

## Nanocrystalline ZnO for *Knoevenagel* Condensation and Reduction of the Carbon-Carbon Double Bond in Conjugated Alkenes

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A novel efficient and eco-friendly nanocrystalline ZnO catalyst was used for the *Knoevenagel* condensation and for the reduction of C=C double bonds at room temperature in the absence of solvents.

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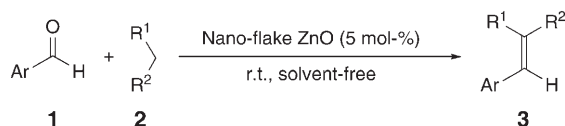
**Introduction.** – Recently nanocrystalline inorganic oxides gained interest because of their different topical characteristics [1–6]. Having variable properties depending on the size of the particles, the inorganic oxides present enormous opportunities. Nanocrystalline semiconducting II–IV metal oxides have been efficiently used as gas sensors and photocatalysts, whereas the catalytic properties of these materials are poorly explored [7–9]. Undoubtedly, one of the most important semiconductor materials is zinc oxide (ZnO). ZnO is a versatile smart material that has key applications as catalysts [10], sensors, piezoelectric transducers [11], transparent conductors [12], and surface-acoustic-wave devices [13]. Nanometer-sized particles of ZnO have very different physical and chemical properties compared with bulk material. When used as catalysts, their catalytic activity is expected to be enhanced not only because of their increased surface area, but also because of the changes of surface properties such as surface defects.

Control over the synthesis of monosubstituted malononitriles (= propanedinitriles) has been a challenging problem in organic chemistry. The most general and direct route to monosubstituted malononitriles is the alkylation of malononitrile, but this method generally produces various amounts of disubstituted malononitriles by over-alkylation when malononitrile is the limiting agent. Indeed, symmetrically disubstituted malononitriles can be efficiently prepared in this manner [14]. Keeping the alkylating agent to a minimum causes the product to be contaminated with significant amounts of unreacted malononitrile, which must be separated from the desired monosubstituted malononitrile [15]. More selective methods for the synthesis of monosubstituted malononitriles follow a two-step reaction sequence. The first step is a *Knoevenagel* condensation between malononitrile and a ketone or aldehyde [16–20]. The intermediate alkylidenedinitrile is reduced in a second step to afford the desired monosubstituted malononitrile [21–24].

*Knoevenagel* condensations (*KC*) [16][17] which are one of the most important C–C bond forming reactions have been widely used in the synthesis of important intermediates or products for perfumes [25], pharmaceuticals [26], calcium antagonists [27], and polymers [28]. Thus, the development of new synthetic procedures for *KC* has

attracted the attention of organic chemists. Recently, various methodologies have been developed for *KC* [16–20]. However, there still remains a need to develop a more efficient method, particularly in view of the disadvantages associated with some of the reported procedures such as the requirement of solvent, additional reagents, heating, long reaction times, costly and moisture-sensitive catalysts, special apparatus, *etc.* While designing a new catalyst, we thought that the use of a more effective electrophilic activating agent should accelerate the overall reaction rate, and a metal oxide, in particular nanocrystalline ZnO, which is composed of both *Lewis* acidic and *Lewis* basic sites [29], might be an ideal candidate for a closer inspection (*Scheme 1*).

Scheme 1. Knoevenagel *Condensation Catalyzed by Nano-Flake ZnO*. For R<sup>1</sup>, R<sup>2</sup>, and Ar, see Table 2.



**Results and Discussion.** – Initially, various ZnO crystals (commercial ZnO (CM-ZnO), nano-flake ZnO (NF-ZnO) (20–30 nm) [30], and nano-particle ZnO (NP-ZnO) ( $35 \pm 5$  nm)) [31] were screened in the *KC* between 4-chlorobenzaldehyde (**1e**; Ar = 4-Cl-C<sub>6</sub>H<sub>4</sub>) and malononitrile (**2**; R<sup>1</sup> = R<sup>2</sup> = CN) (*Scheme 1* and *Table 1*). Among the ZnO samples screened in the *KC*, the NF-ZnO under solvent-free conditions was found to be superior to the other ZnO in terms of yield of product **3e** (Ar = 4-Cl-C<sub>6</sub>H<sub>4</sub>, R<sup>1</sup> = R<sup>2</sup> = CN) and reaction time; this fast transformation did not require any heating.

