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Wells–Dawson heteropolyacid as reusable catalyst for sustainable synthesis of flavones

Daniel O. Bennardi[a], Gustavo P. Romanelli[a,b], Ángel G. Sathicq[b,*], Juan C. Autino[a], Graciela T. Baronetti[c], Horacio J. Thomas[d]

[a] Cátedra de Química Orgánica, Facultad de Ciencias Agrarias y Forestales, UNLP, Calles 60 y 119, B1904AAN La Plata, Argentina
[b] Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. J.J. Ronco" (CINDECA), Departamento de Química, Facultad de Ciencias Exactas, UNLP-CCT-CONICET. Calle 47 N° 257, B1900AJK La Plata, Argentina
[c] Departamento de Ingeniería Química, Facultad de Ingeniería, Universidad de Buenos Aires, Ciudad Universitaria, C1428BG Buenos Aires, Argentina
[d] Planta Piloto Multipropósito PlaPiMu, UNLP-CICPBA, Camino Centenario y 508,1987 Manuel B. Gonnet, Argentina

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ABSTRACT

The behavior of Wells–Dawson ($H_6P_2W_{18}O_{62}\cdot 24H_2O$, WD) acid, both bulk and supported on silica, for the cyclodehydration reaction of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione to obtain flavone was studied in heterogeneous conditions, using toluene as solvent. Catalytic experiences with bulk and supported catalysts with different WD acid loadings and reuse of the catalysts were done. The catalytic activity of supported catalysts was higher than that of the bulk catalyst, and their activity was almost constant after three reaction cycles. The following reaction conditions: reflux toluene and 1% mmol of WD supported on silica (0.4 g WD acid by gram of silica) were used for the preparation of five flavones. Yields above 85% were obtained in 4–5 h.

1. Introduction

It is well known that the use of conventional liquid and Lewis acids such as H_2SO_4, HF, HCl, $AlCl_3$, and $ZnCl_2$ poses risks in handling, containment, disposal and regeneration due to their corrosive and toxic nature. The processes used in the industry for the manufacture of specialty chemicals in the field of pharmaceutical, agrochemical and flavor/fragrance products are largely based on stoichiometric organic synthesis, but they lead to a large quantity of byproducts [1]. For this reason, there is an urgent need to eliminate the aggressive mineral acid-catalyzed processes [2].

The use of solid (heterogeneous) catalysts in organic synthesis and in the industrial manufacture of chemicals is increasingly important since they provide green alternatives to homogeneous catalysts [3,4]. Different solid acid catalysts such as inorganic oxides, mixed oxides, including alumina, silica, titania, zirconia, zeolites, clays, and supported reagents have been used [5].

Catalysis by heteropolyacids (HPAs) and related compounds is a field of increasing importance worldwide. Numerous developments are being carried out in basic research as well as in fine chemistry processes [6]. HPAs possess a very strong acidity, but theyexhibit the characteristic features of bulk-type catalysis (pseudo-liquid bulk type), in which the reagent molecules are absorbed between the polyanions (rather than in a polyanion) in the ionic crystal by replacing crystallization water or expanding the lattice, and the reaction occurs there [7].

The reactions catalyzed by both heterogeneous and homogeneous systems have been reviewed by many researchers. The reactions in which they can be used, from dehydration, cyclization or esterification up to amine oxidation or olefin epoxidation, may find wide applications in fine chemical production, such as fragrances, pharmaceuticals and food [8–14].

Although there are many structural types of HPAs, the majority of the catalytic applications use the most common commercial Keggin-type and then the Wells–Dawson HPAs especially for acid catalysts, owing to their availability and chemical stability [15,16]. The general formula of the Wells–Dawson heteropolyanion is $[(X^{n+})_2M_{18}O_{62}]^{(16-2n)-}$, where X^{n+} represents a central atom, such as phosphorous(V), arsenic(V), sulfur(VI), and fluorine surrounded by a cage of M addenda atoms, such as tungsten(VI), molybdenum(VI) or a mixture of elements, each of them composing MO_6 (M-oxygen) octahedral units. The structure, known as α isomer,

* Corresponding author. Tel.: +54 221 421 1353; fax: +54 221 421 1353.
E-mail address: agsathicq@quimica.unlp.edu.ar (Á.G. Sathicq).

