



**ANOTHER APPLICATION OF ZIRCONIA SULFURIC ACID AS HIGHLY EFFICIENT RECYCLABLE NANO-CATALYST FOR SELECTIVE CROSS-ALDOL CONDENSATIONS OF KETONES WITH AROMATIC ALDEHYDES IN WATER**

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**ABSTRACT**

In this research cross-aldol condensations of aromatic aldehydes with various ketones in the presence of Zirconia Sulfuric Acid (ZrSA) nanoparticle, as heterogeneous catalyst have been reported. The catalyst was prepared according to a previously published literature procedure using inexpensive and readily available starting materials. The highly active catalyst gave excellent yields of the desired cross-aldol products without the occurrence of any self-condensation reactions. Reaction times were short, the procedure and work-up were simple, and no volatile or hazardous organic solvents were necessary. Moreover, the catalyst could be recovered at least three times with only a slight reduction in activity.

**KEYWORDS:** Zirconia Sulfuric Acid (ZrSA); Heterogeneous catalysis; Reusability; Cross-aldol condensation; Refluxing water.

**INTRODUCTION**

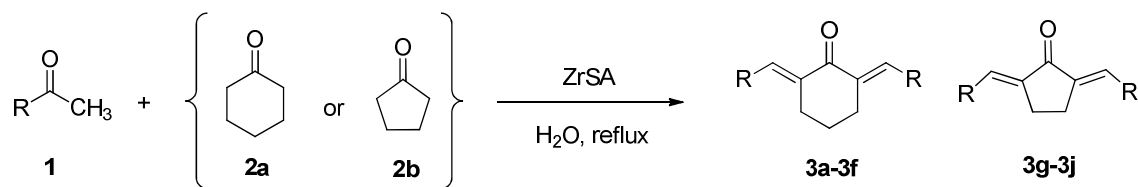
An aldol condensation is a condensation reaction in organic chemistry in which an enol or an enolate ion reacts with a carbonyl compound to form a  $\beta$ -hydroxyaldehyde or  $\beta$ -hydroxyketone, followed by dehydration to give a conjugated enone. This is an important method for the formation of carbon-carbon bonds. For example, cross-aldol condensation of aromatic aldehydes with ketones is an important synthetic reaction for the preparation of  $\alpha,\alpha'$ -bisarylidene cycloalkanones and chalcones. Arylidene cycloalkanone derivatives are intermediates of various pharmaceuticals, agrochemicals and perfumes<sup>i</sup>. These compounds are frequently used for the synthesis of bioactive pyrimidine derivatives<sup>ii</sup>, 2,7-disubstituted tropones<sup>iii</sup>, cytotoxic analogs<sup>iv</sup>. They also find applications in the preparation of nonlinear optical materials<sup>v</sup> and liquid-crystalline polymers<sup>vi</sup>. Arylidene cycloalkanones have also been reported to possess significant biological activities, including antiangiogenic activity<sup>vii</sup>, quinine reductase- inducing activity<sup>viii</sup>, and cholesterol-lowering activity<sup>ix</sup>. Furthermore, they

