



Application of Metal Oxide Nanoparticles as Reusable Heterogeneous Catalysts in the Synthesis of 1,8-Dioxodecahydroacridines (A Comparative Study)

Ahmad Nakhaei^{1*}, Abolghasem Davoodnia², and Sepideh Yadegarian¹

¹Young Researchers and Elite Club, Mashhad Branch, Islamic Azad University, Mashhad, Iran

²Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran
E-mail: nakhaei_a@yahoo.com, nakhaei_a@mshdiau.ac.ir

Abstract

The catalytic performance of three nano-sized metal oxides including Al₂O₃, TiO₂, and Fe₃O₄ nanoparticles, in the synthesis of 1,8-dioxodecahydroacridines by one-pot three-component reaction of aromatic aldehydes, ammonium acetate, and dimedone, has been investigated. Different reaction conditions were studied in the presence of Al₂O₃, TiO₂, and Fe₃O₄ nanoparticles as catalysts. The results showed that nanoFe₃O₄ acts as more effective heterogeneous catalyst than others and the reaction proceeded more easily and gave the highest yields of the products in shorter reaction times under thermal solvent-free conditions. Short reaction times, simple isolation of the products, and usage of eco-friendly catalysts are some features of this procedure. In addition, the catalysts were easily recovered and used in multiple catalytic cycles.

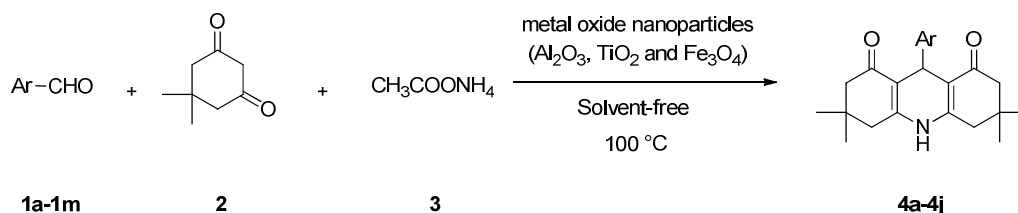
Keywords: Comparative study; Metal oxide nanoparticles; 1,8-Dioxodecahydroacridines; Solvent-free synthesis.

Introduction

The problems associated with most homogeneous catalysts, such as their environmental hazards and difficult recovery, have increased the interest to develop alternative procedures using heterogeneous onesⁱ⁻ⁱⁱⁱ. The potential advantages of heterogeneous catalysts could potentially allow for the development of environmentally benign processes in both academic and industrial settings^{iv-vi}. In recently years, among the various heterogeneous catalysts, nanoparticles have attracted much attention for their high surface area^{vii,viii}. As the particle size decreases, ample external surface area emerged, which allows the accessibility to a large amount of the active centers, and thus the activity of the catalyst increases. Despite various metal oxide nanoparticles have been synthesized and tested as catalysts in organic transformations^{ix-xii}, there have, to the best of our knowledge, been no reports concerning the use of Al₂O₃, TiO₂, and Fe₃O₄ nanoparticles as catalysts for the synthesis of 1,8-Dioxodecahydroacridines, an important class of organic compounds with diverse and

interesting biological activities. These compounds are synthesized *via* the one-pot three-component reaction of aldehyde, ammonium acetate, and dimedone using various catalysts^{xiii-xxii}.

Prompted by these facts and as part of our research program on the development of convenient methods using reusable catalysts for the synthesis of organic compounds^{xxiii-xxix}. We report here the results of our investigation on the application of Al₂O₃, TiO₂, and Fe₃O₄ nanoparticles as heterogeneous catalysts in the synthesis of 1,8-Dioxodecahydroacridines (Scheme 1).



Scheme 1. Nano metal oxides catalyzed synthesis of 1,8-Dioxodecahydroacridines.