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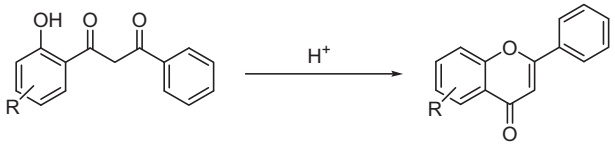


Scheme 1. cyclodehydration of 1-(2-hydroxyphenyl)-1,3-diketones.

possesses two identical "half units" of the central atom surrounded by nine octahedral units XM_9O_{31} linked through oxygen atoms [17]. Recently, we have used Wells–Dawson heteropolyacids in a range of processes such as preparation of heterocycles [18,19] and protection/deprotection of organic functional groups [20–22].

Flavones constitute a large number of natural products with many medicinal applications. Because of their broad range of biological activities this class of molecule has been extensively investigated, and more than 4000 chemically unique flavonoids have been isolated from plants [23]. They exhibit diverse biological and pharmacological activities, for example, antibacterial, antifungal [24,25], anticancer [26], gastro-protective [27], antioxidant [28] and anti-HIV [29]. Furthermore, it has been reported that some flavones have a repelling property against some phytophagous insects and a subterranean termite (*Coptotermes* sp.) acting as an antifeedant [30].

Various strategies have been developed to synthesize flavones. One of the most commonly used methods consists of the cyclodehydration of 1-(2-hydroxyphenyl)-1,3-diketones [31]. This is usually a catalyzed reaction (Scheme 1) and it has been performed in different media. Some reaction conditions employed were the use of excess of sulfuric acid in glacial acetic acid [32], cationic exchange resins in isopropanol [33], $CuCl_2$ in ethanol [31], and ionic liquid under microwave irradiation [34]. Recently, we reported a more suitable method for their synthesis, including heteropolyacids [35–37] and-carbon supported triflic acid [38].

The main goal of the present work was to study the catalytic activity of both bulk and silica-supported WD in the reaction of cyclization of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione to flavone.

2. Experimental

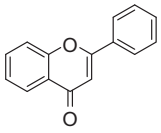
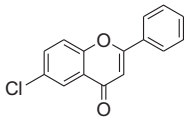
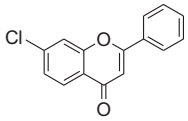
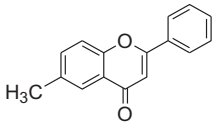
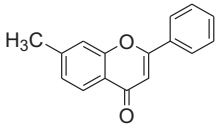
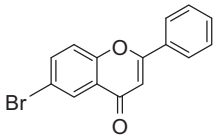
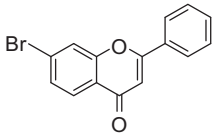
2.1. Preparation of catalysts

$H_6P_2W_{18}O_{62}{\cdot}24H_2O$ (WD) was synthesized as described elsewhere [39] from an aqueous solution of α/β $K_6P_2W_{18}O_{62}{\cdot}10H_2O$ salt. The WD silica-supported catalyst was obtained by wet impregnation of Grace Davison silica (Grade 59, specific area = 250 m^2/g) with an aqueous solution of the synthesized WD. Catalysts containing 0.1, 0.2, 0.4 and 0.6 g/g of WD acid were prepared ($0.1WDSiO_2$, $0.2WDSiO_2$, $0.4WDSiO_2$ and $0.6WDSiO_2$). Then, samples were dried at room temperature in a vacuum desiccator for 8 h.

2.2. Catalyst characterization

Bulk and supported catalysts were characterized by ^{31}P MAS-NMR measurements. The ^{31}P MAS-NMR spectra were recorded in Bruker MSL-300 equipment operating at frequencies of 121.496 MHz. A sample holder of 5 mm diameter and 17 mm in height was used. The spin rate was 2.1 kHz, and several hundreds of pulse responses were collected. Chemical shifts were expressed in parts per million with respect to 85% H_3PO_4 as an external standard for ^{31}P-NMR.

Table 1
Preparation of substituted flavones using $0.4WDSiO_2$ catalyst.[a]

Entry	Flavone	Time (h)	Yield (%)	TOF[b]
1		4.5	87	19.3
2		4.5	86	19.1
3		4.5	85	18.9
4		5	86	17.2
5		5	87	17.4
6		5	83	16.6
7		5	82	16.4

[a] Toluene, reflux. Catalyst: 1% mmol.
[b] Turnover frequency (product mol s × WD mol s^{-1} × h^{-1}).

