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Ceria–Vanadia/Silica-Catalyzed Cascade for C–C and C–O Bond Activation: Green One-Pot Synthesis of 2-Amino-3-cyano-4*H*-pyrans

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We designed a ceria–vanadia/silica ($Ce–V/SiO_2$) heterogeneous catalyst and used it for the green and efficient synthesis of 2-amino-3-cyano-4*H*-pyran derivatives. The green reaction was a multicomponent one-pot condensation of 5,5-dimethylcyclohexane-1,3-dione, aromatic aldehyde, and malononitrile in an eco-compatible solvent (ethanol). The catalyst was synthesized and fully characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) surface area analysis. The reported procedure offers a number of advantages including decreased reaction times, mild conditions, high yields, operational simplicity, and environmentally benign and simple work-up procedures. Furthermore, the catalyst is economical, fully recyclable, and reusable for over five runs while preserving its high activity. The synthesized 2-amino-3-cyano-4*H*-pyran products can later be used for pharmaceutical purposes.

Multicomponent reactions (MCRs) are exciting new synthetic protocols geared toward heterocyclic scaffolds as building blocks of biological and medicinal importance.[1,2] MCRs have many advantages over conventional linear-type syntheses by virtue of their convergence, productivity, facile execution, and high yields.[3] Moreover, MCRs conform to green principles, such as one-pot conversions and atom efficiency, in addition to other conditions optimal for the synthesis of heterocyclic compounds.[4–6] These single-step processes have distinctive suppleness in generating molecular diversity combined with minimization of time, cost efficiency, and moderate reaction conditions.

In the recent past, heterogeneous mixed metal oxide catalysts started to receive greater attention. Such systems are successfully utilized in the augmentation of heterocyclic synthesis and green reaction protocols.[7] Heterogeneous catalytic processes based on metal oxide catalysts are simpler, highly efficient, and eco-friendly with greater selectivity.[8] Heterogeneous catalysts possess added advantages such as thermal stability, shape selectivity, acidic or basic nature, nontoxic crystalline solids, and easy handling.[8] Easy salvage and reusability are additional benefits. Hence, considering current legislation and industry needs, the use of heterogeneous catalysts is a notable option for one-pot synthesis involving multicomponent reactions.

Silica (SiO_2) is an efficient and cheap support material, which can readily promote the activity of the supported metal catalysts. SiO_2 has good acid–base properties, a nontoxic nature, and high chemical thermal stability.[9] It has high surface area and carries a vast concentration of active sites. SiO_2 by itself, or in combination with metals (composites), has been used in organic synthesis.[10] This acid–base bifunctional catalyst has emerged as an attractive option as support material for the activation and stabilization of ceria and vanadia. The crystalline structure of SiO_2 has been reported as a key factor in explaining the structure–activity relationships of mixed oxides of cerium (Ce) and vanadium (V) catalysts as the $Ce–V/SiO_2$ solid material possesses both Brønsted and Lewis acid centers.[11]

Due to variety of therapeutic, pharmacological, biological, and agricultural applications for heterocyclics in the fields of organic, pharmaceutical, medicinal, and combinatorial chemistry, heterocyclic compounds have gained importance as catalysts.[12,13] The pyrans and benzopyrans received significant attention in heterocyclic synthesis,[14] as they possess an oxygen heteroatom and exhibit diverse biological properties such as antibacterial and antifungal,[15] anticancer,[16] anti-inflammatory,[17] antirheumatic,[18] anti-HIV,[19] and anti-Alzheimer activities[20] and is also used for treatment of disorders in the central nervous system.[21] Applications of pyran-containing compounds as ligands in coordination chemistry, herbicidal, and insecticidal in pesticide chemistry are also well documented.[12] A large number of molecules bearing the pyran moiety display a wide-ranging spectrum of pharmacological activities in conditions such as asthma, hypertension, urinary diseases, and ischemia, and currently, many are in use in the treatment of variety of diseases.[22–26] Thus, the synthesis of substituted pyran derivatives has been the topic of many research investigations, and several approaches have been pursued using various catalysts, including hexamethylenetetramine-bromine (HMTAB),[27] $H_6P_2W_{12}O_{62}.H_2O$,[28] rare-earth perfluorooctanoate $(RE(PFO)_3)$,[29] phenylboronic acid,[30] silica-gel-supported polyphosphoric acid (PPA-SiO_2),[31] per-6-amino-β-cyclodextrin,[32] L-proline,[33] 4-dimethylaminopyridine (DMAP),[34] 1-butyl-3-methylimidazolium tetrafluoroborate (Bmim[BF_4]),[35] MNP@P[imEt][Br],[36] tetra-*n*-