Table 1. Knoevenagel *Condensation Catalyzed by Different Crystallites of ZnO* (0.004 g) of 4-Chlorobenzaldehyde (**1e**; Ar = 4-Cl-C<sub>6</sub>H<sub>4</sub>; 1 mmol) and Malononitrile (**2**; R<sup>1</sup> = R<sup>2</sup> = CN; 1 mmol) at 25°

Catalyst	Solvent	Time	Yield [%] <sup>a)</sup>
NF-ZnO	none	10 min	98
NP-ZnO	none	90 min	86
CM-ZnO	none	3 h	10 <sup>b)</sup>
NF-ZnO	CH <sub>2</sub> Cl <sub>2</sub>	3 h	43
NF-ZnO	MeCN	3 h	40

<sup>a)</sup> Yield of isolated **3e** (Ar = 4-Cl-C<sub>6</sub>H<sub>4</sub>, R<sup>1</sup> = R<sup>2</sup> = CN). <sup>b)</sup> The yield was increased by raising the temperature to 80° for 6–7 h.

To widen the scope, NF-ZnO was tested in the *KC* of various benzaldehydes **1a–1e** with activated methylene compounds **2**; the resulting products **3a–3o** were formed in excellent yields (*Table 2*).

Spurred by the success of *KC*, the reduction of some activated conjugated alkenes **3**, which were synthesized by *KC*, was studied by using nanomaterials (*Scheme 2*). To the best of our knowledge, most investigated reductions of C=C bonds in conjugated alkenes proceed much better in protic solvents such as alcohols, water, and/or aqueous EtOH, and such reductions do not occur under solvent-free conditions [21–24].

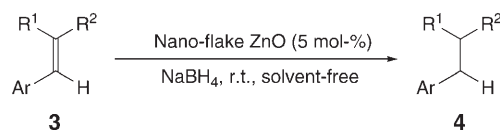
Table 2. Knoevenagel Condensation Catalyzed by NF-ZnO (0.004 g) at 25° under Solvent-Free Conditions (see also Scheme 1)

Aldehyde	Ar	R <sup>1</sup>	R <sup>2</sup>	Product	Time [h]	Yield [%] <sup>a)</sup>
<b>1a</b>	Ph	CN	CN	<b>3a</b>	3.5	90
<b>1b</b>	4-Me-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>3b</b>	3	90
<b>1c</b>	4-MeO-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>3c</b>	2.5	90
<b>1d</b>	2-MeO-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>3d</b>	3	95
<b>1e</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>3e</b>	10 min	98
<b>1f</b>	4-OH-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>3f</b>	3	90
<b>1g</b>	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>3g</b>	10 min	98
<b>1h</b>	3-Cl-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>3h</b>	3	90
<b>1i</b>	2-Cl-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>3i</b>	30 min	90
<b>1j</b>	2-thienyl	CN	CN	<b>3j</b>	2	90
<b>1k</b>	pyridin-4-yl	CN	CN	<b>3k</b>	5 min	98
<b>1l</b>	furan-2-yl	CN	CN	<b>3l</b>	3	95
<b>1e</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CN	CO <sub>2</sub> Et	<b>3m</b>	4	90
<b>1e</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CN	MeO	–	24	0
<b>1e</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	Cl	<b>3n</b>	1	90
<b>1e</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	CO <sub>2</sub> Et	<b>3o</b>	5	90

<sup>a)</sup> Yield of isolated product **3**.

Among the ZnO samples screened in the reduction of 2-(4-chlorophenylmethylene)-malononitrile (**3e**) with NaBH<sub>4</sub> as reducing agent under solvent-free conditions, the NF-ZnO was found to be superior to NP-ZnO and CM-ZnO in terms of yields and reaction times; the yields of product **4e** are 87, 68, and 60% by using the NF-ZnO, NP-ZnO, and assorted crystals of CM-ZnO, respectively (Table 3).

Scheme 2. Reduction of C=C Bonds Catalyzed by Nano-Flake ZnO. For R<sup>1</sup>, R<sup>2</sup>, and Ar, see Table 4.