Experimental

Nano-sized metal oxides, Al₂O₃, TiO₂, and Fe₃O₄ nanoparticles, were purchased from Tecnan Spanish company. All of the other chemicals were purchased from Merck and Aldrich and used without purification. The IR spectra were obtained using a Tensor 27 Bruker spectrophotometer in KBr disks. The ¹H NMR spectra were recorded on Bruker (300, 400 and 500) spectrometers. The melting points were measured on a Stuart SMP3 melting point apparatus.

General procedure for the synthesis of 1,8-Dioxodecahydroacridines 4a-4j catalyzed by nano-sized metal oxides.

A mixture of aldehyde **1a-1j** (1 mmol), dimedone **2** (2 mmol), ammonium acetate **3** (1 mmol), and a nano-sized metal oxide (0.09 g) was heated in an oil bath at 100 °C. The reaction was monitored by TLC. Upon completion of the transformation, the reaction mixture was cooled to room temperature and hot ethanol was added. This resulted in the precipitation of the catalyst, which was collected by filtration (for Al₂O₃, and TiO₂ nanoparticles) or using an external magnet (for Fe₃O₄ nanoparticles). The product was collected from the filtrate after cooling to room temperature and recrystallized from ethanol to give compounds **4a-4j** in high yields. The separated catalyst was washed with hot ethanol, dried at 60 °C under vacuum for 1 h and reused for the same experiment. Purity checks with melting points, TLC and the ¹H 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 **4a-4j** were deduced from their ¹H NMR and FT-IR spectral data and a comparison of their melting points with those of authentic samples.

Characterization data

9-phenyl-3,3,6,6-tetramethyl-1,8-dioxodecahydroacridine (4a) Mp, 288–290 °C (Lit.^{xviii} 220–222); ¹H NMR (400 MHz, CDCl₃, ppm): 0.84 (s, 6H, 2CH₃), 0.95 (s, 6H, 2CH₃), 2.00–2.35 (m, 8H, CH₂), 5.09 (s, 1H, CH), 7.00–7.35 (m, 5H, arom-H); FT-IR (ν, cm⁻¹ KBr disc): 3190, 3090, 2968, 1628, 1610, 1483, 1365, 1232, 1149, 1032, 748.

9-(2-Chlorophenyl)-3,3,6,6-tetramethyl-1,8-dioxodecahydroacridine (4b) Mp, 219–221 °C (Lit.^{xviii} 220–222); ¹H NMR (400 MHz, DMSO-d₆, ppm): 0.95 (s, 6H, 2CH₃), 1.03 (s, 6H, 2CH₃), 1.90 (d, *J* = 16.2 Hz, 2H, CH₂), 2.13 (d, *J* = 16.2 Hz, 2H, CH₂), 2.28 (d, *J* = 16.8 Hz, 2H, CH₂), 2.43 (d, *J* = 16.8 Hz, 2H, CH₂), 5.06 (s, 1H, CH), 7.02 (t, *J* = 7.2 Hz, 1H, arom-H),

7.06–7.20 (m, 2H, arom-H), 7.26 (d, $J = 7.7$, Hz, 1H, arom-H), 9.59 (s br., 1H, NH); FT-IR (v, cm^{-1} KBr disc): 3200, 3072, 2954, 1635, 1608, 1487, 1364, 1223, 1147, 1038, 750.

9-(4-Chlorophenyl)-3,3,6,6-tetramethyl-1,8-dioxodecahydroacridine(4c)Mp, 297–299 °C (Lit.^{xviii} 298–300); ^1H NMR (400 MHz, CDCl_3 , dppm): 0.99 (s, 6H, 2 CH_3), 1.11 (s, 6H, 2 CH_3), 2.18 (d, $J = 16.4$ Hz, 2H, CH_2), 2.24 (d, $J = 16.4$ Hz, 2H, CH_2), 2.28 (d, $J = 16.4$ Hz, 2H, CH_2), 2.35 (d, $J = 16.4$ Hz, 2H, CH_2), 5.08 (s, 1H, CH), 7.15 (br., 1H, NH), 7.19 (d, $J = 8.4$ Hz, 2H, arom-H), 7.31 (d, $J = 8.4$ Hz, 2H, arom-H); FT-IR (v, cm^{-1} KBr disc): 3175, 3058, 2956, 1650, 1609, 1490, 1366, 1222, 1154, 1091, 844.