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butylammonium fluoride (TBAF)[37] amongst others. However, many of these procedures have one or more drawbacks such as moderate yields, requirement of expensive reagents, toxic organic solvents, stoichiometric catalysts, extreme reaction conditions, lengthy procedures, or long reaction times,. Moreover, in many cases, the catalysts used are not recyclable. Therefore, the development of an effective and facile procedure with high generality for the synthesis of 4*H*-pyrans would be timely and of considerable interest.

In continuing our research in developing new methodologies for the synthesis of heterocycles[38,39] and synthesis of biologically active heterocyclic molecules,[40–45] we here communicate an efficient method for the synthesis of 2-amino-3-cyano-4*H*-pyran derivatives (**4a–l**) in high yields in the presence of a heterogeneous and reusable Ce–V/SiO_2 catalyst under green conditions.

To establish the optimum reaction conditions, to maximize the yield, and decrease reaction times, the reaction was investigated under varied conditions of catalysts and solvents. The initial experiment was conducted with 5,5-dimethylcyclohexane-1,3-dione 1 (1 mmol), benzaldehyde **2a** (1 mmol), and malononitrile **3** (1.2 mmol) in aqueous media, without any catalyst at RT, and no reaction was observed. Even after 24 h under reflux conditions, the reaction showed no product (Table 1, entries 1 and 2). The same reaction was repeated with ethanol as solvent, but no product was obtained even after 12 h (Table 1, entry 3). Interestingly, a trace amount of the predicted product was observed, when MgO, Mn/Al_2O_3, or V/Al_2O_3 were used as catalysts in the ethanol media (Table 1, entry 4–6), but no reaction was apparent in presence of strongly basic catalysts, such as piperidine or K_2CO_3 and ethanol as solvent (Table 1, entries 7&8). The acidic catalysts PTSA, SiO_2, and $ZnCl_2$ were attempted, but found to be less effective as reactions gave only 21–34% yield of the expected product (Table 1, entries 9–11). The scope of reaction in the presence of the L-proline and also ionic liquids such as (Bmim)BF_4 and (Bmim)OH was also explored, but yields were low (Table 1, entries 12–14). With CeO_2/SiO_2 and V_2O_5/SiO_2 as a catalyst in ethanol, yields of 55% and 58% were obtained, respectively (Table 1, entries 15, 16). This could be due to the high surface area of V_2O_5 on silica than Ce on silica which increases the availability of vanadium active sites for the reaction. Furthermore, we examined $HClO_4$/SiO_2 catalyst to afford less yield 45%. Then, we investigated the range of Ce–V/SiO_2, which is a bifunctional acid–base catalyst, with ethanol as solvent. The reaction was repeated under similar conditions using Ce–V/SiO_2 which gave an excellent yield of 95% in 1 h once optimum dopant percentage had been established.