Table 3. Reduction of 2-[(4-Chlorophenyl)methylene]malononitrile (**3e**; Ar = 4-Cl-C<sub>6</sub>H<sub>4</sub>, R<sup>1</sup> = R<sup>2</sup> = CN; 1 mmol) with NaBH<sub>4</sub> (1 mmol) Catalyzed by Different Crystallites of ZnO (0.004 g) at 25° under Solvent-Free Conditions

Catalyst	Time [min]	Yield [%] <sup>a)</sup>
NF-ZnO	2	87
NP-ZnO	30	68
CM-ZnO	90	60

<sup>a)</sup> Yield of isolated **4e** (Ar = 4-Cl-C<sub>6</sub>H<sub>4</sub>, R<sup>1</sup> = R<sup>2</sup> = CN).

To widen the scope, a system composed of NF-ZnO under solvent-free conditions was evaluated in the reduction of different activated alkene derivatives with NaBH<sub>4</sub>, i.e. of **3e**, **3h**, **3i**, **3f**, **3g**, **3m**, **3n** (Table 4). When the aryl substituent at the methylene

moiety of the activated alkene **3** is substituted by a Cl-atom such as in **3e**, **3h**, **3i**, **3m**, higher yields are observed than in the case of aryl substituents bearing other groups (*Entries 1–3* and *6*). On the other hand, the NF-ZnO-promoted reductions of activated alkenes **3** bearing 2- or 3-substituted aryl substituents with either electron-withdrawing or electron-donating groups exhibit a decrease of yield when compared with the corresponding 4-substituted analogs, which may be ascribed to the steric hindrance for the unidirectional entry of reacting species (*e.g.*, *Entries 2* and *3*). These catalytic reductions are very impressive when compared with other reducing systems such as  $\text{InCl}_3/\text{NaBH}_4$  (*i.e.*,  $\text{Cl}_2\text{InH}$ ) and  $\text{Al}_2\text{O}_3/\text{NaBH}_4$ , which require more than the stoichiometric amount of reducing agent, offer low selectivity or conversions to the desired products, and need protic solvents (*Table 5*).

Table 4. Reduction of Activated Alkene Derivatives **3** with  $\text{NaBH}_4$  Catalyzed by NF-ZnO at 25° under Solvent-Free Conditions (see also *Scheme 2*)

Entry	Knovenagel adduct	Ar	R <sup>1</sup>	R <sup>2</sup>	Product	Time [min]	Yield [%] <sup>a)</sup>
1	<b>3e</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>4e</b>	2	87
2	<b>3h</b>	3-Cl-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>4h</b>	5	72
3	<b>3i</b>	2-Cl-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>4i</b>	5	83
4	<b>3f</b>	4-HO-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>4f</b>	2	60
5	<b>3g</b>	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>4g</b>	2	65
6	<b>3m</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CN	CO <sub>2</sub> Et	<b>4m</b>	5	90
7	<b>3n</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	Cl	<b>4n</b>	10	53

<sup>a)</sup> Yield of isolated product **4**.

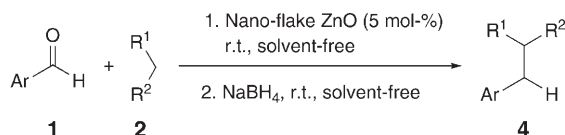
Table 5. Comparison of the Catalytic Efficiency of NF-ZnO and Various Catalysts for the Reduction of **3e**

Catalyst	Time	Yield [%] <sup>a)</sup>
In, EtOH/H <sub>2</sub> O, NH <sub>4</sub> Cl [23a]	10 h	82
InCl <sub>3</sub> /NaBH <sub>4</sub> , MeCN, r.t., H <sub>2</sub> O [23b]	3 h	83
NF-ZnO, r.t.	2 min	87

<sup>a)</sup> Yield of isolated **4e**.

Since the *KC* of malononitrile and 4-chlorobenzaldehyde (**1e**) in the presence of NF-ZnO was accomplished without solvent, we hypothesized that reduction with  $\text{NaBH}_4$  could be performed subsequently in the same pot also under solvent-free conditions. Thus, the condensation of malononitrile and 4-chlorobenzaldehyde (**1e**) was carried out at room temperature by absorption on 5 mol-% of NF-ZnO and determined to be complete (TLC monitoring ( $\text{CH}_2\text{Cl}_2$ ) of malononitrile) within *ca.* 10 minutes. Then  $\text{NaBH}_4$  was added, and all intermediate **3e** was converted to product **4e** within a couple of minutes (*Scheme 3*).

