Title: Tantalum *vs* Niobium MCF nanocatalysts in the green synthesis of chromene derivatives

Authors: Agata Smuszkiewicz, Jesús López-Sanz, Izabela Sobczak, Rosa M. Martín-Aranda, Maria Ziolek, Elena Pérez-Mayoral

PII: S0920-5861(18)30776-4
DOI: https://doi.org/10.1016/j.cattod.2018.06.038
Reference: CATTOD 11527

To appear in: *Catalysis Today*

Received date: 15-3-2018
Revised date: 11-6-2018
Accepted date: 18-6-2018

Please cite this article as: Smuszkiewicz A, López-Sanz J, Sobczak I, Martín-Aranda RM, Ziolek M, Pérez-Mayoral E, Tantalum *vs* Niobium MCF nanocatalysts in the green synthesis of chromene derivatives, *Catalysis Today* (2018), https://doi.org/10.1016/j.cattod.2018.06.038

Tantalum *vs* Niobium MCF nanocatalysts in the green synthesis of chromene derivatives

Agata Smuszkiewicz[1], Jesús López-Sanz[1,2], Izabela Sobczak[2], Rosa M. Martín-Aranda[1], Maria Ziolek[2]*, Elena Pérez-Mayoral[1]*

[1]Departamento de Química Inorgánica y Química Técnica, Universidad Nacional de Educación a Distancia, UNED, Paseo Senda del Rey 9, E-28040 Madrid, Spain

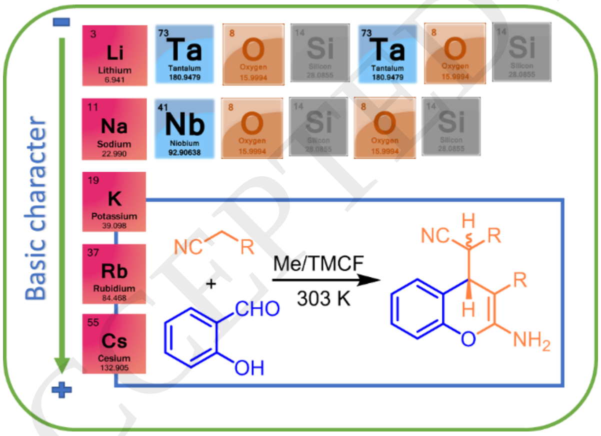
[2]Adam Mickiewicz University, Faculty of Chemistry, Umultowska 89b, 61-614 Poznan, Poland

Corresponding authors:

Elena Pérez Mayoral; eperez@ccia.uned.es

Phone (+34) 91 398 9047; Fax (+34) 91 398 6697

Graphical abstract



Highlights

- Nb and Ta show shared properties but different interaction with alkaline metals in Me/TMCF.
- Me/TaMCF samples showed higher Brönsted basicity than the Me/Nb analogues.
- Me/TaMCF are highly efficient bifunctional catalysts in the synthesis of chromenes.
- Basicity of the Me/TMCF samples are behind of the catalytic behaviour.
- A compromise between basicity and alkaline cation size influences the catalytic performance.

Abstract

TaMCF silicas modified with alkaline metals can be considered a novel family of highly efficient bifunctional catalysts involved in the synthesis of chromene derivatives, from salicylaldehyde 2 and acetonitrile compounds, under mild conditions, showing enhanced catalytic performance than their NbMCF analogues. The observed reactivity was mainly attributed to the higher basicity of the Me/TaMCF but also the texture of the samples. The Me/TaMCF silicas showed higher Brønsted basicity than the Nb ones as indicated by the stronger interaction between alkali metals and Ta in the UV-Vis and the test reaction experiments.

On the other hand, the basicity of Me/TaMCF together the reactivity degree and steric hindrance of the starting acetonitriles are key factors influencing the reaction selectivity. In conclusion, the basicity of the samples plays an important role initiating the reaction by activation of nucleophile but also a compromise between alkaline cation size and basicity is required.

Keywords: Nb and Ta mesoporous silicas, heterogeneous catalysis, multicomponent reactions, chromene derivatives

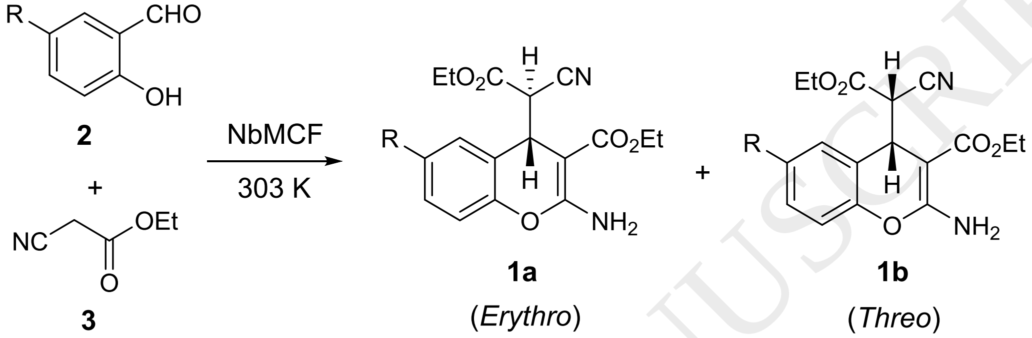
1. Introduction

Niobium and tantalum are transition metals belonging to the group V almost always paired together in nature and showing shared physico-chemical properties. Both elements as their oxide forms are recognized as catalyst supports or active catalysts, even combined with other metals, exhibiting interesting catalytic behavior in relevant organic transformations [1-5] and oxidative processes [6-8].