Table 1. Optimization conditions for the synthesis of 2-amino-3-cyano-4*H*-pyran derivatives by Ce–V/SiO_2 catalyst.[a]

Entry	Catalyst	Solvent	Condition	Time [h]	Yield [%][b]
1	No catalyst	H_2O	RT	24	–
2	No catalyst	H_2O	Reflux	24	–
3	No catalyst	EtOH	Reflux	12	–
4	MgO (50 mg)	EtOH	Reflux	10	Trace
5	Mn/Al_2O_3 (50 mg)	EtOH	Reflux	12	Trace
6	V/Al_2O_3 (50 mg)	EtOH	Reflux	12	Trace
7	Piperidine	EtOH	Reflux	12	–
8	K_2CO_3	EtOH	Reflux	12	–
9	PTSA	EtOH	Reflux	7	21
10	SiO_2	EtOH	Reflux	8	27
11	$ZnCl_2$	EtOH	Reflux	5	34
12	L-proline	EtOH:H_2O	Reflux	4.5	38
13	(Bmim)BF_4	EtOH:H_2O	Reflux	4	32
14	(Bmim)OH	EtOH:H_2O	Reflux	4	29
15	CeO_2/SiO_2	EtOH	RT	2	55
16	V_2O_5/SiO_2	EtOH	RT	2	58
17	$HClO_4$/SiO_2	EtOH	RT	2.5	45
18	1% Ce–V/SiO_2 (30 mg)	EtOH	RT	2.5	79
19	2% Ce–V/SiO_2 (30 mg)	EtOH	RT	1	95
20	4% Ce–V/SiO_2 (30 mg)	EtOH	RT	1	89
21	2% Ce–V/SiO_2 (30 mg)	MeOH	RT	2	89
22	2% Ce–V/SiO_2 (30 mg)	CH_3COCN	RT	2.5	78
23	2% Ce–V/SiO_2 (30 mg)	DMF	RT	2.5	86
24	2% Ce–V/SiO_2 (30 mg)	THF	RT	3	69
25	2% Ce–V/SiO_2 (30 mg)	Toluene	RT	4	65

[a] All products were characterized by IR, ^{1}H NMR, ^{13}C NMR, ^{15}N NMR, and high-resolution mass spectrometry (HRMS) spectral analysis. [b] Isolated yields. (–) No reaction.

The impact of cerium or vanadia loading on silica in tuning its catalytic efficiency was further investigated. To find the ideal loading of Ce–V on SiO_2 on catalyst activity, reactions with 1%, 2%, and 4% Ce–V-doped SiO_2 were carried out under otherwise comparable conditions. The percentage of Ce–V loading was found to have an influence on the reaction yield as well as reaction time (Table 1, entries 18–20). Using 1% Ce–V/SiO_2 catalyst yielded 79% product in 2.5 h under ethanol solvent conditions (Table 1, entry 18). A 2% Ce–V loading was found optimal with 95% yield in 1 h (Table 1, entry 19). A further increase of metal loading (4%) led to a slightly decreased yield (89%) (Table 1, entry 20). We were pleasantly surprised to discover the MCR was successful in only 1 h at RT. The expected substituted pyrans (**4a**) were produced selectively and in good yield (95%) (Table 1, entry 19). Although it took about 1 h for the reaction to complete, the Ce-V/SiO_2-catalyzed reaction was found to start almost immediately. Reaction products were identified and confirmed by spectral and other analytical data. Excellent selectivity and yield could be achieved due the nature of the chosen catalyst with high surface area, which presumably enhanced the accessibility of the substrate to the anchored acidic and basic groups.

The surface properties of the SiO_2 can be modified by loading cations of various properties. An optimal distribution of the acidic and basic sites due to loading of Ce–V on SiO_2 possibly contributed to its enhanced catalytic efficiency, which is evident from the high yield, selectivity, and speed of the reaction achieved in the title reaction. In the proposed MCR, we speculate that the Ce–V/SiO_2 catalyst displays greater efficiency compared with the other catalysts investigated due to a synergetic effect between ceria and vanadia.

