wt.% as SnO₂ (AAS).

General Procedure for the Condensation with Malononitrile

In a glass flask 14 mmol of ketone, 14 mmol of malononitrile, 100 mg of naphthalene as internal standard, 100 mg of the catalyst and, optionally, 2.00 g of toluene were mixed. The reaction mixture was heated to 100 °C and the progress was followed by withdrawing aliquots periodically and analysing them by gas chromatography. Products were characterised by GC-MS and for some cases by NMR spectroscopy.

3a: MS, m/z (%): 146 (57) [M]⁺, 55 (100), 92 (30), 105 (35), 118 (29), 131 (56), 145 (62).

3b: MS, m/z (%): 132 (100) [M]⁺, 67 (65), 77 (48), 78 (28), 104 (66), 105 (43), 131 (75).

3c: MS, m/z (%): 160 (38) [M]⁺, 41 (52), 55 (46), 69 (100), 132 (42), 145 (53), 159 (45).

3d: MS, m/z (%): 160 (84) [M]⁺, 55 (75), 69 (44), 106 (51), 132 (72), 145 (91), 159 (100).

3e: MS, m/z (%): 160 (87) [M]⁺, 41 (39), 56 (43), 69 (100), 132 (83), 145 (86), 159 (69).

3f: MS, m/z (%): 174 (63) [M]⁺, 56 (54), 73 (48), 119 (73), 132 (44), 159 (100), 173 (91).

3g: MS, m/z (%): 202 (1) [M]⁺, 56 (5), 57 (100), 58 (5), 145 (14), 146 (5), 187 (9).

3h: MS, m/z (%): 134 (41) [M]⁺, 42 (93), 56 (84), 79 (76), 93 (100), 105 (76), 106 (60).

3i: MS, m/z (%): 174 (4) [M]⁺, 39 (8), 41 (37), 53 (5), 69 (100), 70 (5), 159 (9).

3j: MS, m/z (%): 176 (1) [M]⁺, 55 (60), 57 (80), 70 (61), 120 (39), 122 (100), 147 (28).

RESULTS AND DISCUSSION

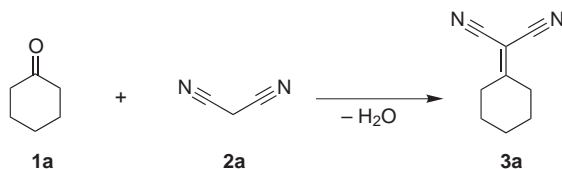
Cyclohexanone (**1a**) was mixed with equimolar amounts of malononitrile (**2a**) and heated to 100 °C. From Table I it can be seen that Sn-MCM-41 as well as Sn-Beta is able to catalyse this reaction. For Sn-MCM-41 the reaction was complete after 6 h, cyclohexylidenemalononitrile (**3a**) being the only observed product (Table I, entry 2). The reaction can be accelerated by adding toluene as solvent and thus the reaction time shortened to 2 h (Table I, entry 1). With Sn-Beta and toluene, the reaction reaches only a conversion of 46% within 6 h (entry 5). This is quite surprising since for the Baeyer-Villiger oxidation Sn-Beta was found to be intrinsically more active than Sn-MCM-41 where the substrate can diffuse without steric constraints. However, these geometrical limitations seem to exist for the condensation products that involve a ring with an exo-double bond bearing other substituents. This rigid system should have diffusion problems within the narrow channel system of Beta zeolite with a pore diameter of 0.6 to 0.7 nm but not within MCM-41 (3.5 nm).

Without any catalyst or with the parent system, i.e., all-silica MCM-41, only a conversion of ~10% is obtained under the same reaction conditions

(Table I, entries 3 and 4). Thus, we can associate most of the catalytic conversion to the presence of Sn. Since some of the Sn can also be present as SnO₂, we have measured the activity of SnO₂ supported on Si-Beta; the conversion was only 7% (Table I, entry 7). These results clearly show that tin has to be incorporated in the siliceous matrix and that has also been the condition for the Baeyer–Villiger reactivity of tin centres as Lewis acids¹.