9-(3-Nitrophenyl)-3,3,6,6-tetramethyl-1,8-dioxodecahydroacridine (4d)Mp, 291–292 °C (Lit.^{xv} 288–290); ^1H NMR (400 MHz, CDCl_3 , dppm): 1.00 (s, 6H, 2 CH_3), 1.13 (s, 6H, 2 CH_3), 2.19 (d, $J = 16.4$ Hz, 2H, CH_2), 2.28 (d, $J = 16.4$ Hz, 2H, CH_2), 2.34 (d, $J = 16.8$ Hz, 2H, CH_2), 2.45 (d, $J = 16.8$ Hz, 2H, CH_2), 5.20 (s, 1H, CH), 6.20 (s, 1H, NH), 7.41 (t, $J = 8.0$ Hz, 1H, arom-H), 7.91 (dt, $J = 7.6$, 1.6 Hz, 1H, arom-H), 7.98 (ddd, $J = 8.2$, 2.4, 0.8 Hz, 1H, arom-H), 8.07 (t, $J = 2.0$ Hz, 1H, arom-H); FT-IR (v, cm^{-1} KBr disc): 3185, 3065, 2960, 1647, 1609, 1528, 1487, 1426, 1397, 1366, 1346, 1256, 1170, 1145.

9-(4-Nitrophenyl)-3,3,6,6-tetramethyl-1,8-dioxodecahydroacridine(4e)Mp, 286–288 °C (Lit.^{xv} 286–288); ^1H NMR (500 MHz, CDCl_3 , dppm): 1.00 (s, 6H, 2 CH_3), 1.14 (s, 6H, 2 CH_3), 2.19 (d, $J = 16.2$ Hz, 2H, CH_2), 2.28 (d, $J = 16.2$ Hz, 2H, CH_2), 2.32 (d, $J = 16.8$ Hz, 2H, CH_2), 2.46 (d, $J = 16.8$ Hz, 2H, CH_2), 5.19 (s, 1H, CH), 6.12 (s br., 1H, NH), 7.54 (d, $J = 8.7$ Hz, 2H, arom-H), 8.11 (d, $J = 8.74$ Hz, 2H, arom-H); FT-IR (v, cm^{-1} KBr disc): 3175, 3057, 2957, 1650, 1610, 1489, 1398, 1366, 1222, 1146, 1090, 843.

9-(4-Methylphenyl)-3,3,6,6-tetramethyl-1,8-dioxodecahydroacridine(4f)Mp, 317–319 °C (Lit.^{xviii} 318–320); ^1H NMR (400 MHz, CDCl_3 , dppm): 0.99 (s, 6H, 2 CH_3), 1.09 (s, 6H, 2 CH_3), 2.17 (d, $J = 16.0$ Hz, 2H, CH_2), 2.24 (d, $J = 16.8$ Hz, 2H, CH_2), 2.25 (d, $J = 16.0$ Hz, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.34 (d, $J = 16.8$ Hz, 2H, CH_2), 5.07 (s, 1H, CH), 7.02 (d, $J = 8.0$ Hz, 2H, arom-H), 7.19 (br., 1H, NH), 7.24 (d, $J = 8.0$ Hz, 2H, arom-H); FT-IR (v, cm^{-1} KBr disc): 3184, 3069, 2959, 1651, 1606, 1492, 1398, 1366, 1222, 1146.