2.3. General procedure for the preparation of substituted flavones

All the starting 1,3-diketones were prepared following a method described elsewhere [21]. A mixture of 1,3-diketone (0.5 mmol) dissolved in 3 ml toluene and catalyst (1% mmol) was refluxed with stirring for the indicated time (see Table 1). The reaction was followed by TLC using TLC aluminum sheets (silica gel 60 F254 Merck). When the reaction time was over, the catalyst was filtered and washed twice with toluene (1 ml). The extracts were combined and washed with NaOH 3 M, then with H_2O, and dried with anhydrous sodium sulfate. The organic solution was concentrated in vacuum. All the solid crude products were recrystallized from methanol. Products were identified by ^1H and ^{13}C NMR with a Bruker Avance DPX-400 instrument, operating at 400 MHz for ^1H and 100 MHz for ^{13}C NMR, and by comparison with authentic samples prepared using sulfuric acid as catalyst.

2.4. Catalytic tests

All the reactions were carried out in glass tubes (10 ml), by adding the corresponding catalyst to a solution of 0.5 mmol of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione in toluene, with stirring and heating at the indicated temperature (range: 65–110 °C). Samples (30 μl each) were withdrawn with a syringe at prescribed intervals. Each sample was diluted with toluene

to a volume of 10 ml. Then the absorbance values of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione contained in the samples were determined at λ = 420 nm using a UV/VIS spectrometer LAMBDA 35, Perkin Elmer. The absorbance values of standard solutions of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione in toluene were determined at λ = 420 nm to build the calibration plot.

The activity of bulk and supported catalysts for the cyclodehydration reaction of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanodione to obtain flavone was studied in heterogeneous conditions, using toluene as reaction solvent. Conversion to flavone as a function of the time was determined by means of UV–vis spectroscopy. In order to estimate the possible catalyst solubilization, additional tests were performed. The $0.4WDSiO_2$ sample (60 mg) was refluxed in toluene (3 ml) for 5 h, filtered and dried in vacuum till constant weight. Loss of mass was not detected. The refluxed toluene was used as solvent for attempting the reaction without adding the catalyst. After 20 h flavone was not detected, and the starting material was quantitatively recovered. Presence of W species in the filtrate was not detected by ICP.