Taking advantage of the proven performance of 2% Ce–V/SiO_2 as catalyst for the MCR, we then focused on further improving the reaction efficiency. We screened for changes in the variation of Ce–V catalyst loading on silica support. The results are summarized (Table 2, entries 1–3) and indicate that an increase in loading of Ce–V on SiO_2 from 10 mg to 30 mg, resulted in an increased yield from 71% to 95%. A further in-

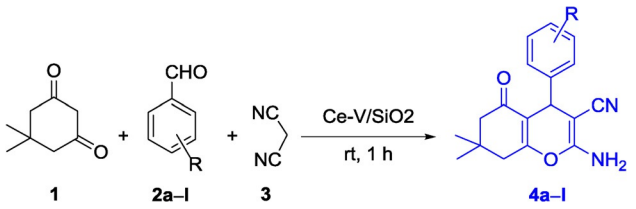
Table 2. Optimization of the amount of 2% Ce–V loading on SiO_2 as catalyst in the reaction.

Entry	Catalyst [mg]	Time [h]	Yield [%]
1	Ce–V/SiO_2 (10)	2.5	86
2	Ce–V/SiO_2 (20)	2.0	89
3	Ce–V/SiO_2 (30)	1	95
4	Ce–V/SiO_2 (40)	1	95
5	Ce–V/SiO_2 (50)	1.5	94

crease in loading of catalyst had only a marginal effect on product yield (Table 2, entries 4&5).

Secondly, because solvents play an important role in design of MCRs, we also studied the influence of solvent in the title reaction. The efficiencies of various solvents including methanol, acetonitrile, dimethylformamide (DMF), tetrahydrofuran (THF), and toluene were compared under otherwise identical reaction conditions. We found that the reaction proceeded smoothly in protic solvents. Among all the screened solvents, EtOH was found to be the superior solvent for this multicomponent reaction. It is noteworthy to mention that from the results of optimization (Table 1, entries 21–25), the reaction temperature and polarity of the solvent appear to be important for this multicomponent reaction to achieve clean products in good to excellent yields. Polar protic solvents enhance the rate of reaction, whereas for the nonpolar solvents, the rate of the reaction was sluggish.

The wider scope of this MCR was further explored with other reagents. Choosing the optimized conditions for the synthesis of **4a**, that is, 30 mg of Ce–V/SiO_2 at RT and ethanol as solvent (Scheme 1), we investigated the reactions with varied



Scheme 1. Synthesis of 2-amino-3-cyano-4*H*-pyran derivatives. Substituents (R) and yields can be seen in Table 3.

structurally different aldehydes (**2a–l**) for the MCR. To our delight, most of the reactions afforded the desired 2-amino-3-cyano-4*H*-pyran derivatives with excellent selectivity (**4a–l**) and yields (87–95%), and with no by-products. The results are summarized in Table 3. Interestingly, the MCRs with substrates bearing both electron-donating and electron-withdrawing groups on the aromatic ring performed well and gave corresponding target molecules in excellent yields. Structures of all the products (**4a–l**) were established and confirmed on the basis of their spectral data: ^{1}H NMR, ^{13}C NMR, ^{15}N NMR (gradient heteronuclear single quantum coherence, GHSQC), and Fourier-transform infrared (FTIR) spectroscopy and high-resolution mass spectrometry (HRMS).

Figure 1 shows the X-ray diffraction (XRD) patterns of the Ce–V/SiO_2 powder catalyst calcined at 450 °C. The CeO_2 diffraction peaks at $2\theta = 29.6°$, 31.7°, 36.5°, 49.1°, and 67.2° com-

Table 3. Synthesis of 2-amino-3-cyano-4*H*-pyran derivatives catalyzed by Ce–V/SiO_2 catalyst.

Entry	R	Product	Yield [%]	Mp [°C]	Lit. Mp [°C]
1	3-OMe	**4a**	92	210–212	–
2	4-OMe	**4b**	93	201–202	201–202[37]
3	2-Br	**4c**	89	197–198	–
4	4-Br	**4d**	92	204–206	–
5	3-Cl	**4e**	94	210–211	–
6	2,3-$(OMe)_2$	**4f**	90	215–217	–
7	2,4-$(OMe)_2$	**4g**	92	220–221	–
8	3,4-$(OMe)_2$	**4h**	90	208–209	–
9	2,4,6-$(OMe)_3$	**4i**	91	232–234	–
10	H	**4j**	95	232–234	234–235[37]
11	2-Furyl	**4k**	93	224–226	–
12	2-NO_2	**4l**	87	231–232	–

(–) New compounds/no literature available.