9-(4-Methoxyphenyl)-3,3,6,6-tetramethyl-1,8-dioxodecahydroacridine(4g)Mp, 273–275°C (Lit.^{xxi} 275–277); ^1H NMR (300 MHz, DMSO-d_6 , dppm): 0.85 (s, 6H, 2 CH_3), 0.99 (s, 6H, 2 CH_3), 1.96 (d, $J = 16.1$ Hz, 2H, CH_2), 2.15 (d, $J = 16.1$ Hz, 2H, CH_2), 2.29 (d, $J = 17.0$ Hz, 2H, CH_2), 2.43 (d, $J = 17.0$ Hz, 2H, CH_2), 3.64 (s, 3H, OCH_3), 4.74 (s, 1H, CH), 6.70 (d, $J = 8.6$ Hz, 2H, arom-H), 7.04 (d, $J = 8.6$ Hz, 2H, arom-H), 9.23 (s br., 1H, NH); FT-IR (v, cm^{-1} KBr disc): 3205, 3072, 2959, 1645, 1607, 1509, 1484, 1396, 1368, 1224, 1145, 1032, 835.

9-(4-Bromophenyl)-3,3,6,6-tetramethyl-1,8-dioxodecahydroacridine(4h)Mp, 239–241 °C (Lit.^{xv} 241–243); ^1H NMR (400 MHz, CDCl_3 , dppm): 0.99 (s, 6H, 2 CH_3), 1.11 (s, 6H, 2 CH_3), 2.18 (d, $J = 16.0$ Hz, 2H, CH_2), 2.25 (d, $J = 16.4$ Hz, 2H, CH_2), 2.27 (d, $J = 16.0$ Hz, 2H, CH_2), 2.37 (d, $J = 16.4$ Hz, 2H, CH_2), 5.06 (s, 1H, CH), 6.85 (br., 1H, NH), 7.25 (d, $J = 8.4$ Hz, 2H, arom-H), 7.33 (d, $J = 8.4$ Hz, 2H, arom-H); FT-IR (v, cm^{-1} KBr disc): 3176, 3059, 2956, 1648, 1609, 1489, 1396, 1366, 1223, 1171, 1146, 1012, 842.

9-(3-Hydroxyphenyl)-3,3,6,6-tetramethyl-1,8-dioxodecahydroacridine(4i)Mp, 199–301 °C (Lit.^{xxi}300); ^1H NMR (400 MHz, DMSO-d_6 , dppm): 0.89 (s, 6H, 2 CH_3), 1.01 (s, 6H, 2 CH_3), 1.99 (d, $J = 16.0$ Hz, 2H, CH_2), 2.16 (d, $J = 16.0$ Hz, 2H, CH_2), 2.31 (d, $J = 16.8$ Hz, 2H, CH_2), 2.43 (d, $J = 16.8$ Hz, 2H, CH_2), 4.73 (s, 1H, CH), 6.42 (d, $J = 7.6$ Hz, 1H, arom-H), 6.56 (d, $J = 7.2$ Hz, 1H, arom-H), 6.62 (s, 1H, arom-H), 6.91 (t, $J = 7.6$ Hz, 1H, arom-H), 9.03 (s br., 1H, NH or OH), 9.24 (s br., 1H, NH or OH); FT-IR (v, cm^{-1} KBr disc): 3414, 3337, 3058, 2957, 1646, 1627, 1596, 1477, 1453, 1363, 1257, 1217, 1144.

9-(4-Hydroxyphenyl)-3,3,6,6-tetramethyl-1,8-dioxodecahydroacridine(4j) Yield, 91 %; mp, 275–277 °C (Lit.^{xxi}271–274); ^1H NMR (400 MHz, DMSO-d_6 , dppm): 0.85 (s, 6H, 2 CH_3), 0.99 (s, 6H, 2 CH_3), 1.96 (d, $J = 16.1$ Hz, 2H, CH_2), 2.14 (d, $J = 16.1$ Hz, 2H, CH_2), 2.29 (d,

$J = 17.0$ Hz, 2H, CH₂), 2.41 (d, $J = 17.0$ Hz, 2H, CH₂), 4.68 (s, 1H, CH), 6.51 (d, $J = 8.4$ Hz, 2H, arom-H), 6.91 (d, $J = 8.4$ Hz, 2H, arom-H), 8.99 (s br., 1H, NH or OH), 9.25 (s br., 1H, NH or OH); FT-IR (ν , cm⁻¹KBr disc): 3415, 3277, 3028, 2954, 1641, 1590, 1475, 1422, 1373, 1263, 1221, 1142.