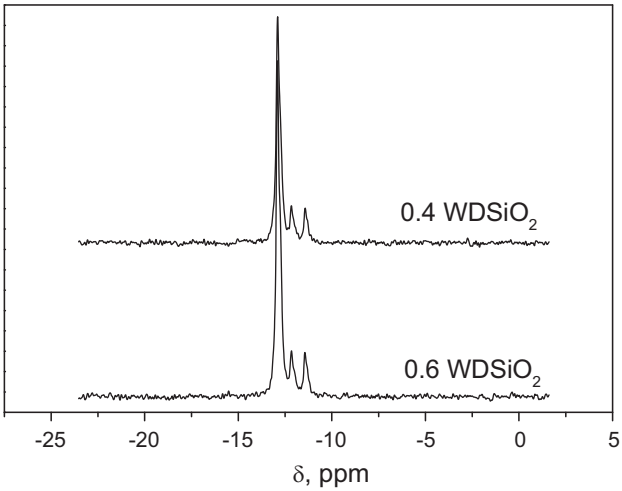


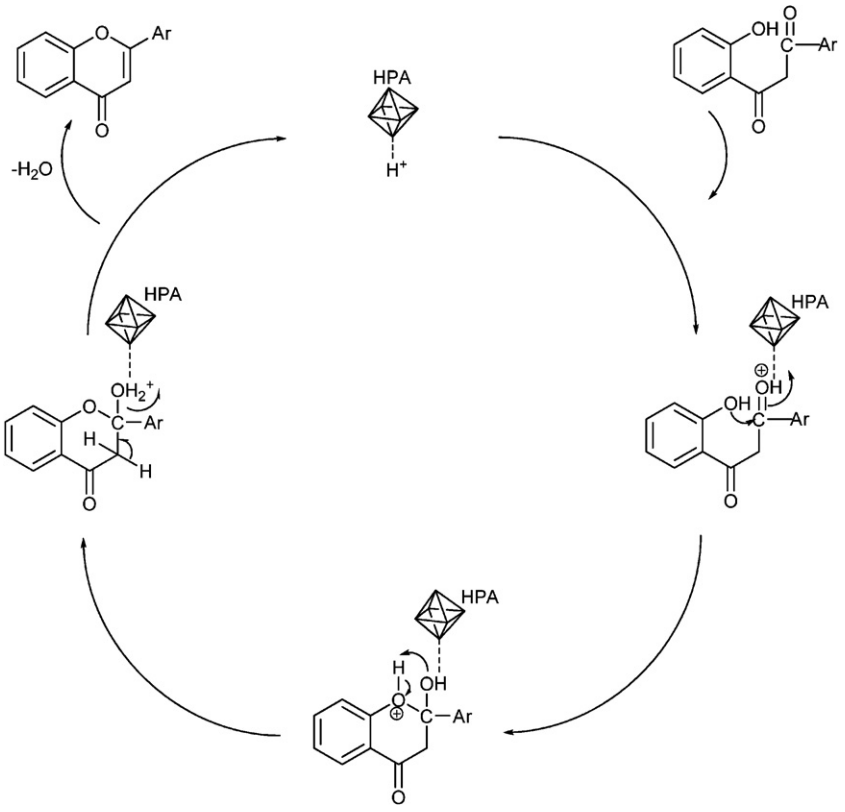
Fig. 1. ^{31}P-NMR spectra of 0.4 and 0.6 $WDSiO_2$.

3. Results and discussion

3.1. Characterization of bulk and supported WD acid

In a previous work [18], bulk WD acid was characterized by ^{31}P MAS-NMR. It is known that this pure acid has two equivalent phosphorus atoms, and consequently it has only one peak in the ^{1}P MAS-NMR spectrum. The chemical shift obtained for synthesized WD was only one peak at −12.8 ppm (using 85% H_3PO_4 as external reference). The ^{31}P MAS-NMR spectra of silica-supported samples ($0.4WDSiO_2$ and $0.6WDSiO_2$, Fig. 1) show a main peak with a chemical shift of −12.7 ppm, which indicates that after the impregnation and drying, the acid is supported keeping its Dawson structure, independent of the loading. In both samples, two new small signals close to −12 and −11 ppm are detected. As has been reported in detail in our previous work [40] for silica supported samples up to $0.2WDSiO_2$, these signals could be related to the presence of $H_6P_2W_{18}O_{62}$ species strongly interacting with the Si–OH groups of the support, and to lacunary species such as $P_2W_{21}O_{71}{}^{-6}$, respectively. These results and those obtained in a previous work [40] indicate that WD keeps its heteropolyoxoanion structure after the impregnation and drying steps when it is supported on SiO_2 using a WD loading in the range 0.1 to 0.6gWD/g SiO_2.

On the other hand, DRX spectra for all the samples only showed the pattern of the support indicating that there exists a good dispersion of WD acid on the silica [40].



Scheme 2.

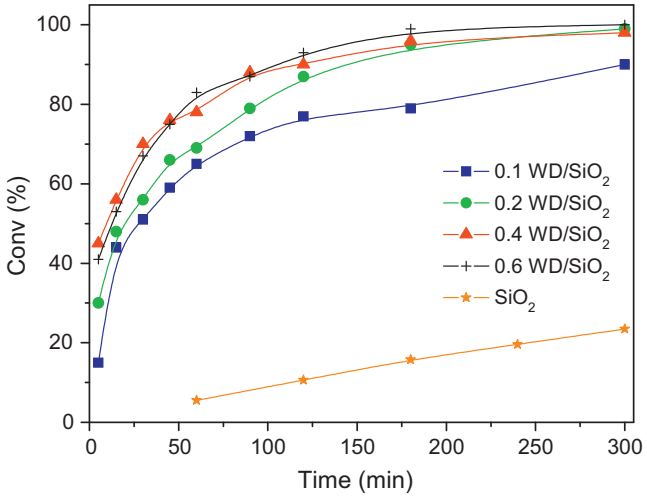


Fig. 2. Conversion of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione to flavone vs. time for supported catalysts (100 mg) with different acid ratios.

