A Cooperative Effect in a Novel Bimetallic Mo–V Nanocomplex Catalyzed Selective Aerobic C–H Oxidation

Hasan Tavallaei, Maasoumeh Jafarpour,* Fahimeh Feizpour, Abdolreza Rezaeifard,* and Alireza Farrokhi

Catalysis Research Laboratory, Department of Chemistry, Faculty of Science, University of Birjand, Birjand 97179-414, Iran

Supporting Information

ABSTRACT: In this study, a new heterobimetallic Mo(VI)–V(V) organosilicon Schiff base complex has been prepared and characterized by different techniques, such as FTIR, Raman, MS, ICP-AES, TGA, and XPS. The bimetallic nanocomplex, revealed by TEM images, showed high oxidation stability and desired activity in the aerobic oxidation of a structurally diverse set of benzylic alcohols in ethanol as a safe solvent. Further, oxidation of benzylic hydrocarbons successively occurred, producing the target compounds in high yields and excellent selectivities. Our results demonstrated a cooperative effect between Mo(VI) and V(V) as redox active sites in an organosilicon Schiff base framework. A facile and practical reusability of the solid catalyst at the end of the reaction was observed.

1. INTRODUCTION

Nowadays, the development of new synthetic strategies that take green chemistry into consideration has become a very imperative topic. Because catalysis can be considered as one of the central themes in green chemistry,1–3 optimizations of existing chemical transformations associated with the development of practical and environmentally friendly processes depend appreciably on the improvement of catalyst performance. In particular, transition-metal-based catalysts render an effective manner to achieve the optimal conditions in terms of high efficiency and selectivity of the processes.4–6 Nature as a provenance of specific and highly efficient catalysts containing two or more metal centers in the active site has long been definitely well-known.7,8 In this context, inspired by it, several research groups have developed bimetallic catalytic systems for various organic and bioorganic transformations.9–12 Cooperative and synergistic benefits together with these processes further enhance their potential to high performance.

Recently, bimetallic complexes have attracted extensive investigations into their synthesis and development in catalysis.13–18 In general, incorporating multiple metal centers into a single ligand structure can promote reactivity and selectivity.19 Also, the ability to orchestrate with other catalytic modes in a complementary pathway is arguably attributed to the development of these robust complexes.20–22 On the other hand, the properties of bimetallic catalysts are significantly different from their related monometallic systems, which accrued from the “synergistic” effects.23,24 Nevertheless, it would be interesting to include such compounds in considering assays because of the potentially superior performance of bimetallic catalysts as compared to their monometallic counterparts.

Owing to their varied characteristics and tunable compositions, they are intensely used in a variety of applications as catalytic reforming reactions,25 adsorbents,26 pollution control,27 and valuable conversions.28–31 Despite these priorities, most of the bimetallic complexes are still limited to noble metals, including Pd, Pt, Au, Ru, and Rh, which are costly and unavailable.32–36 Therefore, to achieve the full potential of this strategy, exploitation of more naturally abundant metals deserves future attention. So, it is of great interest to improve the understanding and design of novel heterogeneous bimetallic catalysts.

Selective oxidation reactions as a significant class of clean chemical transformations have been extensively used in the synthetic organic chemistry at both laboratorial and industrial levels.37,38 Although there are widespread means of achieving this conversion, typically most of them rely on the use of hazardous terminal oxidants or cause the generation of by-products. With a view to tackling problems for such oxidations and due to environmental concerns, more sustainable chemical processes have been promoted.39–41 Today, a clean and environmentally friendly process using environmentally benign oxidants, such as oxygen, which is among the cheaper and lesser polluting stoichiometric oxidants, is preferred.42–45 Therefore, the use of a catalytic system with implementation of a transition-metal-based catalyst in combination with oxygen as an alternative oxidant would potentially lead to significant improvements over many existing systems. Molybdenum complexes have attracted...
considerable interest, especially as catalysts for oxidation reactions in recent years. However, as far as we know, only a few reports have described the catalytic activity of molybdenum-based bimetallic catalysts in oxidation reactions. Besides, Mo is a well-known multivalent element, which is predicted to display very close redox potentials to vanadium. Therefore, we developed a Mo–V bimetallic complex for the aerobic oxidation transformation.

In view of the above and in continuation of our interest in exploring green oxidation methods, herein, we wish to describe an efficient aerobic benzylic C–H oxidation to the corresponding carbonyl compounds using a Mo(VI)–V(V) bimetallic nanocomplex containing an organosilane Schiff base ligand (HL). The nanocomplex could be readily recovered and reused five times without significant loss of its catalytic activity (Scheme 1).