Results and discussion

First, the reaction between 4-chlorobenzaldehyde **1c** (1 mmol), dimedone **2** (2 mmol), and ammonium acetate **3** (1 mmol) for the synthesis of compound **4c** was selected as the test reaction and optimized with different nano metal oxide catalysts in terms of various parameters like catalyst amount, effect of solvent, and influence of temperature. A summary of the optimization experiments is provided in Table 1. As seen, although all used nano metal oxide catalysts show good catalytic effects in the model reaction, but Fe₃O₄ nanoparticles improves the reaction more effectively than others, obtaining higher yields of **4c**. For finding the best catalyst amount, we started the experiments using 0.01 g of each catalyst. Moderate yields of the product were obtained in this condition. Increasing the amount of each of the catalysts increased the yields of the product **4c**. The optimal amount was 0.09 g (Entry 16) under solvent-free conditions; increasing the amount of the catalyst beyond this value had no significant effect on the yields and reaction times. Subsequently, the effect of different solvents on the reaction rate as well as the product yield was investigated. As can be seen from Table 1, for all used catalysts, the best results were achieved under solvent-free conditions. The effect of temperature on the reaction was also studied in the same model reaction. It was observed that the yield increased as the reaction temperature was raised, and at 100 °C the product **4c** was obtained in excellent yield. Moreover, to substantiate the important role of the catalyst, the reaction was carried out at 100 °C in the absence of the catalyst under solvent-free conditions (Entry 1). As a result, only low yield of the product was formed, indicating that the catalyst is necessary for the reaction.

Table 1. Synthesis of compound **4c** in the presence of the Al₂O₃, TiO₂, and Fe₃O₄ nanoparticles as catalysts under different reaction conditions.

Entry	Nano metal oxide	Catalyst amount (g)	Solvent	T (°C)	Time (min)	Yield* (%)
1	----	----	----	100	160	21
2	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.01	----	80	59/61/57	40/40/44
3	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.01	----	90	56/55/49	43/43/49
4	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.01	----	100	48/47/45	48/51/57
5	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.03	----	80	41/43/40	50/57/59
6	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.03	----	90	36/40/35	58/63/68
7	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.03	----	100	30/35/31	60/66/71
8	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.05	----	80	27/24/22	66/69/73
9	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.05	----	90	27/25/20	70/72/79
10	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.05	----	100	24/23/20	73/75/81
11	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.07	----	80	22/21/19	66/78/84
12	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.07	----	90	20/20/18	73/79/87
13	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.07	----	100	20/20/18	80/83/89
14	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.09	----	80	20/20/18	83/87/90
15	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.09	----	90	20/19/16	87/90/92
16	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.09	----	100	20/18/16	89/95/97
17	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.11	----	80	20/20/20	80/85/88
18	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.11	----	90	20/20/20	82/86/89
19	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.11	----	100	18/17/17	84/86/92
20	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.09	----	110	18/16/16	85/87/95
21	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.09	EtOH	Reflux	115/115/90	57/65/76
22	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.09	MeOH	Reflux	115/115/90	50/60/70

23	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.09	CH ₂ Cl ₂	Reflux	115/115/90	33/41/47
24	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.09	CH ₃ CN	Reflux	115/115/90	40/43/54
25	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	0.09	CH ₃ CO ₂ Et	Reflux	115/115/90	30/35/45

Reaction conditions: 4-chlorobenzaldehyde **1b** (1 mmol), dimedone**2** (2 mmol) , and ammonium acetate **3** (1 mmol). * Isolated yields.