have been used as key starting materials for the synthesis of a new class of spiropyrrolidine antimicrobial and antifungal agents<sup>x</sup>, tetraazadispiro[4.1.4.3]tetradeca-2,9-dien-6-ones<sup>xi</sup>, tricyclic thiazolo[3,2-a]thiapyrano[4,3-d] pyrimidines, which are potential anti-inflammatory agents<sup>xii</sup>, and other important heterocyclic compounds<sup>xiii</sup>. Aldol condensations are traditionally catalyzed by strong acids or bases such as HCl<sup>xiv,xv</sup>, p-toluenesulfonic acid<sup>xvi</sup>, and potassium or sodium hydroxide<sup>xvii,xviii</sup>. Although, the presence of a strong acid or base mostly induces the reverse reaction as well as self-condensation reactions, and thus the yields of the desired products can be low. Recently, researchers have performed the reaction in ionic liquids<sup>xix,xx</sup>. However, the use of homogeneous catalysts complicates product separation and catalyst recovery<sup>xxi,xxii</sup>, and thus there have been efforts to replace homogeneous catalysts with easy-to-handle, noncorrosive, reusable, and environmentally friendly heterogeneous catalysts. For example, aldol condensations have been carried out with heterogeneous catalysts such as BF<sub>3</sub>-Et<sub>2</sub>O<sup>xxiii</sup>, Mg(HSO<sub>4</sub>)<sub>2</sub><sup>xxiv</sup>, sulfamic acid<sup>xxv</sup>, Yb(OTf)<sub>3</sub><sup>xxvi</sup>, InCl<sub>3</sub><sup>xxvii</sup>, hydrotalcite<sup>xxviii</sup>, a fluoroalkylated 1,4-disubstituted [1,2,3]triazole organocatalyst<sup>xxix</sup>, bis(p methoxyphenyl)telluroxide<sup>xxx</sup>, Cp<sub>2</sub>ZrH<sub>2</sub> in combination with metal salts<sup>xxxi</sup>, NaOAc<sup>xxxii</sup>, silica chloride<sup>xxxiii</sup>, a sulfonated carbon nanocage<sup>xxxiv</sup>, polystyrene-supported sulfonic acid<sup>xxxv</sup>, cetyl trimethyl ammonium bromide<sup>xxxvi</sup>, and KF-Al<sub>2</sub>O<sub>3</sub><sup>xxxvii</sup>. Although these methods may be effective, but have some problems. Major drawbacks of these procedures include expensive reagents, use of large amounts of toxic organic solvents, prolonged heating and side reactions. All of these disadvantages make further improvement of the synthesis of such molecules essential. Therefore, the development of a new greener and more convenient method for the synthesis of these compounds is highly desirable.

Acid-catalysts are one of the most frequently applied processes in chemical industry, which has been a major area of research interest<sup>xxxviii</sup>. Commonly, liquid inorganic acids including H<sub>2</sub>SO<sub>4</sub>, HCl and H<sub>3</sub>PO<sub>4</sub> are part of the homogeneous acid catalysts. Despite their application in the wide production of industrial chemicals, many disadvantages such as high toxicity, corrosive nature, hazards in handling and difficult separation from the products make them not so useful. Furthermore, the synthesis using homogeneous catalysts have major problem of catalyst recovery and reuse. These difficulties are not in the range of green chemistry. According to these disadvantages, in order to improve drawbacks of these catalysts, replacement of them by novel, nontoxic, eco-friendly, recyclable heterogeneous catalysts with improved efficiency have been the important topics of researchers during the last decades. Heterogeneous catalysts show important role in many aspects of environmental and economic in many industrial processes. They presented some excellence including great reactivity, operational simplicity, low toxicity, non-corrosive nature and the potential of the recyclability. Furthermore, most of the heterogeneous catalysts show better product selectivity, so that by-product can be easily separated<sup>xxxix</sup>. One of the important routes for developing novel heterogeneous catalysts is immobilizing of homogenous precursors on a solid support<sup>xl</sup>.

The metal oxide nanoparticles such as TiO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, and ZnO are reported as useful heterogeneous catalyst agents in the synthesis of organic compounds<sup>xxxix,xli</sup>. Zirconia (ZrO<sub>2</sub>) is one of the most important metal oxide nanoparticles with high surface area, mechanical strength and thermal stability which have widely application in chemical industry especially as catalyst.

As part of our research on the development of reusable catalysts for the synthesis of organic compounds<sup>xxxix-l</sup>, we reported here ZrSA as greener catalyst for selective cross-aldol condensation of aromatic aldehydes **1** with various ketones **2a**, and **2b** in refluxing water. This reusable heterogeneous catalyst showed high catalytic activity in short reaction times without side reaction like self-condensation (Scheme 1).