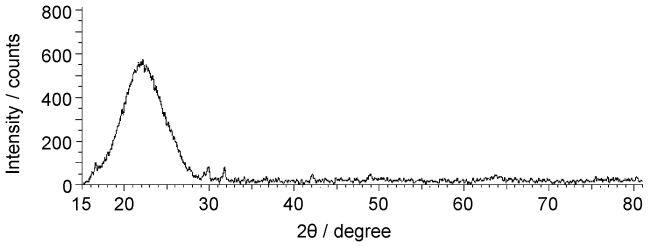


Figure 1. XRD spectra of Ce–V/SiO_2 catalyst.

pare well with the standard database file (JCPDS34-0394). The mixed oxide shows the Ce–VO_4 phase in accord with the standard database file JCPDS12-757, with sharp diffraction peaks at $2\theta = 22.2°$, 26.2°, 32.2°, 42°, 54.6°, and 71.8°. As can be seen from the figure, the vanadium oxide sample showed sharp diffraction peaks at $2\theta = 17.3°$, 29.1°, 38.1°, and 49° (JCPDS41-1426). There are no other peaks, except V_2O_5, CeO_2, and $CeVO_4$ in XRD patterns for the Ce–V/SiO_2 sample, implying bulk purity.

The scanning electron microscopy (SEM) micrograph (Figure 2a) displays agglomeration of metal oxide particles which is caused by the calcination of the Ce–V/SiO_2 catalyst, and these aggregates are in the size range from 0.81–2.00 μm. Energy-dispersive X-ray spectroscopy (EDS) semi-quantitative analysis of this catalyst showed that Ce and V are homogenously distributed in the catalyst (Figure 2b), and the metal ratio (Ce:V:Si) is also in agreement with the inductively coupled plasma (ICP) elemental analysis. The catalyst morphologies as indicated by the SEM image clearly point out the homogeneity in shapes for the sample and high crystallinity. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis showed that the cerium to vanadium metal ratio is equal. The transmission electron microscopy (TEM) micrograph (Figure 3) showed that the calcined catalyst has a cubic-like structure, which is characteristic of typical vanadate. These cubic planar structures are in the size of 21 ± 3 nm. The selected area diffractions showed that catalyst is polycrystalline in nature, which is further supported by the XRD diffractogram.

The nitrogen adsorption–desorption isotherms for the Ce-V/silica supported catalyst are shown in Figure 4. All the prepared catalysts have a similar pattern in adsorption–desorption