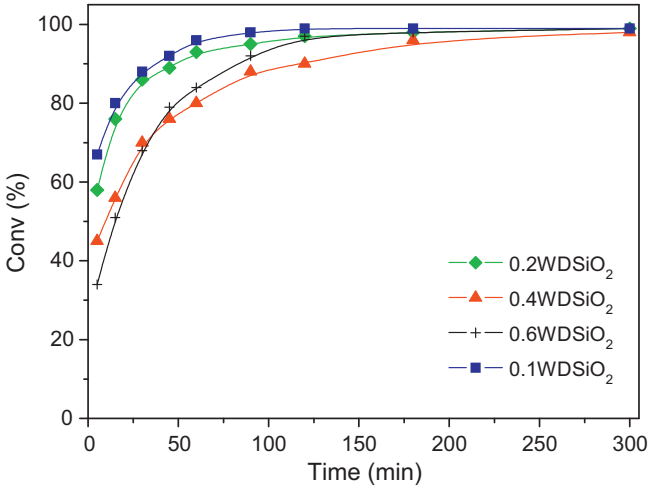


Fig. 3. Conversion of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione to flavone vs. time for supported catalyst maintaining the initial reagent to active phase ratio constant.

3.2. Catalyst activity

In a previous paper [41] the pseudo liquid or surface-type behavior of Wells–Dawson acid in organic reactions in liquid phase was analyzed theoretically and experimentally. As previously shown [31], $H_5O_2^+$ species, bridged to secondary structures, built the tertiary heteropolyanion structure and then a cage-type structure was obtained. This three-dimensional framework was connected with all its neighbors, so all its acid active sites inside the cage could take part in catalysis by the diffusion of reagents from the solution.

Through theoretical calculations and experimental results we have shown that there is a direct relationship between polarity of organic molecules and the ability to diffuse inside the catalyst cage or framework. A nonpolar molecule does not diffuse inside and only interacts with surface acidic sites, but a polar molecule can move into the cage and then all internal acidic sites are available. When diffusion occurs, the number of active sites grows sharply. In this way, the higher the diffusion is, the closer the behavior of a bulk catalyst to a supported one results.

The 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione has two carbonyl groups in ß position so it is possible to believe that it is a polar molecule. Then we propose two different types of reactions, the first one in order to see if the catalyst shows a pseudo-liquid or surface-type behavior, and the second one to analyze the influence of different substituent groups and their positions on the substrate reactivity.

For the first, we used bulk and supported catalysts, and four catalysts with different charges of WD were prepared. Measurements at different reaction temperatures were also made. The variation of conversion as a function of time was also analyzed, and additional runs were made in order to see if the supported catalyst presents a deactivation process.

The probable mechanism for the reaction of cyclodehydration of 1,3-diketones has been described in the bibliography [42,43]. By using 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione as reagent (Scheme 2), the intramolecular nucleophilic attack leading to the ring closure is catalyzed by acidic sites; this addition is followed by elimination of water and regeneration of protons. In our case the acidic sites are provided by the WD.

Fig. 2 shows the results obtained for the cyclodehydration reaction of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione to flavone using supported catalysts with different WD loadings ($0.1WDSiO_2$, $0.2WDSiO_2$, $0.4WDSiO_2$ and $0.6WDSiO_2$).

Additional tests carried out with the support as catalyst indicate that the support has a very low catalytic activity, only 20% after 5 h of reaction. In this figure a noticeable increase in catalytic activity for supported catalysts can be observed. An increase in WD loading produces a conversion increment following the sequence $0.1WDSiO_2 < 0.2WDSiO_2 < 0.4WDSiO_2 \approx 0.6WDSiO_2$. For the highest WD content the catalytic activity is similar to $0.4WDSiO_2$ sample.