Consequently, the principal and first action of the catalyst in this condensation should be the coordination of the ketone substrate to the tin centre (Scheme 2). However, an attack of malononitrile onto the activated carbonyl group from the homogeneous phase is unlikely since the reacting carbon atom has no free electron pair to make a new carbon–carbon bond, and no strong basic sites are assumed to be present in the reaction mixture. Interestingly, when only the carbonyl group is activated as it is the case with Brønsted acid sites of Al-Beta, the condensation with malononitrile is

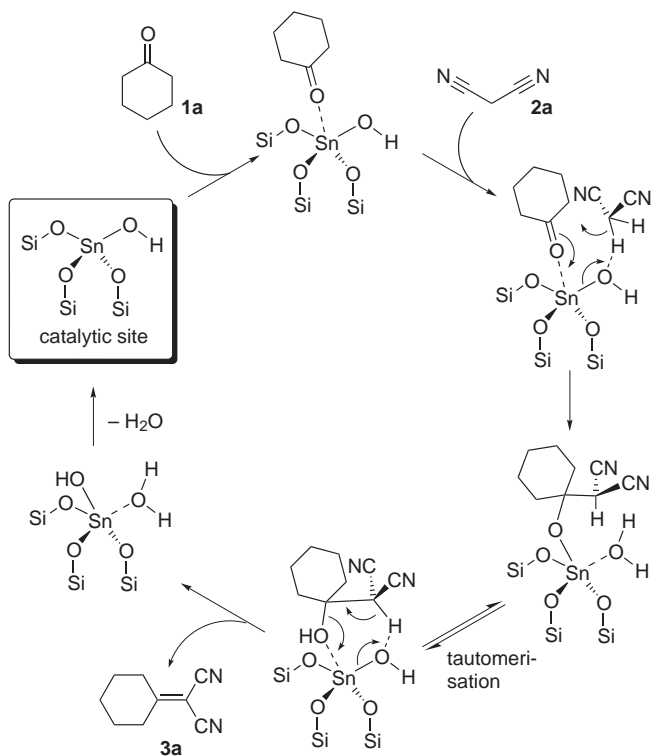
TABLE I
Condensation of cyclohexanone (**1a**) with malononitrile (**2a**) catalysed with different molecular sieves



Entry	Catalyst	Solvent	Time, h	Yield, %	Selectivity, %
1	Sn-MCM-41	toluene	2	99	99
2	Sn-MCM-41	–	6	99	99
3	MCM-41	–	6	12	99
4	–	–	6	10	99
5	Sn-Beta	toluene	6	46	99
6	Si-Beta	toluene	6	4	99
7	Si-Beta/SnO ₂	toluene	6	7	99
8	Sn-Beta ^a	toluene	6	2	99
9	Al-Beta ^b	toluene	6	10	10 ^c

^a Sn-Beta calcined in the absence of any water to avoid the formation of the (SiO)₃Sn–OH centres. ^b Synthesized in a fluoride medium; Si/Al ratio 100. ^c Main product is the aldol condensation product in 80% selectivity.

observed only as side reaction (uncatalysed reaction) and the aldol condensation of two cyclohexanone molecules is the main reaction pathway but reaching only low conversion levels (Table I, entry 9). In agreement with this, when Sn-Beta was calcined in a different way to avoid the formation of the $(\text{SiO})_3\text{Sn}-\text{OH}$ centres, and to produce a material with, almost essentially, Sn framework centres coordinated to four framework silyloxy groups, then no catalytic activity is observed (Table I, entry 8). We have therefore to conclude that the presence of the Sn-Lewis acid is not sufficient and a Sn-OH group, where malononitrile can be activated, is also required. Therefore, in the tin-containing molecular sieves, instead of activation of malononitrile by deprotonation, malononitrile can be coordinated by hydrogen bonding with the oxygen of the Sn-OH, and the reaction may