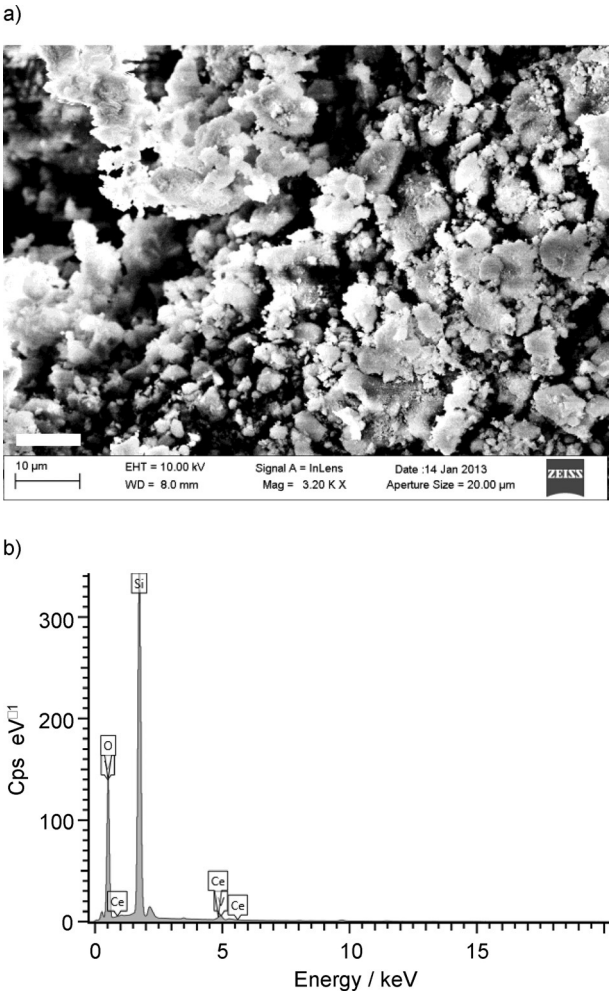


Figure 2. a) SEM image of Ce–V/SiO_2 catalyst (white scale bar = 10 µm); b) SEM-EDX image of Ce–V/SiO_2 catalyst.

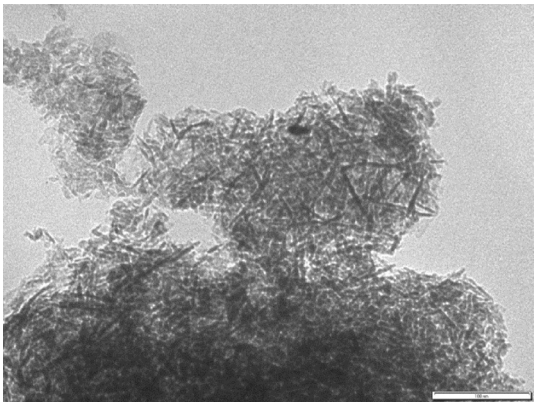


Figure 3. TEM spectra of Ce–V/SiO_2 catalyst (white scale bar = 100 nm).

isotherms and display the characteristic hysteresis loop of a type-IV isotherm (IUPAC) lying in the p/p° range of 0.7–0.85, demonstrating mesoporous character and indicates a small pore size and good homogeneity of the catalyst. A quite narrow and monomodal pore size distribution was obtained for the Ce–V doped on silica. This further indicated that the

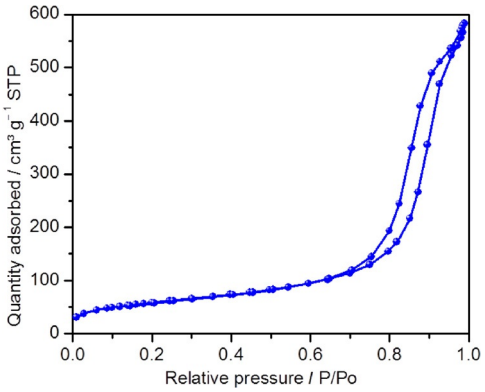


Figure 4. N_2 adsorption and desorption spectra and pore size distribution of Ce–V/SiO_2 catalyst.

average pore size has increased with increasing the loading amount of silica. For the 2 wt% Ce–V loaded catalyst, the parameters are specific surface area (17.1 $m^2 g^{-1}$), pore size (0.0139 $cm^3 g^{-1}$), and total pore volume (74 Å^3). The low surface area of the prepared catalysts compared with the bare silica support was probably due to the good dispersion of Ce–V on the surface of silica.

The reusability of any heterogeneous catalyst is one of the most important parameters for potential commercial applications. The reusability of the catalyst was assessed in the synthesis of 2-amino-3-cyano-4*H*-pyran derivatives (Figure 5). Gratifyingly, the heterogeneous Ce–V/SiO_2 could be recovered effectively from the reaction mixture by simple filtration and by washing the catalyst twice with acetone and drying at 70–80 °C under reduced pressure for 2 h to make it ready for a later run. There was no loss of Ce–V loading on silica observed which was confirmed by ICP-OES analysis. The catalyst was tested for six runs. It was observed that recovered catalyst can be recycled in subsequent runs with minimal loss of its activity only after five runs, which might be due to the agglomeration of Ce–V.