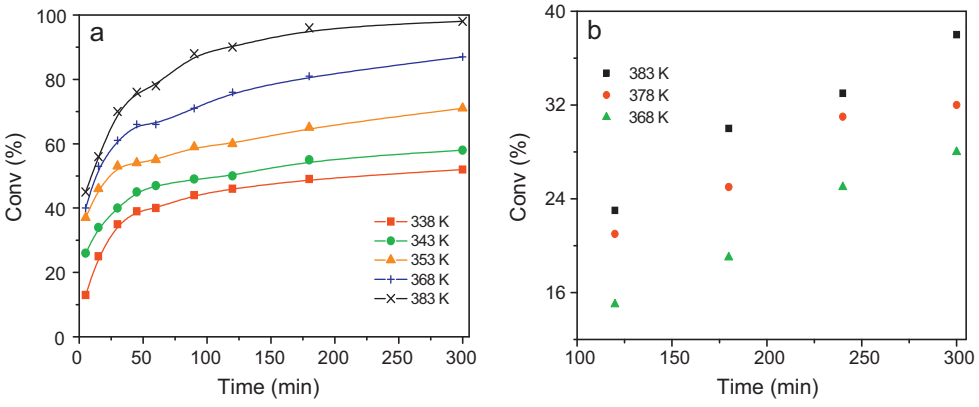


Fig. 4. Conversion of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione to flavones vs. time, at different reaction temperatures, (a) 0.4 $WDSiO_2$ catalyst, (b) bulk catalyst.

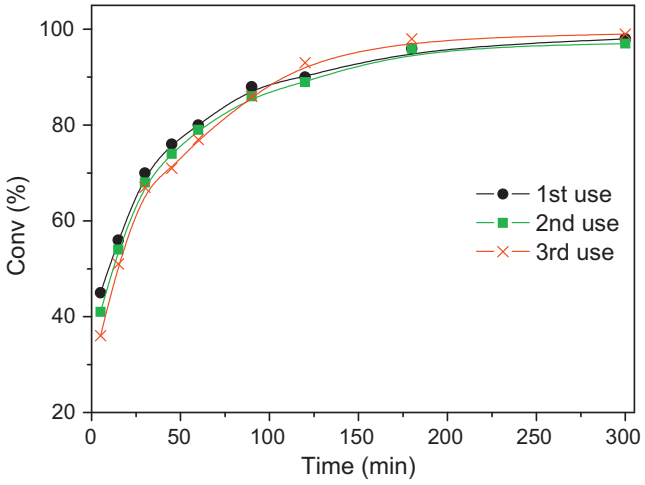


Fig. 5. Reuse of 0.4WDSiO$_2$. Conversion of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione vs. time.

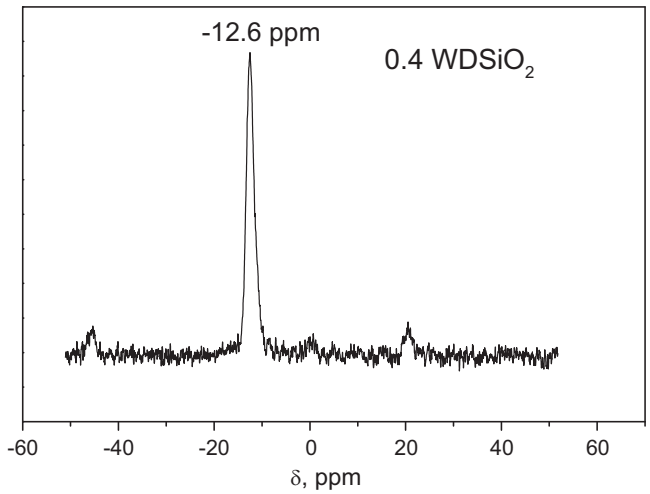


Fig. 6. ^{31}P-NMR spectra of 0.4 WDSiO$_2$ after the third reaction cycle.

On the other hand, catalytic tests keeping the ratio between initial reagent and amount of active phase constant were done (Fig. 3). For this purpose we used a variable mass of catalyst. It can be observed that the conversion values are similar for samples with low acid content in the range 0.1–0.2. In the same way, for the high acid content in the range 0.4–0.6 the conversion values are similar. These results may indicate that the acid dispersion is higher in the samples with the lower acid content.

3.2.1. Temperature effect

The effect of temperature in the range 65–110 °C on the reaction of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione to obtain flavone, using 0.4 WDSiO$_2$, was studied. This catalyst showed the best catalytic conversion by gram of catalyst (see Fig. 2).

Fig. 4 shows that the conversion is higher as temperature increases. Fig. 4a shows the conversion of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione to flavones versus time, at different reaction temperatures using 0.4 WDSiO$_2$ catalyst, being obtained conversions higher than 90% at reflux in toluene in 3 h. Fig. 4b shows the conversion of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione to flavones versus time, using a bulk catalyst.