In the last decades, the development of Nb-containing molecular sieves has undergone a significant progress [9-10]. Such materials have been widely investigated in the synthesis of valuable products because of their catalytic properties. Our research groups both in cooperation have recently contributed to this progress reporting new families of aminopropyl organosilicas functionalized with transition metals centers, especially niobium, involved in the synthesis of *N*-alkylimidazoles under sonochemical conditions [11], Knoevenagel condensation [12], C=C isomerization reaction of safrole for the synthesis of interesting compounds useful in perfume manufacture [13] and the preparation of relevant nitrogen heterocyclic systems such as substituted quinolines and naphtiridines through the Friedländer reaction [14-15]. All of them can be considered bifunctional catalysts in which both functionalities can act in cooperation producing an enhancement of the overall reaction yields. The presence of Nb in the silica framework is responsible of an increasing of the basicity of the amine functions but also the metal center is involved in the reaction, probably by stabilizing the corresponding transition structures, as demonstrated by computational methods.

There are also some reports comprising the use of tantalum mesoporous silica catalysts although as a crushing minority. For instance, silica-supported alkoxo-tantalum complexes have been used in the deperoxidation of cyclohexyl hydroperoxide [16], Ta/SBA15 for the olefin epoxidation by using a benign oxidant such as H_2O_2 aqueous solution [17] or even chiral ligand modifying Ta/MCM-41 catalysts implied in the enantioselective oxidation of thioanisole [18]. Ziolek and co-workers have also participated on increasing the knowledge to stablish differences on the catalytic behavior of Nb or Ta-containing mesoporous silicas by using those in several organic transformations, highlighting the production of biofuels additives on sulphonated MCF materials modified with Nb and Ta [19] and acetalation of glycerol [20].

Interestingly, basicity can be also introduced on Nb doped mesoporous silicas by modifying within alkaline cations. In this sense, we also recently reported a new series of NbMCF mesoporous silicas modified with alkali metals useful as bifunctional catalysts yielding 2-amino-4*H*-chromenes in good to excellent yields, heterocyclic scaffolds of importance because of their therapeutic uses (Scheme 1) [21]. Our theoretical results indicated that the presence of alkaline oxides on Me/NbMCF catalysts (where M is Li, Na, K, Rb and Cs), showing strong basicity, activates the nucleophile initiating the reaction, whereas the Nb center is implied on the approaching of the reactants also stabilizing the aldolization transition structure.



Scheme 1. Synthesis of 2-amino-4*H*-chromenes over NbMCF silicas modified with alkaline metals.

Following our ongoing investigations and considering that Ta nanocatalysts have barely been explored in the synthesis of valuable compounds, the goal of this paper is aimed to stablish differences on the catalytic behavior between comparable series of TMCF mesoporous silicas (where T is Nb or Ta), modified with alkaline metals, in the multicomponent synthesis of 2-amino-4*H*-chromenes **1** (Scheme 1). Having in mind our previous results, it would be reasonable to expect cooperative effects between Ta and alkaline metals but also probably varying the appropriate basicity in comparison to the catalytic performance for the NbMCF series.

2. Materials and Methods

2.1. Synthesis of NbMCF and TaMCF mesoporous silicas

MCF materials were prepared by one-pot synthesis method described in Ref. [22]. For the preparation of NbMCF and TaMCF, the synthesis procedure was modified in order to introduce niobium and tantalum sources, niobium ethoxide and tantalum ethoxide, respectively. The source of Nb or Ta was added to the mixture 10 min after TEOS admission (TEOS/Nb and TEOS/Ta molar ratio = 64). Moreover, 1,3,5trimethylbenzene (TMB) / Pluronic ratio = 0.75 was applied (8 g, 1.4 mmol of Pluronic and 6 g, 49.92 mmol of TMB).

2.2. Modification of NbMCF and TaMCF materials with alkali metals

NbMCF and TaMCF supports were impregnated by using the incipient wetness method with aqueous solution of $MeCH_3COO$ (Me = Li, Na, K, Rb, Cs). The outgassed NbMCF and TaMCF were filled in with the appropriate amount of an aqueous solution of alkali metal acetate (CH_3COOLi, CH_3COONa, CH_3COOK, CH_3COOR, CH_3COOCs, a volume of the solution was a little bit higher than the pore volume of the support) and rotated and heated in an evaporator flask at 373 K. The impregnated powder was dried at 373 K for 18 h and then calcined at 723 K for 10 h. Two series of catalysts were obtained: Me/NbMCF and Me/TaMCF, where Me = alkali metal. The amount of alkali metal acetate used for the impregnation was calculated for the loading of metal equal to 0.5 mmol per 1 g of support. Such value gives rise to the following weight percent of metals: Li-0.35%; Na-1.15%; K-1.96%; Rb-4.27; Cs-6.65%. The surface area of the modified materials differs from that of the parent one and therefore the mole number of alkali metal cations calculated per m^2g^{-1} of the supports was calculated and shown in Table 1.

2.3. Characterization of the samples

The materials prepared were characterized using XRF, N_2 adsorption/desorption, UV–vis and test reactions.

X-ray fluorescence (XRF) was applied using MiniPal-Philips. The measurements were done using calibration curves prepared from mixtures of silica and Nb_2O_5 and silica and Ta_2O_5 (Si/Nb and Si/Ta from 5 to 300).

The N_2 adsorption/desorption isotherms at 77 K on materials studied were recorded using a static volumetric apparatus ASAP 2020 (Micromeritics). Before each sorption measurement the samples were outgassed at 383–393 K overnight until the residual pressure was lower than 0.7 Pa.

UV–vis spectra were recorded using a Varian-Cary 300 Scan UV–visible Spectrophotometer. Sample powders were placed into the cell equipped with a quartz window. The spectra were recorded in the range from 800 to 190 nm. Spectralon was used as a reference material.

2,5-Hexanedione cyclisation and dehydration was performed using a tubular, down-flow reactor that was carried out at atmospheric pressure, with nitrogen as the carrier gas. 0.05 g of catalyst was activated for 2 h at 673 K under nitrogen flow (40 cm^3 min^{-1}). Subsequently, 0.5 cm^3 of 2.5-hexanedione was passed continuously over the catalyst at 623 K. The substrate was delivered with a pump system and vaporized before being passed through the catalyst with the flow of nitrogen carrier gas (40 cm^3 min^{-1}). The reaction products were collected for 30 min downstream of the reactor in the cold trap (mixture of 2-propanoland liquid nitrogen) and analyzed by gas chromatography (CHROM-5, Silicone SE-30/Chromosorb G column).