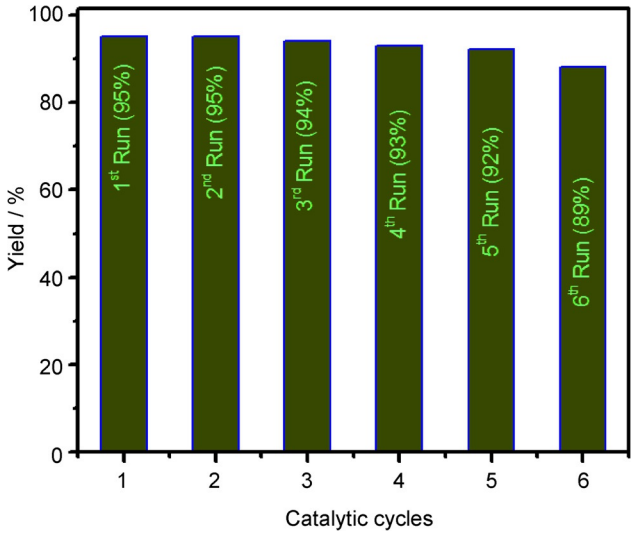


Figure 5. Recyclability of Ce–V/SiO_2 catalyst.

In conclusion, we report an environmentally benign and an efficient one-pot multicomponent green synthesis of 2-amino-3-cyano-4*H*-pyran derivatives using Ce–V/SiO_2 as catalyst in green solvent and with good atom efficiency. This simple and recyclable heterogeneous catalyst, Ce–V/SiO_2 shows high catalytic activity for multicomponent reactions. The current method has several advantages such as short reaction times, excellent yields, high purity of products, cost-effectiveness, use of small amounts of inexpensive catalyst, and use of an environmentally benign green solvent.

Experimental Section

Ce–V-loaded silica mixed oxide (Ce–V) with a Ce:V molar ratio of 1:1 was synthesized by the wet impregnation method.[46–48] $Ce(NO_3)_3{\cdot}6H_2O$, (62 mg for 1%, 124 mg for 2% and 250 mg for 4%; Aldrich-99%) and $VOSO_4{\cdot}xH_2O$, (63 mg for 1%, 126 mg for 2% and 252 mg for 4%; Aldrich-97%) were dissolved in distilled water (50 mL), and this was followed by the addition of SiO_2 (2.0 g, Aldrich). The reaction mixture was continuously stirred for 4 h at RT, and the mixture was further dried in an oven at 110 °C overnight, and then calcined in air flow at 500 °C for 4 h to obtain the various 1, 2, and 4 wt% of mixed oxides of Ce/V-loaded silica catalysts.

General procedure for the synthesis of 2-amino-3-cyano-4*H*-pyran derivatives. A mixture of 5,5-dimethylcyclohexane-1,3-dione 1 (1 mmol), aromatic aldehyde 2 (1 mmol), and malononitrile 3 (1.1 mmol) were dissolved in EtOH (10 mL) at RT. The 2% Ce–V/SiO_2 catalyst (30 mg) was added to the reaction mixture and continuously stirred for 1 h. The completion of the reaction mixture was monitored by thin-layer chromatography (TLC) analysis (Scheme 1). After completion of the reaction, the solid heterogeneous catalyst was filtered. The obtained catalyst was washed with acetone (10×3 mL), dried in vacuo at 70–80 °C for 2 h, and kept aside for use in the next reaction. The filtrate was concentrated to obtain the crude product, which was purified by recrystallization in EtOH to afford the target compounds. Structures of all the products (**4a–l**) were established and confirmed on the basis of their spectral data, ^{1}H NMR, ^{13}C NMR, ^{15}N NMR (GHSQC), FTIR, and HRMS. The details of the product characterization are presented in the Supporting Information.

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Keywords: 4*H*-pyrans · ceria–vandia/silica (Ce–V/SiO_2) · green chemistry · heterogeneous catalysts · one-pot multicomponent reactions · recyclable

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