Comparing the conversion values of supported and bulk catalysts at different temperatures it was observed that the difference between them were not so high as expected considering that the amount of employed catalyst was always the same and the supported ones have a well disperse active phase. So, these results could be explained in terms of pseudo-liquid behavior of bulk catalyst, as we described before. The difference with supported ones can be explained in terms of diffusion of reagents and products inside and outside crystallites on supported catalysts.

We assume that the difference in conversion between bulk and supported catalysts can be explained considering that they have microporous and mesoporous structures respectively, with 0.5 and 2.5 nm pore radius, so the diffusion factor in the whole reaction has a different influence on both systems.

3.2.2. Catalyst reuse

The catalytic behavior after three reaction cycles of 0.4WDSiO$_2$ catalyst was studied according to the protocol described in detail in the experimental section. Fig. 5 shows the conversion after each reaction cycle. All conversions are similar, indicating that the catalytic activity remains constant after three reaction cycles. The ^{31}P MAS-NMR spectra of silica-supported sample (0.4WDSiO$_2$ Fig. 6) after three reaction cycles shows only one peak corresponding to Wells–Dawson structure indicating that after the reaction cycles the structure of the heteropolyoxoanion keeps intact.

However, the small peaks (close to −12 and −11 ppm) in the used sample (Fig. 1), asigned to the $H_6P_2W_{18}O_{62}$ species strongly interacting with the Si–OH groups of the support, and to lacunary species such as $P_2W_{21}O_{71}{}^{-6}$, for the fresh sample have not been detected.

This fact would be indicating that during the procedure of washing before each new reaction cycle these species are lost.

3.2.3. Preparation of substituted flavones

The following reaction conditions: reflux toluene and 1% mmol 0.4WDSiO$_2$ catalyst were employed for the preparation of substituted flavones. The obtained results are listed in Table 1. The experiments were conducted until the 1,3-diketone was consumed or until no changes in the composition of the reaction mixture were observed. In all the cases, the desired products were obtained with high selectivity, almost free of secondary products. The unchanged starting materials were recovered nearly quantitatively. No stereoelectronic effects on the yields due owing to the substituent were observed.

4. Conclusions

In this work the performance of catalysts with Wells–Dawson ($H_6P_2W_{18}O_{62}\cdot 24H_2O$) structure was studied in the cyclodehydration reaction of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione to obtain flavone. The tests were carried out in heterogeneous conditions, at different reaction temperatures. The activity of the supported catalysts was higher than that of the bulk catalyst. Moreover, the activity of the supported catalyst remained almost constant after three cycles; it can be separated and recovered for further use.

The utilization of these solid catalysts provided interesting yields (above 85%) in the cyclization reaction of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanediones to substituted flavones, in reaction times of 4.5–5 h.