In an effort to determine the scope and limitation of this novel one-pot *KC*-reduction methodology, various aldehydes **1** were treated with malononitrile under the conditions developed for **1e**, which resulted in excellent yields of the corresponding products **4** (*Table 6, Entries 1–11*). We also found that the reaction of some other activated methylene compounds with **1e** were successful under these conditions, but the

Scheme 3. One-Pot Synthesis of Monosubstituted Malononitriles. For R<sup>1</sup>, R<sup>2</sup>, and Ar, see Table 6.

rates for the condensation on NF-ZnO decreased with less reactive methylene compounds (Entries 12–16), whereas the reduction with NaBH<sub>4</sub> proceeded without incident.

Table 6. Overall Yield of the One-Pot Synthesis of **4** by the KC-Reduction Methodology (see also Scheme 3)

Entry	Aldehyde	Ar	R <sup>1</sup>	R <sup>2</sup>	Product	Yield [%] <sup>a)</sup>
1	<b>1a</b>	Ph	CN	CN	<b>4a</b>	95
2	<b>1c</b>	4-MeO-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>4c</b>	98
3	<b>1d</b>	2-MeO-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>4d</b>	95
4	<b>1e</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>4e</b>	98
5	<b>1f</b>	4-OH-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>4f</b>	95
6	<b>1g</b>	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>4g</b>	98
7	<b>1h</b>	3-Cl-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>4h</b>	95
8	<b>1i</b>	2-Cl-C <sub>6</sub> H <sub>4</sub>	CN	CN	<b>4i</b>	95
9	<b>1j</b>	2-thienyl	CN	CN	<b>4j</b>	95
10	<b>1k</b>	pyridin-4-yl	CN	CN	<b>4k</b>	98
11	<b>1l</b>	furan-2-yl	CN	CN	<b>4l</b>	95
12	<b>1e</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CN	CO <sub>2</sub> Et	<b>4m</b>	90
13	<b>1e</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CN	MeO	–	0
15	<b>1e</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	Cl	<b>3n</b>	90
16	<b>1e</b>	4-Cl-C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	CO <sub>2</sub> Et	<b>3o</b>	90

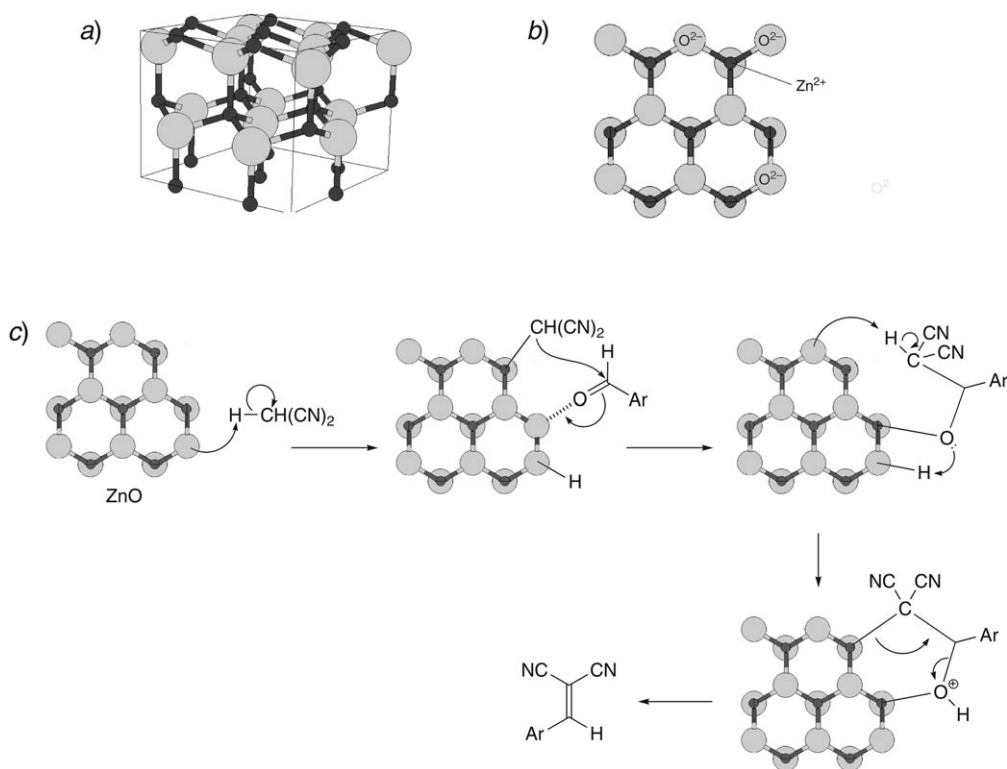
<sup>a)</sup> Yield of isolated product **4**.