Thereafter, the applicability of the method was evaluated for the synthesis of other 1,8-Dioxodecahydroacridines using a wide range of aromatic aldehydes. Our observations are recorded on Table 2. Fe₃O₄ nanoparticles proved to be the better catalyst than nano-sized Al₂O₃ and TiO₂ in terms of yield and reaction time.

Table 2. synthesis of 1,8-Dioxodecahydroacridines **4a-j**, catalyzed by metal oxide nanoparticles

Comp. no	Ar	Catalyst	Time (min)	Yield* (%)
4a	C ₆ H ₅	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	23/18/13	78/84/89
4b	2-ClC ₆ H ₄	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	23/20/17	81/86/90
4c	4-ClC ₆ H ₄	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	20/18/16	89/95/97
4d	3-O ₂ NC ₆ H ₄	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	19/20/13	85/92/94
4e	4-O ₂ NC ₆ H ₄	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	25/20/15	89/93/96
4f	4-MeC ₆ H ₄	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	28/26/22	87/90/93
4g	4-MeOC ₆ H ₄	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	20/18/16	85/91/93
4h	4-BrC ₆ H ₄	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	27/25/22	80/85/90
4i	3-HOC ₆ H ₄	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	29/20/17	88/91/96
4j	4-HOC ₆ H ₄	Al ₂ O ₃ /TiO ₂ /Fe ₃ O ₄	31/20/15	79/85/92

Reaction conditions: 4-chlorobenzaldehyde **1c** (1 mmol), dimedone**2** (2 mmol) , and ammonium acetate **3** (1 mmol), nano metal oxide(0.09 g), 100 °C, solvent-free. * Isolated yields.

On the other hand, the reusability of three nano catalysts in model reaction was also investigated. For this purpose, after separation of the catalyst according to the procedure outlined in the experimental section, the recovered catalysts were washed with hot ethanol and subsequently dried at 60 °C under vacuum for 1 h before being reused in a similar reaction. All the three catalysts could be used at least five times without significant reduction in its activity (89/95/97, 89/93/96, 87/91/95, 86/90/93 and 85/88/92% yields for nano Al₂O₃/TiO₂/Fe₃O₄ catalysts in first to fifth use, respectively) which clearly demonstrates the practical reusability of these catalysts (Fig. 1). However, in the case of Fe₃O₄ nanoparticles, easy magnetic separation, as explained in experimental section, makes this catalyst attractive in view of green chemistry and catalysis science.