R= 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> (**3a**), 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> (**3b**), 4-ClC<sub>6</sub>H<sub>4</sub> (**3c**), Ph (**3d**), 4-MeOC<sub>6</sub>H<sub>4</sub> (**3e**), 4-MeC<sub>6</sub>H<sub>4</sub> (**3f**),  
4-MeOC<sub>6</sub>H<sub>4</sub> (**3g**), 4-MeC<sub>6</sub>H<sub>4</sub> (**3h**), 4-ClC<sub>6</sub>H<sub>4</sub> (**3i**), Ph (**3j**)

**Scheme 1.** ZrSA catalyzed cross-aldol condensation.

## RESULTS AND DISCUSSION

### Characterization of the catalyst

For our investigations, the catalyst ZrO<sub>2</sub>-SO<sub>3</sub>H (ZrSA) was prepared according to the literature procedure<sup>li</sup>. The ZrSA catalyst was characterized by FT-IR, and pH analysis. The FT-IR spectrum of the nano-ZrO<sub>2</sub> and ZrO<sub>2</sub>-SO<sub>3</sub>H are shown in Figure 2(1) and (2), respectively. In Figure 2(1), the characteristic vibrational bands of the Zr-O bond at 576 and 752 cm<sup>-1</sup>, as well band belonging to the Zr-OH group at 1627 cm<sup>-1</sup>. The FT-IR spectrum of the catalyst also contained absorbance band at 3421 cm<sup>-1</sup>, which indicated the presence of water. These observations proved nano-ZrO<sub>2</sub> structures and are consistent with the previously reported evidences<sup>li</sup>. The FT-IR spectrum of the ZrSA catalyst prepared in the current study (Figure 2(2)) revealed new bonds at 820-890 and 1060-1180 cm<sup>-1</sup> which are related to the O=S=O asymmetric and symmetric stretching vibration and S-O stretching vibration of the sulfonic groups (-SO<sub>3</sub>H), respectively. The appeared broad band around 2700-3600 cm<sup>-1</sup> related to the OH stretching absorption of the SO<sub>3</sub>H group. All these specifications acknowledge nano-ZrO<sub>2</sub> structure that has functionalized with sulfonic acid groups. The density of the SO<sub>3</sub>H groups was measured using NaOH (0.1 N) as titrant by acid-base potentiometric titration. The amount of SO<sub>3</sub>H in the catalyst was 2.45 mmol/g.

### Evaluation of catalytic activity of ZrSA in cross-aldol condensations

The catalytic activity of this material was evaluated in the synthesis of fluoroquinolone derivatives. At first, we used the reaction of cyclohexanone (**2a**, 1 mmol), and 4-chlorobenzaldehyde (**1**, 2 mmol) as the model ketone and aromatic aldehyde, respectively, to afford product **3c**. In order to get the effective reaction conditions, the reaction was optimized in terms of various parameters like catalyst amount, effect of solvent, and influence of temperature (Table 1). Low yields of the product **3c** were obtained in the absence of the catalyst in refluxing EtOH or H<sub>2</sub>O (entries 1 and 2) or in the presence of the catalyst under solvent-free conditions at high temperatures (entries 3 and 4) indicating that the catalyst and solvent are necessary for the reaction. As can be seen from Table 1, among the tested solvents such as H<sub>2</sub>O, EtOH, MeOH, CHCl<sub>3</sub>, CH<sub>3</sub>CN, and also solvent-free conditions and various amounts of the catalyst, the reaction was more facile and proceeded to give the highest yield, using 0.08 g of ZrSA in H<sub>2</sub>O at reflux temperature (entry 12). All subsequent reactions were carried out in these optimized conditions.