Acknowledgements

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References

[1] P.L. Mills, R.V. Chaudhari, Catal. Today 37 (1997) 367–404.
[2] B. Reddy, P. Sreekanth, P. Lakshmanan, J. Mol. Catal. A: Chem. 237 (2005) 93–100.
[3] A. Corma, H. García, Chem. Rev. 103 (2003) 4307–4365.
[4] I. Ledneczki, M. Darányi, F. Fulop, A. Molnár, Catal. Today 100 (2005) 437–440.
[5] G. Yadav, Catal. Surv. Asia 9 (2005) 117–137.
[6] M. Misono, N. Nojiri, Appl. Catal. A: Gen. 64 (1990) 1–30.
[7] T. Okuhara, Catal. Today 73 (2002) 167–176.
[8] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113–252.
[9] I. Kozhevnikov, Chem. Rev. 98 (1998) 171–198.
[10] I. Kozhevnikov, J. Mol. Catal. A: Chem. 262 (2007) 86–92.
[11] M. Misono, I. Ono, G. Koyano, G. Aoshima, Pure Appl. Chem. 72 (2002) 1305–1311.
[12] M. Misono, C.R. Acad. Sci., Ser. IIc: Chim 3 (2000) 471–475.
[13] N. Mizuno, M. Misono, Curr. Opin, Solid State Mater. Sci. 2 (1997) 84–89.
[14] L. Pizzio, P. Vázquez, C. Cáceres, M. Blanco, Appl. Catal. A, Gen 256 (2003) 125–139.
[15] I. Kozhevnikov, Catal. Rev. Sci. Eng. 37 (1995) 311–352.
[16] M. Pope, Heteropoly and Isopoly Oxometalates, Springer, Berlin, 1983.
[17] L. Briand, G. Baronetti, H. Thomas, Appl. Catal. A: Gen. 256 (2003) 37–50.
[18] G. Romanelli, D. Bennardi, D. Ruiz, G. Baronetti, H. Thomas, J. Autino, Tetrahedron Lett. 45 (2004) 8935–8939.
[19] G. Romanelli, A. Sathicq, J. Autino, H. Thomas, G. Baronetti, Synth. Commun. 37 (22) (2007) 3907–3916.
[20] G. Romanelli, G. Baronetti, H. Thomas, J. Autino, Tetrahedron Lett. 43 (42) (2002) 7589–7591.
[21] G. Romanelli, H. Thomas, G. Baronetti, J. Autino, Tetrahedron Lett. 44 (2003) 1301–1303.
[22] J. Sambeth, G. Romanelli, J. Autino, H. Thomas, G. Baronetti, Appl. Catal. A: Gen. 378 (1) (2010) 114–118.
[23] N. Ahmed, H. Ali, J.E. van Lier, Tetrahedron Lett. 46 (2005) 253–256, and references cited herehin.
[24] S. Alam, J. Chem. Sci. 116 (2004) 325–331.
[25] H. Göker, D. Boykin, S. Yildiz, Bioorg. Med. Chem. 13 (2005) 1707–1714.
[26] S. Martens, A. Mithöfer, Phytochemistry 66 (2005) 2399–2407.
[27] J. Ares, P. Outt, J. Randall, P. Murray, P. Weisshaar, L. Obrien, B. Ems, S. Kakodkar, G. Kelm, W. Kershaw, K. Werchowski, A. Parkinson, J. Med. Chem. 38 (1995) 4937–4943.
[28] H. Chu, H. Wu, Y. Lee, Tetrahedron 60 (2004) 2647–2655.
[29] J. Wu, X. Wang, Y. Yi, K. Lee, Bioorg. Med. Chem. Lett. 13 (2003) 1813–1815.
[30] M. Morimoto, K. Tanimoto, S. Nakano, T. Ozaki, J. Agric. Food Chem. 51 (2003) 389–393.
[31] G. Kabalka, A. Mereddy, Tetrahedron Lett. 46 (2005) 6315–6317.
[32] T. Wheeler, Organic Synth. 32 (1952) 72.
[33] Y. Hoshino, N. Takeno, Bull. Chem. Soc. Jpn. 60 (1987) 1919–1920.
[34] S. Sarda, M. Pathan, V. Paike, P. Pachmase, W. Jadhav, R. Pawar, Arkivoc 16 (2006) 43–48.
[35] D. Bennardi, G. Romanelli, J. Jios, J. Autino, G. Baronetti, H. Thomas, Arkivoc (xi) (2008) 123–130.
[36] D.O. Bennardi, D.M. Ruiz, G.P. Romanelli, G.T. Baronetti, H.J. Thomas, J.C. Autino, Lett. Org. Chem. 5 (8) (2008) 607–615.
[37] G. Romanelli, E. Virla, P. Duchowicz, A. Gaddi, D. Ruiz, D. Bennardi, D. Dell Valle Ortiz, J. Autino, J. Agric. Chem. Food. 8 (10) (2010) 6290–6295.
[38] D.O. Bennardi, G.P. Romanelli, J.C. Autino, L.R Pizzio, Catal. Commun. 10 (5) (2009) 576–581.
[39] G. Baronetti, L. Briand, U. Sedran, H. Thomas, Appl. Catal. A, Gen. 173 (1998) 265–272.
[40] J. Jíos, J. Autino, A. Pomilio, An. Asoc. Quím. Argent. 83 (1995) 183–189.
[41] J. Sambeth, G. Romanelli, J. Autino, H. Thomas, G. Baronetti, Appl. Catal. A: Gen. 378 (2010) 114–118.
[42] J. Jios, Doctoral Thesis, Universidad Nacional de La Plata, Facultad de Ciéncias Exactas, La Plata, 1996.
[43] D. Bennardi, G. Romanelli, J. Autino, L. Pizzio, P. Vázquez, C. Cáceres, M. Blanco, React. Kinet. Mech. Catal. 100 (2010) 165–174.