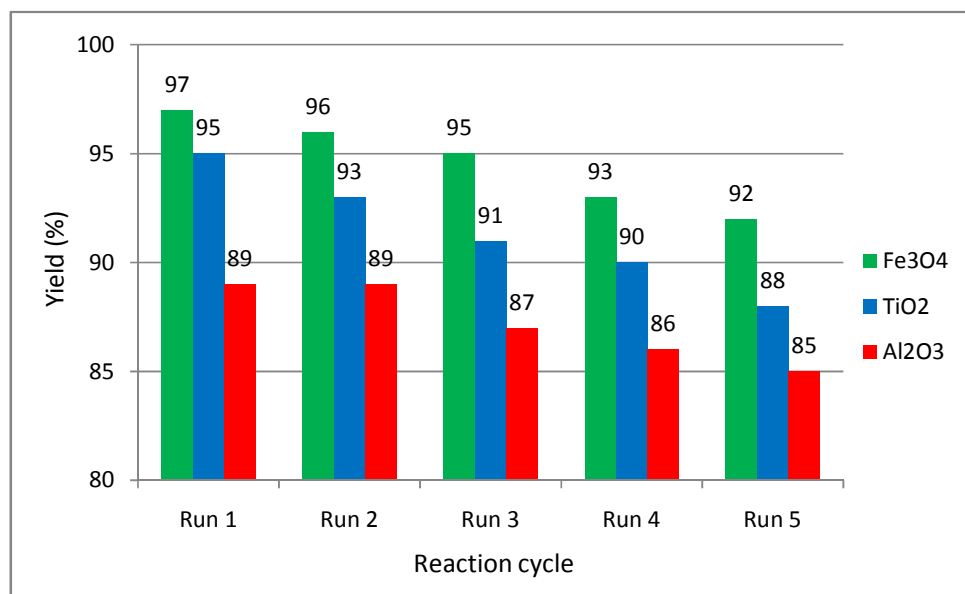


Fig. 1. Effect of recycling on catalytic activity of Al₂O₃, TiO₂, and Fe₃O₄ in the synthesis of **4c** in model reaction.

The applicability and efficiency of our catalysts were compared with some of the reported methods for the synthesis of 1,8-Dioxodecahydroacridines. This comparison is shown in Table 3. It is clear from the data that our procedure with nanoFe₃O₄ as catalyst gave high yields of the products in shorter reaction times than the other conditions. Moreover, magnetically recyclable of Fe₃O₄ nanoparticles makes it superior over other reported methods.

Table 3. Comparison of the efficiencies of different catalysts for the one-pot three-component synthesis of 1,8-Dioxodecahydroacridines.

Catalyst	Conditions			Time (min)	Yield (%)	Ref.
	Solvent	T/°C	Other			
[Hmim]TFA	-----	80	-----	240–420	78–89	xiii
Brønsted acidic imidazolium salts	H ₂ O	Reflux	-----	240	79–91	xiv
Zn(OAc) ₂	H ₂ O	Reflux	-----	120–180	84–94	xv
Proline	H ₂ O/EtOH	65	-----	300–360	73–88	xvi
Amberlyst-15	CH ₃ CN	Reflux	-----	270–390	81–95	xvii
CeCl ₃ ·7H ₂ O	[bmim][BF ₄]	100	-----	180	82–94	xviii
Silica-bonded s-sulfonic acid	EtOH	Reflux	-----	60–270	84–96	xix
Silica-bonded N-propyl sulfamic acid	EtOH	Reflux	-----	120–300	86–93	xx
3-(Carboxymethyl)-1-methyl-1Himidazol-3-ium trifluoroacetate	H ₂ O/EtOH	reflux	-----	60–90	81–90	xxi
[CMIM][CF ₃ COO]						
Carbon-Based Solid Acid	-----	100	-----	15–50	80–92	xxii
Al ₂ O ₃ Nanoparticles	-----	100	-----	19-31	78-89	This work
TiO ₂ Nanoparticles	-----	100	-----	18-26	84-95	This work
Fe ₃ O ₄ Nanoparticles	-----	100	-----	13-22	89-97	This work

Conclusion

In conclusion, the catalytic activity of three commercially available nano-sized metal oxides including Al_2O_3 , TiO_2 , and Fe_3O_4 were compared in the synthesis of 1,8-Dioxodecahydroacridines by one-pot three-component reaction of aldehyde, dimedone, and ammonium acetate. The reactions proceeded under solvent-free conditions at $100\text{ }^\circ\text{C}$ giving the high yields of the products in short reaction times. Among the three tested nano catalysts, Fe_3O_4 nanoparticles proved to be the better catalyst than others in terms of yield, reaction time, and easy separation. Some attractive features of these protocols are high yields, short reaction times, easy work-up, high catalytic activity and recyclability and reusability of the catalyst. The catalysts could be used at least five times without substantial reduction in their catalytic activities.

Acknowledgment

The authors express their gratitude to the Islamic Azad University, Mashhad Branch for its financial support.