SCHEME 2





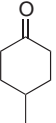
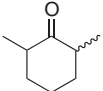
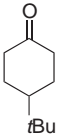
Proposal of the mechanism of the condensation of cyclohexanone (**1a**) with malononitrile (**2a**) catalysed with tin-containing molecular sieves

proceed in a cyclic process involving 6 atoms and 3 electron pairs as depicted in Scheme 2. Subsequent tautomerisation followed by a second cyclic electron shift liberates product **3a** and produces the water molecule. This is a plausible mechanism for the reaction and a further indication of a hydrogen-bonding (weakly "basic") site adjacent to the tin centre. It should be noted that the weak acid-base pairs present in solid catalysts have been shown to be highly efficient catalysts for aldol condensation reactions¹⁵.

Several other cyclic ketones **1b–1g** were chosen for the condensation with malononitrile (**2a**) in the presence of the Sn-MCM-41 catalyst. It can be seen that the relative activity of different substrates is similar to that in the tin-catalysed Baeyer–Villiger oxidation² (Table II). The reactivity of cyclopentanone (**1b**) is slightly lower than that of cyclohexanone (**1a**) in both types of reactions. In the Baeyer–Villiger oxidation, better results (higher conversion, the same reaction time) have been observed for the 4-substituted derivatives than for unsubstituted cyclohexanone² (**1a**). Indeed, in the condensation with malononitrile, 4-*tert*-butylcyclohexanone (**1g**) is converted almost completely after 3 h, versus 6 h for cyclohexanone (Table II, entries 1 and 7). In the 4-methylcyclohexanone case (**1e**), only 2-h reaction time is necessary (Table II, entry 5). In contrast, 2,6-dimethylcyclohexanone (**1f**) requires more than 24 h for full conversion (entry 6) and also 2-methylcyclohexanone (**1c**) is converted more slowly than one would expect. This is probably due to the fact that the tin centres are embedded in channel walls and the methyl substituents make the approach and coordination of the carbonyl group difficult. As it has also been observed for the Baeyer–Villiger reaction, aromatic ketones (such as propiophenone) are not converted at all. Similar activities for the Baeyer–Villiger reaction of cyclic ketones with hydrogen peroxide and the condensation of cyclic ketones with malononitrile indicate a similar catalytic action of the tin site in activation of the ketones in the two reactions. It is interesting to note that while linear ketones do not perform well in the Baeyer–Villiger oxidation catalysed with tin-containing molecular sieves, they react in the condensation with malononitrile (Table III). Certainly, their reaction times are longer than those of the cyclic ketones, and up to 24-h reaction time, as in the case octan-3-one, are required (**1j**; Table III, entry 3). The linear ketone that is converted fastest is alkenone **1i** which has the ketone group in position 2. It seems that the longer are the substituents at the carbonyl group, the longer is the reaction time. Analogous results have been obtained in the epoxidation of olefins and oxidation of alcohols with H₂O₂ and *tert*-butylhydroperoxide using Ti-zeolite catalysts¹⁶. These results were

TABLE II

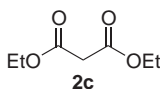
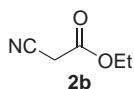
Reaction times, yields and selectivities for the condensation of malononitrile with cyclic ketones **1a–1g** catalysed with Sn-MCM-41. (The values in parentheses were obtained without catalyst.)

Entry	Substrate		Time, h	Yield, %	Selectivity, %	Conversion ^a , %
1		1a	6	99 (10)	99 (90)	42
2		1b	6	93 (0)	98	32
3		1c	6	86 (13)	98 (90)	47
4		1d	4	92 (2)	99 (39)	–
5		1e	2	93 (3)	99 (95)	46
6		1f	24	85 (0)	98	–
7		1g	3	95 (4)	99 (90)	54

^a Conversion of the ketone in the Baeyer–Villiger oxidation in *tert*-butyl methyl ether as solvent after 7-h reaction time; taken from ref.²

attributed to geometrical constraints in approach of the reactant towards the Ti centres in the zeolite framework.