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Catalyst. Just recently, we have reported the synthesis of a new organosilicon aldehyde from the oxidation of (3-chloropropyl)trimethoxysilane and used it as an appropriate linker for designing new heterogeneous catalysts through formation of the imine bond, generating a new HL (Supporting Information). When we added Mo and VO acetate salts to the ethanolic solution of the title HL under ultrasonic agitation, a new heterobimetallic Mo(IV)–V(V) nanocomplex was acquired (Scheme 2), which is the subject of this work.

ICP-AES analysis revealed that the contents of Mo and V are 0.35 and 0.089 wt %, respectively. The FTIR spectrum of the bimetallic Mo(VI)–V(V) nanocomplex (Figure 1) reveals the presence of major bands at 802, 908, and 862 cm⁻¹, which are attributed to the stretching vibrations of V=O groups as a bridge and the symmetric and asymmetric stretching vibrations of the cis-Mo=O₂ moiety. The peaks at 2955 and 1442 cm⁻¹ are related to the C–H stretching vibration of methylene groups. Evidently, the peak at 1665 cm⁻¹ can be assigned to the C=N stretching mode of the imine bond. The absorption bands at 1127–1142 cm⁻¹ correspond to the Si–O bond.

More evidence for the integrity of this structure was obtained by the Raman spectrum. The bimetallic nanocomplex exhibited four main vibration modes in 647, 806, 862, and 910 cm⁻¹ (Figure 2). The peak at 806 cm⁻¹ can be assigned to the stretching vibration of V=O groups as a bridge. The absorption bands at 862 and 910 cm⁻¹ can be assigned to the symmetric and asymmetric stretching vibrations of the cis-Mo=O₂, respectively. The most intense peak at 647 cm⁻¹ may be assigned to the stretching of the Mo=O=V bond.
To investigate the surface chemical composition and chemical state of elements in the bimetallic Mo(VI)−V(V) complex, XPS measurements were carried out in the region from 0 to 1100 eV and calibrated on the basis of C 1s (285 eV) (Figure 3). The respective peaks for Si 2p, Mo 3d, N 1s, V 2p, and O 1s confirmed the presence of these elements in the prepared complex (Figure 3a). From Figure 3b, the spectra of Mo species were seen to exhibit two peaks at 233 and 235.8 eV, which correspond to the characteristic signals of Mo(VI).\(^{61}\) The observed peak at 517.4 eV (Figure 3c) was assigned to VO(V) species, in terms of the V 2p\(^{3/2}\) orbital. Furthermore, the peak at a binding energy of 522.1 eV was attributed to the V 2p\(^{1/2}\) orbital.\(^{62}\)

TEM observations clearly revealed a semispherical morphology for the title bimetallic complex with sizes ranging between 75 and 93 nm (Figure 4).

To study the stability of the bimetallic complex against temperature, the TGA experiment was performed from room temperature to 800 °C at a heating rate of 10 °C/min. As can be seen in Figure 5, the nanocomplex started to degrade at 343 °C, which indicates the desired stability of the catalyst. The organic parts decomposed completely at 643 °C.

XRD was employed to investigate the crystallinity of the prepared complex, and a wide peak at 2\(\theta\) about 20° demonstrated well an amorphous structure as depicted in Figure 6.

### 2.2. Catalytic Activity

Initially, blank experiments were performed under O\(_2\) (1 atm) for the oxidation of 1-phenyl ethanol (1 mmol) as a model substrate using NHPI (N-hydroxy phthalimide) in ethanol (2 mL). No product was observed in the absence of catalyst or NHPI, even after 12 h of stirring under...
reflux conditions. Then, the catalytic activities of MoO$_2$(acac)$_2$ and VO(acac)$_2$ salts and molybdlenum and vanadyl Schiff base complexes as monometallic complexes were examined at the same reaction and conditions. The results presented in Figure 7 clearly showed the superiority of the title Mo(VI)−V(V) bimetallic nanocomplex than the other catalysts for the oxidation of 1-phenyl ethanol.

Afterward, to achieve the standard condition for this reaction, different factors were evaluated, such as the nature and amount of solvent, temperature, oxidant nature, and the quantity of NHPI or catalyst. The schematic examination can be found in Figure 8. The results in Figure 8a recommended EtOH as a green solvent enabling the reaction to proceed faster than those in MeCN, EtOAc, and solvent-free conditions. Also, the reaction did not proceed in water. Further investigation demonstrated an improvement in the reaction yield by reducing the solvent amount to 0.5 mL and increasing the temperature to 75 °C (Figure 8b,c).