References

- i. P. Hu, and M. Long, *Appl. Catal. B* 181,103(2016).
- ii. A.H. Chughtai, N. Ahmad, H.A. Younus, A. Laypkov, and F. Verpoort, *Chem. Soc. Rev.* 44, 6804 (2015).
- iii. A. Davoodnia, R. Mahjoobin, and N.Tavakoli-Hoseini, *Chin. J. Catal.* 35,490 (2014).
- iv. M. Hara, *ChemSusChem* 2,129(2009).
- v. Z. Zarnegar, J. Safari, and Z. Mansouri-Kafroudi, *Catal. Commun.* 59, 216(2015).
- vi. A. Davoodnia, Z.B. Atefeh, H. Behmadi, *Chin. J. Catal.* 33, 1797(2012).
- vii. Z. Hassani, *Lett. Org. Chem.* 11,546(2014).
- viii. H. Mirzaei, and A.Davoodnia, *Chin. J. Catal.* 33,1502(2012).
- ix. F. Javadi, and R.Tayebee, *Microporous Mesoporous Mater.* 231, 100(2016).
- x. M. Hosseini-Sarvari, and S. Najafvand-Derikvandi, *C. R. Chim.* 17, 1007(2014).
- xi. M.Z. Kassae, R. Mohammadi, H. Masrouri, and F.Movahedi, *Chin. Chem. Lett.* 22, 1203(2011).
- xii. Z. Mirjafary, H. Saeidian, A. Sadeghi, and F.M. Moghaddam, *Catal. Commun.* 9, 299 (2008).
- xiii. M. Dabiri, M. Baghbanzadeh, and E. Arzroomchilar, *Catal. Commun.* 9, 939 (2008).
- xiv. W. Shen, L.M. Wang, H. Tian, J. Tang, and J.J. Yu, *J. Fluorine Chem.* 130, 522 (2009).
- xv. S. Balalaie, F. Chadegani, F. Darviche, and H.R. Bijanzadeh, *Chin. J. Chem.* 27, 1953 (2009).
- xvi. K. Venkatesan, S.S. Pujari, and K.V. Srinivasan, *Synth. Commun.* 39, 228 (2009).
- xvii. B. Das, P. Thirupathi, I. Mahender, V.S. Reddy, and Y.K. Rao, *J. Mol. Catal. A: Chem.* 247, 233 (2006).
- xviii. X. Fan, Y. Li, X. Zhang, G. Qu, and J. Wang, *Heteroat. Chem.* 18, 786 (2007).
- xix. K. Niknam, F. Panahi, D. Saberi, and M. Mohagheghnejad, *J. Heterocyclic Chem.* 47, 292 (2010).
- xx. F. Rashedian, D. Saberi, and K. Niknam, *J. Chin. Chem. Soc.* 57, 998 (2010).
- xxi. D. Patil, D. Chandam, A. Mulik, P. Patil, S. Jagadale, R. Kant, V. Gupta, and M. Deshmukh, *Catal. Lett.* 144, 949 (2014).
- xxii. A. Davoodnia, A. Khojastehnejad, and N. Tavakoli-Hoseini, *Bull. Korean Chem. Soc.* 32, 2243 (2011).

- xxiii. A. Nakhaei, S. Yadegarian, and A. Davoodnia, *Heterocycl.Lett.*6, 329 (2016).
- xxiv. A. Nakhaei, A. Davoodnia, and A. Morsali, *Res. Chem. Intermed.*41, 7815(2015).
- xxv. A. Nakhaei, A. Davoodnia, *Chin. J. Catal.*35, 1761(2014).
- xxvi. S. Yadegarian, A Davoodnia, and A. Nakhaei, *Orient. J. Chem.*31, 573(2015).
- xxvii. A. Davoodnia, and A. Nakhaei, *Synth. React. Inorg.Metal-Org. Nano-Met. Chem.*46, 1073(2016).
- xxviii. A. Davoodnia, A. Nakhaei, and N. Tavakoli-Hoseini, *Z. Naturforsch. B*, 71, 219 (2016).
- xxix. M. Rohaniyan, A. Davoodnia, and A. Nakhaei, *Appl. Organometal. Chem.* 30, 626 (2016)

Received on October 5, 2016.