Whereas the ketone substrate can be varied, the CH-acid compound cannot be replaced as in the classical Knoevenagel reactions. There, ethyl cyanoacetate (**2b**) or diethyl malonate (**2c**) often replace malononitrile (**2a**).



However, when compounds **2b** or **2c** were reacted with cyclohexanone in the presence of Sn-MCM-41, no conversion could be detected. A possible explanation can be the competitive adsorption of the ester functionalities on the Lewis-acid tin sites, which then become blocked for the ketone activation. Indeed, for the Baeyer-Villiger oxidation of cyclohexanone, this type of competitive adsorption and inhibition of the catalyst has been demonstrated. The presence of the lactone product clearly decreased the initial rate of the reaction.

TABLE III

Reaction times, yields and selectivities for the solvent-free condensation of malononitrile with linear ketones **1h–1j** catalysed with Sn-MCM-41. (The values in parentheses were obtained without catalyst.)

Entry	Substrate		Time, h	Yield, %	Selectivity, %
1		1h	8	81 (1)	98
2		1i	7	91 (11)	99 (99)
3		1j	24	84 (5)	98 (98)

In summary, we have shown here that tin-containing zeolites are able to catalyse the condensation of ketones with malononitrile. Since the catalyst lacks strong basic sites, it appears that the pair formed from Sn and the associated hydroxyl group (Sn–OH), where the oxygen is weakly basic and flexible, can activate both cyclohexanone and malononitrile. If this is the case, it looks reasonable that in the Baeyer–Villiger oxidation, Sn activates the ketone increasing the density of positive charge on the carbon of the carbonyl group, while the nucleophilicity of H₂O₂ is increased by a strong hydrogen bonding with the weak basic oxygen of the hydroxyl group in the Sn–OH.

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REFERENCES

1. Corma A., Nemeth L. T., Renz M., Valencia S.: *Nature* **2001**, *412*, 423.
2. Renz M., Blasco T., Corma A., Fornés V., Jensen R., Nemeth L.: *Chem. Eur. J.* **2002**, *8*, 4708.
3. Corma A., Renz M.: *Chem. Commun.* **2004**, 550.
4. Corma A., Domine M. E., Nemeth L., Valencia S.: *J. Am. Chem. Soc.* **2002**, *124*, 3194.
5. Corma A., Domine M. E., Valencia S.: *J. Catal.* **2003**, *215*, 294.
6. Weitkamp J., Hunger M., Ryma U.: *Microporous Mesoporous Mater.* **2001**, *48*, 255.
7. MacQuarrie D. J., Jackson D. B., Tailland S., Utting K. A.: *J. Mater. Chem.* **2001**, *11*, 1843.
8. Rodriguez I., Iborra S., Corma A., Rey F., Jordá J. L.: *Chem. Commun.* **1999**, 593.
9. Inaki Y., Kajita K., Yoshida H., Ito K., Hattori T.: *Chem. Commun.* **2001**, 2358.
10. Climent M. J., Corma A., Iborra S., Epping K., Veltz A.: *J. Catal.* **2004**, *225*, 316.
11. Texier-Boullet F., Foucaud A.: *Tetrahedron Lett.* **1982**, *23*, 4927.
12. Cabello J. A., Campelo J. M., Garcia A., Luna D., Marinas J. M.: *J. Org. Chem.* **1984**, *49*, 5195.
13. Valencia S., Corma A. (to UOP): U.S. 5 968 473, 1999; *Chem. Abstr.* **1999**, *131*, 301204.
14. Corma A., Navarro M. T., Renz M.: *Chem. Commun.* **2001**, 2190.
15. Climent M. J., Corma A., Fornés V., Guil-Lopez R., Iborra S.: *Adv. Synth. Catal.* **2002**, *344*, 1090.
16. Corma A., Esteve P., Martínez A.: *Appl. Catal., A* **1996**, *143*, 87.