NF-ZnO indeed displayed the highest activity compared to that of CM-ZnO, and NF-ZnO has *Lewis* acid sites (Zn<sup>2+</sup>) and *Lewis* basic sites (O<sup>2-</sup>) [29]. In the *KC*, an O<sup>2-</sup> site of NF-ZnO takes up a proton of the malononitrile, and the resulting carbanion forms a complex with the Zn<sup>2+</sup> site (the Zn<sup>2+</sup> sites are also interacting with the C=O groups of the aldehyde (Scheme 4)). Hence, the *KC* proceeds *via* the dual activation by NF-ZnO of both substrates, the nucleophile and the electrophile. The *Lewis* acid sites of NF-ZnO also activate NaBH<sub>4</sub> for the solvent-free reductions.

The above results indicate that the efficiency of the catalytic activity is dependent on the particle size and particle shape of ZnO. The SEM (scanning electron microscope) micrograph, FT-IR spectrum, and X-ray diffraction plot of NF-ZnO and NP-ZnO are illustrated in Fig. 1 and 2, respectively.

**Conclusion.** – We established that NF-ZnO is a highly active catalyst for both *KC* and reductions of C=C bonds in activated conjugated compounds. Thus, NF-ZnO with its well-defined shape and size shows higher activity than other catalysts. The advantages of this safe protocol include a simple reaction setup not requiring

Scheme 4. a) Wurtzite Structure of Crystalline ZnO. b) Wurtzite Structure of Crystalline ZnO in Front View. c) Proposed Mechanism for Knoevenagel Condensation Catalyzed by NF-ZnO.



specialized equipment, very mild reaction conditions, high product yields, short reaction times, and the limitation of solvents.

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#### Experimental Part

**General.** Commercial ZnO (CM-ZnO) was purchased from *Merck*. Samples of conventional ZnO, of nano-flake ZnO (NF-ZnO (20–30 nm)), and of nano-particle ZnO (NP-ZnO (35 + 5 nm)) were synthesized as reported in [30][31], the latter two are characterized in *Figs. 1* and *2*.

**Nanoflake Zinc Oxide (NF-ZnO).** In a typical experiment, zinc acetate dihydrate (10 mmol) and CO(NH<sub>2</sub>)<sub>2</sub> (0.2 mol) were dissolved in deionized H<sub>2</sub>O (200 ml) at r.t. (→ transparent soln.), and the soln. was refluxed for 12 h. The mixture was cooled in cold water to stop the reaction. The product was centrifuged and washed with deionized H<sub>2</sub>O and abs. EtOH and dried at 80° for 8 h. The NF-ZnO (2 g) was obtained by calcining the precursor in a furnace in air at 400° for 2 h [30].

**Nanoparticle Zinc Oxide (NP-ZnO).** Zinc acetate dihydrate (10.98 g) was dissolved in EtOH (300 ml) at 60°. Oxalic acid dihydrate (12.6) which was previously dissolved in EtOH (200 ml) at 50° was added slowly under stirring to the Zn(OAc)<sub>2</sub> soln. at 60°. A thick white gel formed, which was kept at 80° for drying. Then the solid was calcined at 500° for 2 h to yield NP-ZnO (5 g) [31].