2.4. Catalytic performance

The reactions were performed in a liquid phase under atmospheric pressure in a multi-experiment work station StarFish (Radley's Discovery Technologies UK). *In a typical procedure,* 2-hydroxybenzaldehyde (**2**) (2 mmol), and ethyl cyanoacetate (**3**) (4 mmol) were added to the 3-necked vessel of 10 mL of capacity, equipped with condenser and thermometer and magnetic stirred (0.8 cm). Subsequently, the catalyst (50 mg) was added and the reaction mixture was stirred (250 rpm) at room temperature, 303 K, during the appropriated reaction time shown in figures or tables. The samples were taken at different reaction times by diluting a small amount of the reaction mixture in dichloromethane (0.5 mL). Subsequently, the catalyst was filtered off and the solvent evaporated in vacuo.

Activation of the catalyst samples was carried out at 333 K overnight. The reactions were followed by TLC chromatography performed on DC-Aulofolien/Kieselgel 60 F245 (Merck) using mixtures of CH_2Cl_2/ EtOH in 98:2 as eluent. The characterization of the reaction products was carried out by ^{1}H NMR. NMR spectra were recorded with a Bruker AVANCE DPX-300 (300 MHz for^{1}H). ^{1}H chemical shifts (δ) in $CDCl_3$ or DMSO are given from internal tetramethylsilane. Mass spectral data (ESI-MS) was performed with a mass spectrometer MAXIS II (Bruker) equipped with electrospray ionization (ESI) interface operating in positive ion mode.

^{1}H NMR spectra of chromenes **1** [30], **7** [31] and **10** [31] are in good agreement with those previously reported.

All reagents and solvents were purchased from Aldrich, Fluka and Alfa-Aesar.

3. Results and discussion

3.1. Structure and Texture characterization of TaMCF materials

The mesoporous structure of TaMCF samples prepared was confirmed by the N_2 adsorption/desorption isotherms (Figure 1). The isotherm of TaMCF is typical of mesostructured cellular foams exhibiting a H1 type hysteresis loop at a relatively high pressure (p/p_0) with parallel adsorption and desorption branches [22]. This type of isotherm is slightly distorted by modification of TaMCF with alkali metal sources. Similar properties were observed for niobium containing series [21]. Textural parameters of the samples studied calculated from N_2 adsorption/desorption isotherms are shown in Table 1. Both TMCF supports show large surface areas (500 - 700 m^2/g). These values significantly decrease for the samples modified with alkali metals, the surface area decreasing with the growth of the alkali metal loading. Pore volume is changed in the same order.

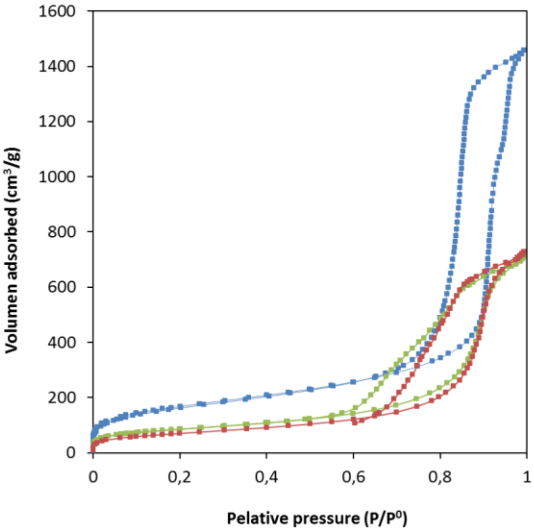


Figure 1. Nitrogen adsorption/desorption isotherms for TaMCF (*blue*), Li/TaMCF (*red*) and Na/TaMCF (*green*).

Table 1. Textural parameters and metal loading for M/TMCF materials

Catalyst	**S_{BET}**	**$V_p{}^b$ [cm^3g^{-1}] BdB FHH adsorption**	**Metal Loading [$mol/m^2g^{-1}\cdot10^{-6}$]**
TaMCF	556	2.5	--
Li/TaMCF	301	1.2	1.66
Na/TaMCF	251	1.2	1.99
K/TaMCF	228	1.0	2.19
Rb/TaMCF	257	1.0	1.94
Cs/TaMCF	211	0.9	2.37
NbMCF[a]	717	2.8	--
Li/NbMCF[a]	331	1.6	1.51
Na/NbMCF[a]	341	1.5	1.47
K/NbMCF[a]	303	1.7	1.65
Rb/NbMCF[a]	250	1.3	2.00

Cs/NbMCF[a]	234	1.4	2.14

[a] See ref 21. [b] V_p = pore volume.

3.2. The loading and location of Nb and Ta in MCF materials

The loading of niobium and tantalum was estimated on the basis of XRF data and is shown in the form of Si/Nb and Si/Ta ratios and metal wt. % (Table 2).

Table 2. Nb and Ta loading in MCF materials.

Sample	Si/Nb/Ta as assumed	Si/Nb (XRF)	Nb, wt. % (XRF)	Si/Ta (XRF)	Ta, wt. % (XRF)
NbMCF	64	169	0.8	-	-
TaMCF	64	-	-	98	2.9

In both materials (NbMCF and TaMCF) the efficiency of metal incorporation in the framework of MCF is lower than assumed. However, it is clear that much higher efficiency of tantalum inclusion than niobium was achieved. It is in agreement with literature data, which proved that the introduction of niobium into the framework of molecular sieves is more difficult than tantalum and typically gives materials with low niobium concentration [23, 24].