**Table 1.** Optimization of reaction conditions for the synthesis of compound **3c** catalyzed by ZrSA\*.

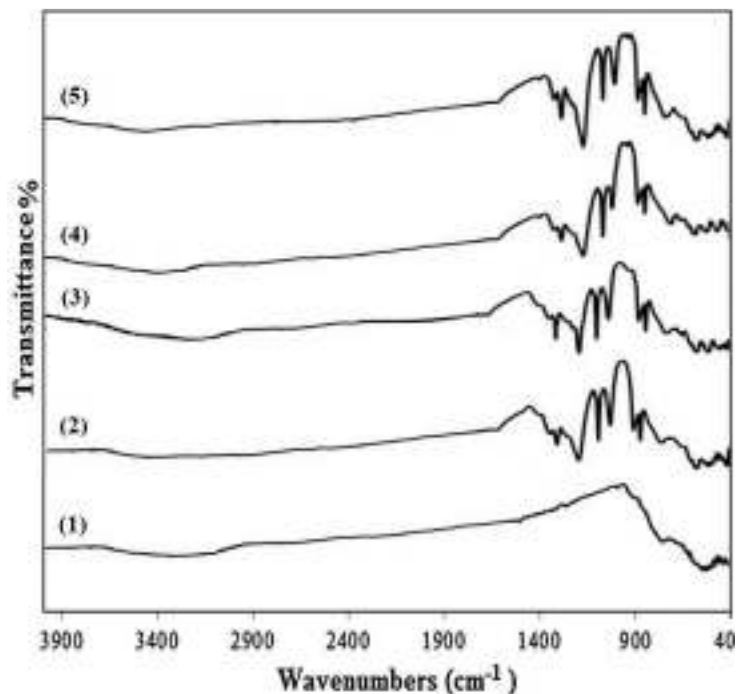
Entry	Catalyst (g)	Solvent	T/°C	Time/min	Isolated Yield/%
1	None	H <sub>2</sub> O	Reflux	110	19
2	None	EtOH	Reflux	110	14
3	0.08	Solvent-free	100	34	32

4	0.08	Solvent-free	120	34	35
5	0.02	EtOH	Reflux	66	19
6	0.04	EtOH	Reflux	46	31
7	0.06	EtOH	Reflux	35	32
8	0.08	EtOH	Reflux	29	82
9	0.02	H <sub>2</sub> O	Reflux	37	25
10	0.04	H <sub>2</sub> O	Reflux	24	54
11	0.06	H <sub>2</sub> O	Reflux	16	88
12	0.08	H <sub>2</sub> O	Reflux	17	96
13	0.08	H <sub>2</sub> O	80	25	92
14	0.08	H <sub>2</sub> O	r.t.	35	87
15	0.1	H <sub>2</sub> O	Reflux	16	94
16	0.02	MeOH	Reflux	47	16
17	0.04	MeOH	Reflux	45	34
18	0.06	MeOH	Reflux	35	81
19	0.08	MeOH	Reflux	25	87
20	0.02	CHCl <sub>3</sub>	Reflux	35	16
21	0.04	CHCl <sub>3</sub>	Reflux	33	39
22	0.06	CHCl <sub>3</sub>	Reflux	30	78
23	0.08	CHCl <sub>3</sub>	Reflux	25	89
24	0.02	CH <sub>3</sub> CN	Reflux	65	14
25	0.04	CH <sub>3</sub> CN	Reflux	57	33
26	0.06	CH <sub>3</sub> CN	Reflux	46	61
27	0.08	CH <sub>3</sub> CN	Reflux	35	80

\* Reaction conditions: cyclohexanone (**2a**, 1 mmol), and 4-chlorobenzaldehyde (**1**, 2 mmol)

Encouraged by the remarkable results obtained with the above reaction conditions, and in order to show the generality and scope of this new protocol, we extended the reaction of aldol condensations with cyclohexanone, cyclopentanone and a series of aromatic aldehydes under the optimized reaction conditions. As shown, all reactions proceed very clean to give the corresponding products **3a–3j** without any self-condensation in high yields over short reaction times. Purity checks with melting points, TLC and the <sup>1</sup>H NMR spectroscopic data reveal that only one product is formed in all cases and no undesirable side-products are observed. The structures of all known products were deduced from their <sup>1</sup>H NMR and FT-IR spectral data and a comparison of their melting points with those of authentic samples<sup>xxiii-xxxvii</sup>.

We also used the model reaction under optimized reaction conditions to evaluate the reusability of the ZrSA catalyst. After completion of the reaction, the catalyst was recovered as described in the experimental section. The separated catalyst was washed with hot ethanol and subsequently dried at 50 °C under vacuum for 1 h before being reused in a similar reaction. The catalyst could be used at least five times without significant reduction in its activity (96, 96, 94, 93 % yields in first to fourth use, respectively) which clearly demonstrates the practical reusability of this catalyst. Furthermore, the FT-IR spectra of the recovered catalysts (Figure 1(3)–(5)) were almost identical to the spectrum of the fresh catalyst (Figure 1(2)), indicating that the structure of the catalyst was unchanged by the reaction.