**Knoevenagel Condensation of 1 and 2: General Procedure.** A benzaldehyde (**1**; 1 mmol) and an activated methylene compound **2** (1 mmol) were added to NF-ZnO (5 mol-%, 0.004 g) in a mortar. The

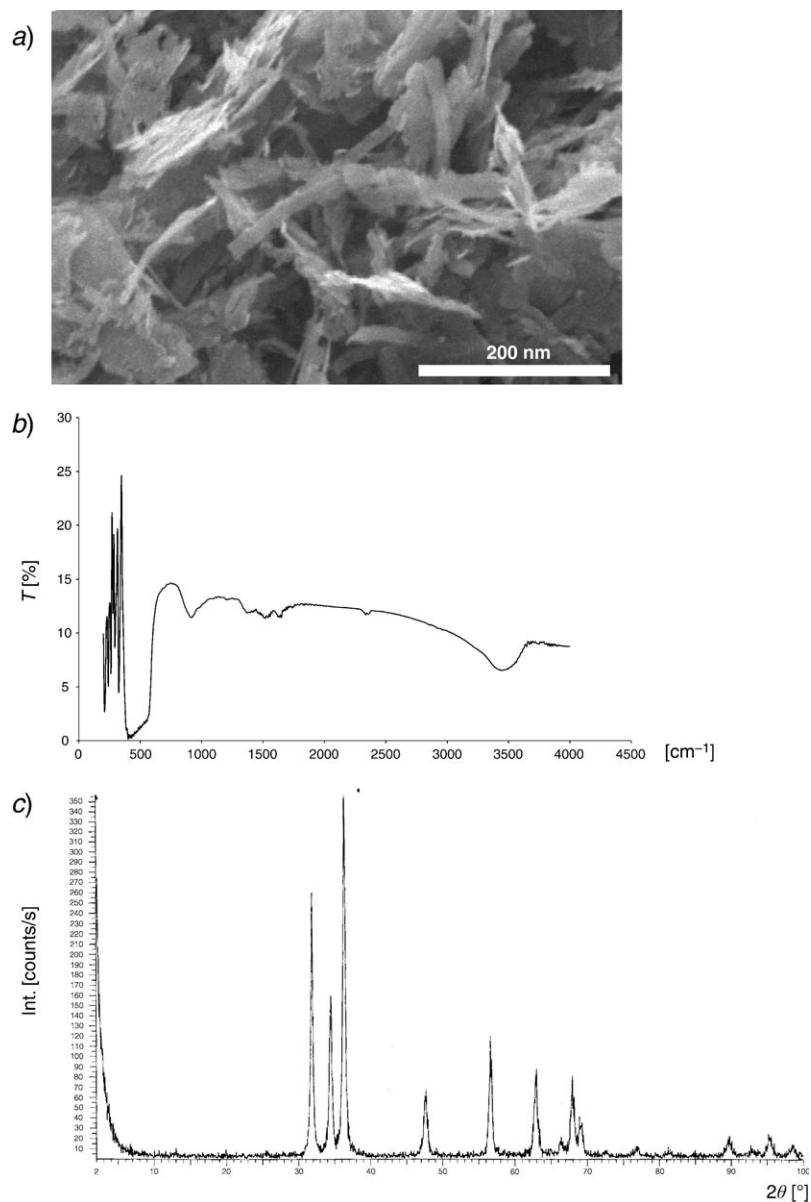


Fig. 1. a) SEM Micrograph of NF-ZnO. b) FT-IR Spectrum of NF-ZnO. c) X-Ray diffraction plot of NF-ZnO.

mixture was ground with a pestle, and the progress of the reaction was monitored by TLC (AcOEt/hexane 2:8). After the reaction was complete, AcOEt was added, and the mixture was centrifuged to separate the catalyst. The org. solvent was evaporated, and the residue was purified by chromatography (silica gel). The structures of the obtained *Knoevenagel* adducts **3** were confirmed by the <sup>1</sup>H-NMR and IR data and comparison with authentic samples obtained commercially or prepared by reported methods [18–20].