The location of niobium and tantalum introduced during the synthesis of MCF material was studied by UV–vis spectroscopy by identification of metal coordination. The UV-vis spectra of NbMCF support and samples after modification with alkali metals (Figure 2) show the presence of two UV bands at ca 225 and 260 nm. The first band is typical of charge transfer in tetrahedrally coordinated niobium species located in a silica skeleton [25, 26]. The second should be assigned to penta - coordinated niobium species located in the silica framework as was proved in [27]. It is worth of notice, that the band corresponding to octahedrally coordinated polynuclear niobium species (at 330 nm) was not detected in UV-vis spectra of NbMCF.

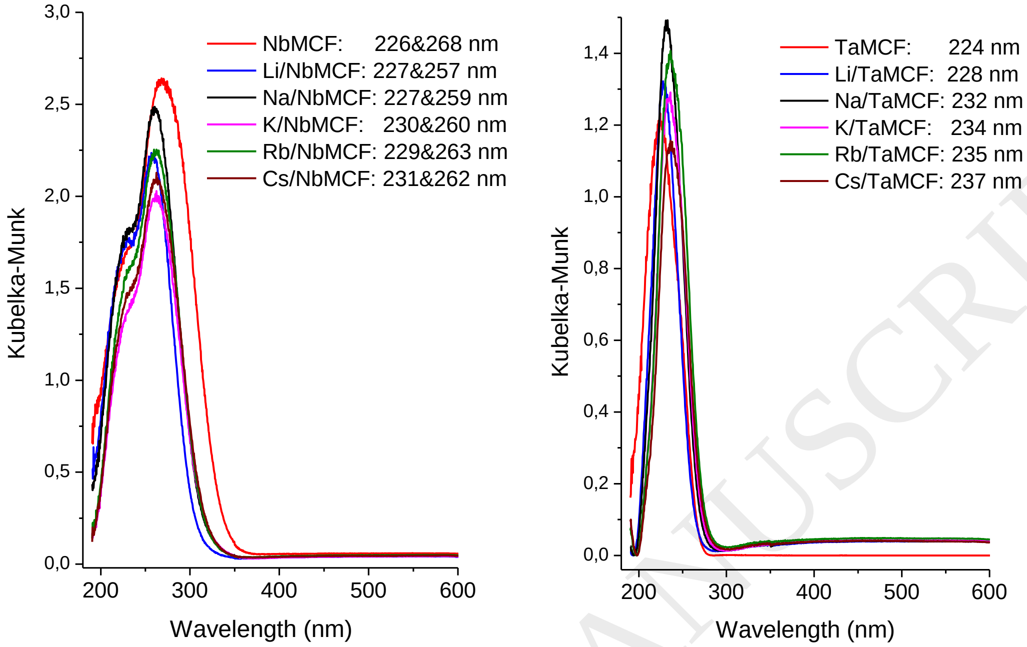


Figure 2 UV-vis spectra of NbMCF (A) [21] and TaMCF (B) materials before and after modification with alkali metals.

In contrast, the UV-vis spectra of TaMCF samples show one symmetric band at 224 nm which is typical of tretra-coordinated Ta species. These results indicate the location of niobium and tantalum in the MCF framework. Some variation in the position of the bands in UV–vis spectra of NbMCF and TaMCF materials after modification indicates the interaction of alkali metal species with niobium or tantalum in the supports. This interaction is higher for the series of tantalum containing materials as deduced from the value of red shift of the bands at ca. 225 nm (13 nm for Cs/TaMCF vs 5 nm for Cs/NbMCF).

3.3. Acid-base properties of catalysts—test reaction

The cyclisation of 2,5-hexanedione has been used as Brønsted acid–base test [28]. The formation of 2,5-dimethylfuran (DMF) occurs on Brønsted acidic centers, whereas in the production of 3-methyl-2-cyclopentenone (MCP) Brønsted basic centers take part. On the basis of the ratio of selectivity to MCP/selectivity to DMF, the sequence of the basicity of the prepared catalysts can be determined. According to literature the basicity of the catalyst is stated if MCP/DMF >1 [28-29]. When MCP/DMF < 1 the catalyst exhibits acidic properties, while for MCP/DMF ~1 the acid–base character of catalysts is postulated.

Table 3 summarizes the results of this test reaction. The conversion of 2,5-hexanedione depends strongly on the composition of the support. The activity is higher for NbMCF than TaMCF, both materials exhibiting acidic properties (MCP/DMF < 1).

Table 3: The results of 2,5-hexanedione cyclisation at 623 K.

Catalyst	**MCP/DMF**	**Conversion (%)**	**Selectivity (%)**	
			DMF	**MCP**
NbMCF	0.2	72	84	16.0
Li/ NbMCF	58	55	1.7	98.3
Na/ NbMCF	49	52	2.0	98.0
K/ NbMCF	90	87	1.1	98.9
Rb/ NbMCF	332	61	0.3	99.7
Cs/ NbMCF	499	68	0.2	99.8
TaMCF	0.2	44	82	18.0
Li/ TaMCF	99	71	1.0	99.0
Na/ TaMCF	199	82	0.5	99.5
K/ TaMCF	499	71	0.2	99.8
Rb/ TaMCF	499	54	0.2	99.8
Cs/ TaMCF	499	67	0.2	99.8

After alkali metal loading the conversion of 2,5-hexanedione slightly decreases on NbMCF with the exception of K/NbMCF (the maximum of activity). For TaMCF modified samples the conversion increases reaching the maximum for Na/TaMCF sample. The introduction of alkali metals leads to the significant increase in the selectivity to MCP (98-99.8%) for all alkali modified catalysts studied. The results indicates that impregnation with alkali metal sources generates Brønsted basic centers. Basicity, expressed by MCP/DMF ratio, is higher for the series of tantalum modified support. This observed behavior point out the role of interaction between alkali metal and transition metal in the support.