**Figure 1.** FT-IR spectra of ZrO<sub>2</sub> (1), fresh catalyst ZrSA ((2), first run), and recovered catalysts (3-5)

Although we did not investigate the reaction mechanism, the ZrSA could act as Brønsted acid related to the –SO<sub>3</sub>H groups and therefore promote the necessary reactions. The catalyst would play a significant role in increasing the electrophilic character of the electrophiles in the reaction.

## EXPERIMENTAL

All chemicals were available commercially and used without additional purification. The catalyst was synthesized according to the literature<sup>11</sup>. Melting points of the compounds were recorded on a Stuart SMP3 melting point apparatus. The IR spectra were obtained using a Tensor 27 Bruker spectrophotometer as KBr disks. The <sup>1</sup>H NMR (400 MHz) spectra were recorded with Bruker 400 spectrometer.

### *General experimental procedure for cross-aldol condensation catalyzed by ZrSA*

A mixture of cyclohexanone (**2a**, 1 mmol) or cyclopentanone (**2b**, 1 mmol), an aromatic aldehyde **1** (2 mmol), and ZrSA (0.08 g) as catalyst in H<sub>2</sub>O (5 ml) was heated under reflux for the appropriate time. The reaction was monitored by TLC. Upon completion of the transformation, hot ethanol was added and the catalyst filtered through sintered glass Büchner funnel under hot conditions. The catalyst was washed with a small portion of hot ethanol. After cooling, the combined filtrate was allowed to stand at room temperature. The precipitated solid was collected by filtration, and recrystallized from ethanol to give compounds 3a-3j in high yields.

### *Characterization data*

**2,6-Bis(3-nitrobenzylidene)cyclohexanone (3a)** Yield: 93%; 19 min; M.p.: 192–194 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.88 (quin, 2H, *J* = 6.1 Hz, CH<sub>2</sub>), 3.21 (t, 4H, *J* = 6.1 Hz, 2CH<sub>2</sub>), 7.71 (t, 2H, *J* = 7.9 Hz, arom-H), 7.63 (d, 2H, *J* = 7.6 Hz, arom-H), 7.84 (s, 2H, 2CH(vinyl)), 8.26 (d, 2H, *J* = 7.9 Hz, arom-H), 8.32 (s, 2H, arom-H); IR (KBr disc): ν 3077, 2949, 1728, 1582, 1501, 1398 1259, 841 cm<sup>-1</sup>.

**2,6-Bis(4-nitrobenzylidene)cyclohexanone (3b)** Yield: 94%; 18 min; M.p.: 160–162 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.90 (quin, 2H, *J* = 6.1 Hz, CH<sub>2</sub>), 3.10 (t, 4H, *J* = 6.0 Hz, 2CH<sub>2</sub>), 7.58–8.2 (m, 8H, arom-H), 8.32 (s, 2H, 2CH(vinyl)); IR (KBr disc): ν 3080, 2933, 1710, 1589, 1499, 1339 1258, 846 cm<sup>-1</sup>.

**2,6-Bis(4-chlorobenzylidene)cyclohexanone (3c)** Yield: 96%; 17 min; M.p.: 149–151 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.87 (quin, 2H, *J* = 6.1 Hz, CH<sub>2</sub>), 2.89 (t, 4H, *J* = 6.1 Hz, 2CH<sub>2</sub>), 7.33–7.45 (m, 8H, arom-H), 7.73 (s, 2H, 2CH(vinyl)); IR (KBr disc): ν 2933, 1676, 1611, 1589, 1270, 826 cm<sup>-1</sup>.