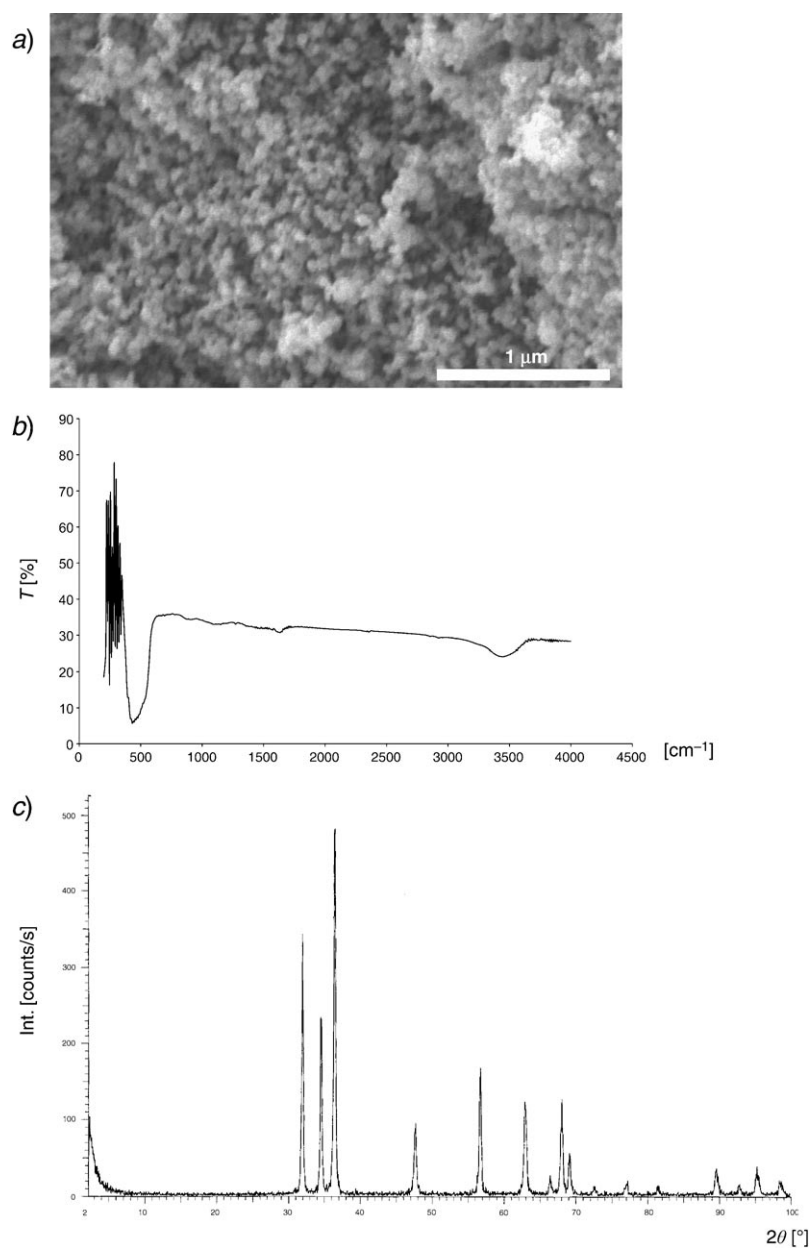


Fig. 2. a) SEM Micrograph of NP-ZnO. b) FT-IR Spectrum of NP-ZnO. c) X-Ray diffraction plot of NP-ZnO.

*Reduction of Knoevenagel Adducts 3: General Procedure.* The Knoevenagel adduct **3** (1 mmol) and NaBH<sub>4</sub> (1 mmol) were added to NF-ZnO (5 mol-%, 0.004 g) in a mortar. The mixture was ground with a pestle, and the progress of the reaction was monitored by TLC (silica gel, CH<sub>2</sub>Cl<sub>2</sub>; nearly identical R<sub>f</sub>



values of educt and product but only the educt was detected under UV light at 254 nm).  $\text{CH}_2\text{Cl}_2$  (30 ml) was added, and the mixture was centrifuged to separate the catalyst. Then the soln. was poured into a separatory funnel with ice-water (20 ml). Excess hydride was destroyed, and the soln. was acidified with 3M HCl (8 ml). The org. phase was dried and concentrated, and the crude oily residue was purified by column chromatography (hexane/AcOEt 9:1). The structures of the obtained colorless oily reduction products **4** were confirmed by the  $^1\text{H-NMR}$  and IR data and comparison with authentic samples obtained commercially or prepared by reported methods [21–24].

*One-Pot Preparation of 4.* A benzaldehyde **1** (1 mmol), an activated methylene compound **2** (1 mmol), and NF-ZnO (5 mol-%, 0.004 g) were mixed in a mortar. The mixture was ground with a pestle, and the progress of the reaction was monitored by TLC (AcOEt/hexane 20:80). After the reaction was complete,  $\text{NaBH}_4$  (1 mmol, 0.04 g) was added, and the mixture was ground with a pestle, and after 5–10 min the reaction was complete (TLC monitoring). Workup was carried out as described above for the reduction of *Knoevenagel* adducts.

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