3.4. Catalytic performance

The mesoporous silicas under study were explored in the synthesis of chromene derivatives **1** (Scheme 1), at 303K, under solvent-free conditions. Remarkably, the T/MCF supports were inactive in the reaction obtaining the unaltered reactant mixture after 4h of reaction time. The Figure 4 depicts the conversion values of salycilaldehyde **2** in the presence of Me/TMCF catalysts. A rapid look at the Figure 3 confirms the analogous reactivity trends of the Me/TMCF catalysts in the reaction as function of the basicity of the samples, in such a manner that the conversion values notably diminished when increasing the basicity of the samples. In this sense, the reactivity order for the T/NbMCF silicas is as follow: Li/NbMCF > Na/NbMCF > K/NbMCF > Rb/NbMCF > Cs/NbMCF [21]. Although this order is also maintained in the case of using T/TaMCF catalysts, it was observed similar catalytic behavior from Na/TaMCF to Rb/TaMCF samples leading to intermedia conversion values, probably attributed to the texture of the samples. Although both series Me/NbMCF and Me/TaMCF showed slight differences concerning the pore volume, it could be though that the S_{BET} variation can influence the catalytic behavior of the samples. In this sense, while for the Me/NbMCF serie it was observed an increase of metal loading but also the decreasing of S_{BET} from Li to Cs samples, the Me/TaMCF catalysts, where Me is Na, K and Rb, showed similar S_{BET} and V_p and metal loadings affording the corresponding chromenes **1** with barely different conversion values probably. However, considerable decreasing of the conversion was obtained for the most basic samples, Cs/TaMCF, as expected.

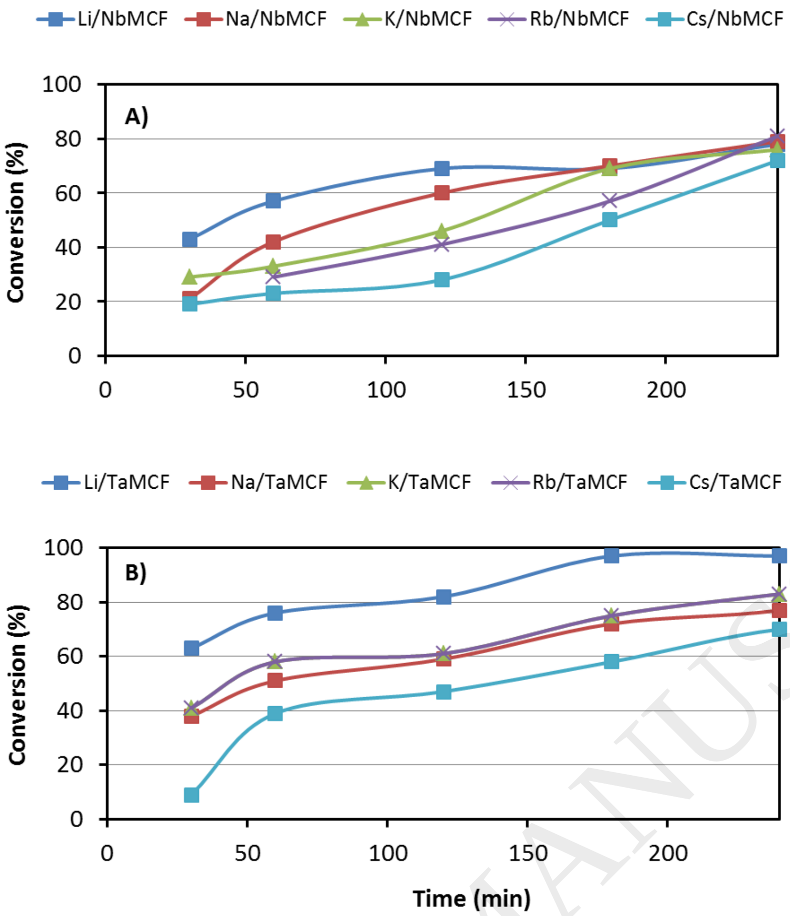


Figure 3. Synthesis of 2-amino-4*H*-chromenes **1** catalyzed by M/TMCF mesoporous silicas, at 303K, under solvent-free conditions.

Comparing both series of catalysts, the highest conversion values were observed for the M/TaMCF samples, this circumstance being clearly visualized from Figure 4. Our results demonstrate that the conversion decreased with the basicity of the samples, the alkaline cation size having a deep impact on the catalytic performance. These results are in accordance with those previously postulated by us for the NbMCF catalysts. Thus, the reactive specie able to initiate the reaction should comprise the enolate from ethyl cyanoacetate **3**, formed by abstraction of the proton at α-position, involving the alkaline oxides as highly exothermic step which proceeds without activation barrier [21]. The computational study concerning the NbMCF catalysts strongly suggested the involvement of Nb in the reaction by stabilizing the transition structures favoring the reactant interactions. In the same context, our experimental observations indicate that the presence of Ta in the silica framework clearly influences the catalytic performance suggesting its participation in the reaction.

It is important to note, that the reaction regioselectivity is maintained for all the investigated catalysts leading to diastereomeric mixtures of chromenes **1a**/**1b**, selectivity to **1a** as the most thermodynamically stable isomer being up to 60% (Figure 5). Finally, we also carried out reused experiments using the most efficient catalyst, Li/TaMCF, in the synthesis of chromenes **1** almost maintaining its activity during at least three consecutive cycles (96, 93, 90%; 3h).