**2,6-Di(benzylidene)cyclohexanone (3d)** Yield: 95%; 18 min; M.p.: 118–120 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.88 (quin, 2H, *J* = 6.0 Hz, CH<sub>2</sub>), 2.93 (t, 4H, *J* = 6.0 Hz, 2CH<sub>2</sub>), 7.25–7.48 (m, 10H, arom-H), 7.80 (s, 2H, 2CH(vinyl)); IR (KBr disc): ν 3082, 3032, 2925, 1661, 1599, 1570, 1445, 1274, 1145, 771 cm<sup>-1</sup>.

**2,6-Bis(4-methoxybenzylidene)cyclohexanone (3e)** Yield: 92%; 16 min; M.p.: 163–165 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.82 (quin, 2H, *J* = 6.2 Hz, CH<sub>2</sub>), 2.88 (t, 4H, *J* = 6.2 Hz, 2CH<sub>2</sub>), 3.78 (s, 6H, 2CH<sub>3</sub>), 7.00–7.50 (m, 8H, arom-H), 7.81 (s, 2H, 2CH(vinyl)); IR (KBr disc): ν 3015, 2945, 1623, 1549, 1516, 1239, 1025, 829 cm<sup>-1</sup>.

**2,6-Bis(4-methylbenzylidene)cyclohexanone (3f)** Yield: 89%; 23 min; M.p.: 167–169 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.82–1.86 (m, 2H, CH<sub>2</sub>), 2.42 (s, 6H, 2CH<sub>3</sub>), 2.92 (t, 4H, *J* = 5.9 Hz, 2CH<sub>2</sub>), 7.20–7.40 (m, 8H, arom-H), 7.81 (s, 2H, 2CH(vinyl)); IR (KBr disc): ν 2938, 2914, 1660, 1600 1516, 1239, 1025, 829 cm<sup>-1</sup>.

**2,5-Bis(4-methoxybenzylidene)cyclopentanone (3g)** Yield: 92%; 20 min; M.p.: 212–214 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.07–3.15 (m, 4H, 2CH<sub>2</sub>), 3.85 (s, 6H, 2CH<sub>3</sub>), 6.95–7.00 (m, 4H, 4CH), 7.57–7.60 (m, 6H, 6CH); IR (KBr disc): ν 3080, 2962, 2892, 1661, 1596, 1535, 1375, 1241, 829 cm<sup>-1</sup>.

**2,5-Bis(4-methylbenzylidene)cyclopentanone (3h)** Yield: 93%; 19 min; M.p.: 246–248 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.30 (s, 6H, 2CH<sub>3</sub>), 3.08 (s, 4H, 2CH<sub>2</sub>), 7.20 (s, 4H, 4CH), 7.45–7.53 (m, 6H, 6CH); IR (KBr disc): ν 3111, 2998, 2856, 1660, 1559, 1491, 1356, 1284, 872 cm<sup>-1</sup>.

**2,5-Bis(4-chlorobenzylidene)cyclopentanone (3i)** Yield: 90%; 17 min; M.p.: 229–231 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.12–3.18 (m, 4H, 2CH<sub>2</sub>), 7.40–7.45 (m, 4H, 4CH), 7.51–7.55 (m, 6H, 6CH); IR (KBr disc): ν 3086, 2972, 2881, 1659, 1584, 1521, 1370, 1239, 832 cm<sup>-1</sup>.

**2,5-Di(benzylidene)cyclopentanone (3j)** Yield: 94%; 18 min; M.p.: 187–189 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.11–3.17 (m, 4H, 2CH<sub>2</sub>), 7.33–7.42 (m, 6H, 6CH), 7.60–7.64 (m, 6H, 6CH); IR (KBr disc): ν 3091, 2958, 2853, 1662, 1549, 1501, 1369, 1251, 839 cm<sup>-1</sup>.

## CONCLUSION

We showed that ZrSA efficiently catalyzed the selective cross-aldol condensation of ketones with aromatic aldehydes in refluxing water. The method was fast and high yielding, the work-up was easy, and only one product was formed, as indicated by thin-layer chromatography and <sup>1</sup>H NMR spectroscopy. In addition, the reaction was environmentally friendly because it was in water as solvent. Moreover, the catalyst could be easily recycled by filtration and reused at least three times with only a slight reduction in activity.

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Received on March 5, 2017.