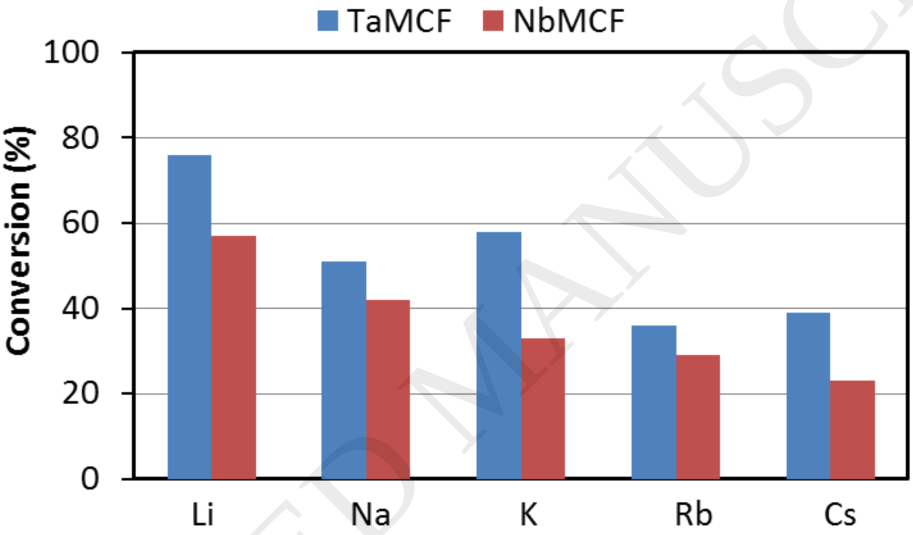


Figure 4. Synthesis of 2-amino-4*H*-chromenes **1** catalyzed by Me/TMCF mesoporous silicas, at 303K, under solvent-free conditions, after 1h of reaction time.

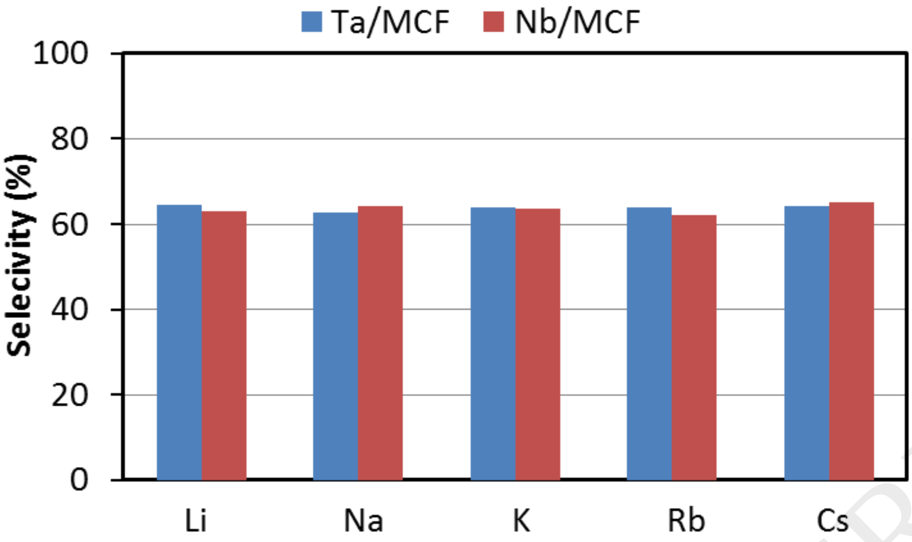
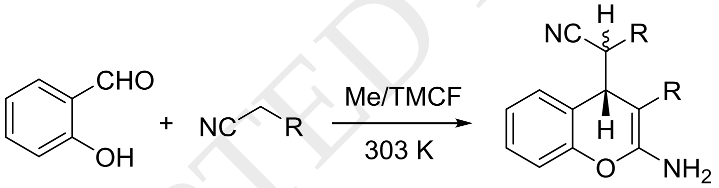


Figure 5. Synthesis of 2-amino-4*H*-chromenes **1** catalyzed by Me/TMCF mesoporous silicas, at 303K, under solvent-free conditions, after 1h of reaction time.

Considering the above commented results, we decide to investigate some modified TaMCF catalysts in the reaction when using other cyano components, more and less reactive than ethyl acetate **3** (Scheme 2).

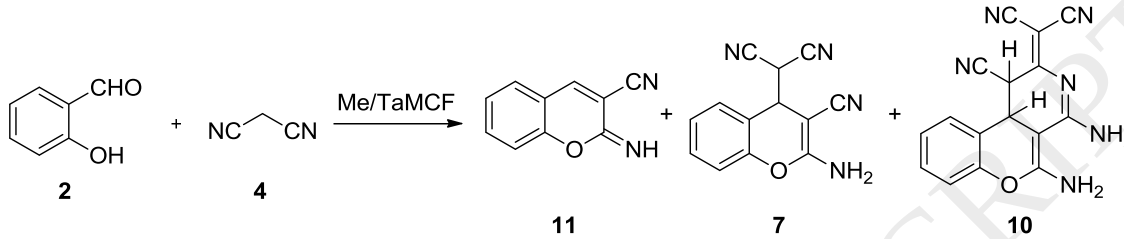


4: R = CN
5: R = SO_2Me
6: R = SO_2Bu^t

7: R = CN
8: R = SO_2Me
9: R = SO_2Bu^t

Scheme 2. Synthesis of 2-amino-4*H*-chromenes over TMCF silicas modified with alkaline metals.

Thus, we carried out the reaction using malononitrile **4**, operating under the same experimental conditions, in the presence of Me/TaMCF catalysts (where Me = Li, K and Cs), providing compound **10** as major reaction product, resulting of the nucleophilic addition of third malononitrile molecule to the initially formed chromene **7** (Scheme 3) [31]. Considering these results, we try the reaction in the presence of increased amounts of malononitrile (reactant ratio **2**/**4** = 2:6). Changes in the reaction mixture were detected almost instantaneously. At this regard, an analysis of the ^{1}H NMR spectra of the reaction crude confirmed the presence of the intermediate compounds **7** and **11**, also demonstrated by MS spectrometry (Scheme 3).



Scheme 3. Reaction between salicylaldehyde **2** and malononitrile **4** catalyzed by Me/TMCF mesoporous silicas (Me = Li, K, Cs), at 303K, under solvent-free conditions.

As can be seen in Figure 6, the reaction in the presence of Me/TaMCF catalysts takes place very quickly providing high conversion values close to 80% in only 30 min of reaction time in the presence of the Li/TaMCF and K/TaMCF samples. The most basic catalyst, Cs/TaMCF, afforded lower conversion values as compared with the Li or K analogues as expected. It is noticeable that while the reaction promoted by Li/TaMCF catalyst afforded the chromene **10** as unique reaction product, selectivity to **10** was diminished when the reaction was carried out in the presence of K/TaMCF (91%) or Cs/TaMCF (87%) catalysts, after 30 min of reaction time. In these cases, the basicity of the samples could be also related with the reaction selectivity. It is important to note that although malononitrile is the most reactive cyano compound explored herein, the blank experiment yielded the corresponding chromene **10** in almost 5% after 2h of reaction time.

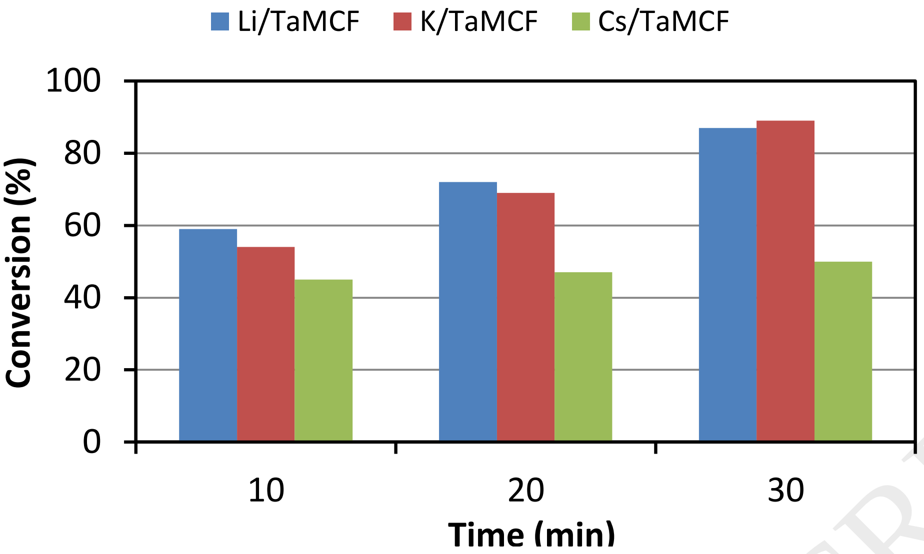


Figure 6. Conversion values for the reaction between salicylaldehyde **2** and malononitrile **4** catalyzed by Me/TMCF mesoporous silicas (Me = Li, K, Cs), at 303K, under solvent-free conditions.

Finally, we tested the most efficient catalysts in the reaction between salycilaldehyde **2** and two different sulfonyl acetonitriles **5** and **6**, in these cases in the presence of tetrahydrofuran as solvent, leading to the corresponding reaction products although with decreases conversion values. Remarkably, the blank experiments when using ethyl cyanoacetate **3** but also sulfonyl acetonitriles **5** and **6** afforded mixtures of unaltered reactants after 4h of reaction times. More specifically, in Figure 8 it is represented the conversion values *vs* time when using *tert*-butyl sulfonylacetonitrile **6** in the presence of Li/TaMCF and K/TaMCF exclusively yielding the corresponding *erythro*-chromene **9** with decreased conversion values (Scheme 2). In both cases, basicity but also the porosity of the materials and the presence of *tert*-butylsulphonyl group as bulky substituent in compound **6** seem strongly to limit the formation of the less stable isomer, the *threo*-isomer. These results are in accordance with those obtained in the reaction between salyciladehyde **2** and methyl sulfonyl acetonitrile **5** catalyzed by K/TaMCF silica leading to a mixture of *Erythro*/*Threo* isomers (6:1 ratio) of chromene **8** in 15% of yield after 4h of reaction time.

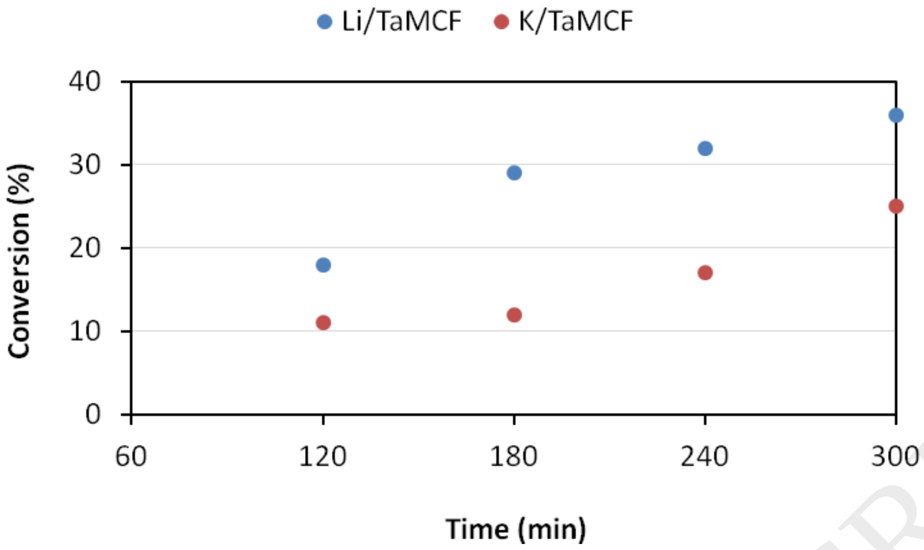


Figure 7. Synthesis of compound **9** catalyzed by Li/TaMCF and K/TaMCF catalysts.

4. Conclusions

We report herein for the first time a new family of Ta/MCF silicas modified with alkaline metals as highly efficient bifunctional catalysts for the synthesis of chromene derivatives, as pharmacologically interesting compounds, from salicylaldehyde **2** and distinct acetonitrile compounds, under mild reaction and solvent-free conditions. An enhancement of the catalytic performance of these TaMCF samples was observed in comparison with those for Nb ones, conversion values increasing from the Cs to Li modified TaMCF samples with maintained selectivity. Our experimental observations suggest an optimum basicity of the samples, being the less basic sample considered the most active catalyst, Li/TaMCF. It is reasonable to think that this notably augmented catalytic performance for Me/TaMCF silicas could be attributed to the enhanced Brønsted basicity provided by the stronger interaction between alkali metals and Ta than between Me-Nb as demonstrated by test reaction and UV-vis experiments.

The basicity of Me/TaMCF catalysts and the reactivity and steric hindrance of the starting acetonitriles are determinant factors which affect the reaction selectivity. However, it was found that the basicity plays an important role initiating the reaction but also a compromise between alkaline cation size and basicity is required.

5. Acknowledgements

This work has been supported in part by Spanish Ministry (projects CTM2014-56668-R) and National Science Centre in Poland (Project No. 2014/15/B/ST5/00167).

6. References

[1] M. A. Ali, S. M. A. H. Siddiki, K. Kon, K. Shimizu, ChemCatChem 7 (2015) 2705-2710.

[2] M. A. Ali, S. M. A. H. Siddiki, K. Kon, J. Hasegawa, K. Shimizu, Chem. -A Eur. J. 20 (2014) 14256-14260.

[3] C. Garcia-Sancho, J. M. Rubio-Caballero, J. M. Merida-Robles, R. Moreno-Tost, J. Santamaria-Gonzalez, P. Maireles-Torres, Catal. Today 234 (2014) 119-124.

[4] X. Lang, X. Chen, J. Zhao, Chem. Soc. Rev. 43 (2014) 473-486.

[5] J. Ohyama, R. Kanao, Y. Ohira, A. Satsuma, Green Chem. 18 (2016) 676-680.

[6] I. Sobczak, K. Jagodzinska, M. Ziolek, Catal. Today 158 (2010) 121–129.

[7] J. C. Rooke, T. Barakat, S. Siffert, B. L. Su, Catal. Today 192 (2012) 183-188.

[8] M. Ziolek, I. Sobczak, P. Decyk, L. Wolski, Catal. Commun. 37 (2013) 85–91.

[9] M. Ziolek, I. Sobczak, Catal. Today 285 (2017) 211–225.

[10] E. Pérez Mayoral, E. Soriano V. Calvino-Casilda, M. L. Rojas-Cervantes, R. M. Martín-Aranda, Catal. Today 285 (2017) 65–88.

[11] D. Blasco-Jiménez, A. J. Lopez-Peinado, R. M. Martin-Aranda, M. Ziolek, I. Sobczak. 2009. Catal. Today 142 (2009) 283-287.

[12] D. Blasco-Jimenez, I. Sobczak, M. Ziolek, A. J. Lopez-Peinado, R. M. Martin-Aranda. 2010. Catal. Today 152 (2010) 119-125.

[13] I. Sobczak, M. Ziolek, E. Pérez-Mayoral, D. Blasco-Jiménez, A. J. López-Peinado, R.M. Martín-Aranda, Catal. Today 179 (2012) 159-163.

[14] A. Smuszkiewicz, E. Pérez-Mayoral, E. Soriano, I. Sobczak, M. Ziolek, R. M. Martín-Aranda, A. J. López-Peinado, Catal. Today 218 (2013) 70– 75.

[15] A. Smuszkiewicz, J. López-Sanz, E. Pérez-Mayoral, E. Soriano, I. Sobczak, M. Ziolek, R. M. Martín-Aranda, A. J. López-Peinado, J. Mol. Catal. A: Chem. 378 (2013) 38-46.

[16] R. Petroff Saint-Arroman, B. Didillon, A. de Mallmann, J. M. Basset, F. Lefebvre, Appl. Catal. A 337 (2008) 78–85.

[17] D. A. Ruddy, T. Don Tilley, J. Am. Chem. Soc. 130 (2008) 11088–11096.

[18] M. Fadhlia, I. Khedhera, J. M. Fraile, J. Mol. Catal. A: Chem. 410 (2015) 140–148.

[19] K. Stawicka, M. Trejda, M. Ziolek, Appl. Catal. A 467 (2013) 325–334.

[20] V. Calvino-Casilda, K. Stawicka, M. Trejda, M. Ziolek, M.A. Bañares J. Phys. Chem. C 118 (2014) 10780−10791.

[21] A. Smuszkiewicz, J. López-Sanz, I. Sobczak, M. Ziolek, R. M. Martín-Aranda, E. Soriano, E. Pérez-Mayoral, Catal. Today 277 (2016) 133–142.

[22] J. S. Lettow, Y. J. Han, P. Schmidt-Winkel, P. Yang, D. Zhao, G. D. Stucky, J. Y. Ying, Langmuir 16 (2000) 8291–8295.

[23] M. Trejda, A. Wojtaszek, A Floch, R. Wojcieszak, E. M. Gaigneaux, M. Ziółek, Catal. Today 158 (2010) 170 – 177.

[24] A. Wojtaszek, M. Ziolek, F. Tielens, J. Phys. Chem. C 116 (2012) 2462–2468.

[25] M. Nashimura, K. Asakura, Y. Iwasawa, J. Chem. Soc., Chem. Commun. 15 (1986) 1660–1661.

[26] B. Kilos, A. Tuel, M. Ziolek, J. C. Volta, Catal. Today 118 (2006) 416–424.

[27] D. C. Tranca, A. Wojtaszek-Gurdak, M. Ziolek, F. Tielens, Phys. Chem. Chem. Phys. 17 (2015) 22401-22411.

[28] R. M. Dessau, Zeolites 10 (1990) 205–206.

[29] J. J. Alcaraz, B. J. Arena, R. D. Gillespie, J. S. Holmgren, Catal. Today 43 (1998) 89–99.

[30] a) R. M. N. Kalla, S. J. Byeon, M. S. Heo, I. Kim, Tetrahedron 69 (2013) 10544-10551. b) J. Velasco, E. Pérez-Mayoral, V. Calvino-Casilda, A. J. López-Peinado, M. A. Bañares, E. Soriano, J. Phys. Chem. B 119 (2015) 12042−12049.

[31] F. Yang, Z. Wang, H. Wang, C. Wang, L. Wang, RSC Adv. 5 (2015) 57122-57126.