Figure 7. Comparison of oxidation of 1-phenyl ethanol (1 mmol) in the presence of NHPI (0.1 mmol) in EtOH (2 mL) by various catalysts at 75 °C under O$_2$ (1 atm) after 2 h.

![Figure 7](image)

Figure 8. Screening of (a) solvent nature [catalyst (0.013 g), NHPI (0.1 mmol), temperature (75 °C)], (b) solvent amount [catalyst (0.013 g), NHPI (0.1 mmol), temperature (75 °C)], (c) temperature [catalyst (0.013 g), EtOH (0.5 mL), NHPI (0.1 mmol)], (d) NHPI amount [catalyst (0.013 g), temperature (75 °C), EtOH (0.5 mL)], (e) catalyst amount [NHPI (0.06 mmol), temperature (75 °C), EtOH (0.5 mL)], and (f) various oxidants in the oxidation of 1-phenyl ethanol (1 mmol) catalyzed by the Mo−V complex under O$_2$ (1 atm) after 2 h.

![Figure 8](image)
The efficiency of oxidation was affected remarkably by the amount of NHPI, indicating that a radical process prevails to a great extent in the present system (Figure 8d). Also, a survey of the results in Figure 8e indicated that the finest activity was observed with 0.013 g of the catalyst; hence, it was taken as the most appropriate quantity of the Mo−VO complex under the conditions employed in this work. On the basis of the data in Figure 8f, among the common oxidants examined, TBHP and O2 were conceivable, giving relatively higher yields for this transformation; nevertheless, O2 is superior because of the economic factor and the eco-friendly advantage.

Having obtained the optimized conditions, the aerobic oxidation of various benzylic alcohols was examined (Table 1). Structurally and electronically diverse benzylic alcohols were oxidized under the optimized conditions, as shown in Table 1. The results are presented in Table 1. *The reactions were run with substrate (1 mmol), NHPI (0.06 mmol), and catalyst (13 mg) under O2 (5−7 mL/min) at 75 °C in EtOH (0.5 mL). The products were identified by comparison with authentic sample retention times of GC analysis and NMR spectra. The selectivities of products were >99% based on GC analysis.

Table 1. Oxidation of Benzylic Alcohols Using the NHPI/O2 Oxidative System Catalyzed by the Mo(VI)−V(V) Nanobimetallic Complex

| Entry | Alcohol | Product | Time (h) | Yield (%) |
|-------|---------|---------|----------|-----------|
| 1     |         |         | 8        | 80        |
| 2     |         |         | 6        | 94        |
| 3     |         |         | 11       | 93        |
| 4     |         |         | 8        | 92        |
| 5     |         |         | 10       | 94        |
| 6     |         |         | 1        | 95        |
| 7     |         |         | 2        | 100       |
| 8     |         |         | 1        | 94        |
| 9     |         |         | 6        | 65        |
| 10    |         |         | 5        | 62        |
| 11    |         |         | 8        | 54        |
| 12    |         |         | 7        | 94        |
| 13    |         |         | 7        | 48        |

*The reactions were run with substrate (1 mmol), NHPI (0.06 mmol), and catalyst (13 mg) under O2 (5−7 mL/min) at 75 °C in EtOH (0.5 mL). The products were identified by comparison with authentic sample retention times of GC analysis and NMR spectra. The selectivities of products were >99% based on GC analysis.
generally excellent substrates for this system, and no overoxidation of alcohols occurred. Our results exhibited the oxidation performance affected by the electronic properties of substrates. Electron-withdrawing groups on the phenyl rings of alcohols accelerated the reaction (Table 1, entry 6), whereas electron-donating ones retarded it (Table 1, entries 2–5). On the basis of the results, the steric hindrance of alcohols was not dominant. Furthermore, secondary benzylic alcohols gave moderate to excellent yields (Table 1, entries 7–10).

Table 2. Oxidation of Benzylic Hydrocarbons Using NHPI/O2 Oxidative System Catalyzed by the Mo(VI)–V(V) Bimetallic Nanocomplex

| Entry | Alkane                  | Product     | Time (h) | Yield (%) |
|-------|-------------------------|-------------|----------|-----------|
| 1     | Phenethyl ethane        | Phenylacetone | 1        | 100       |
| 2     | 2-Methoxyphenethyl ethane | 2-Methoxyphenylacetone | 7        | 94        |
| 3     | 2-Nitrophenethyl ethane | 2-Nitrophenylacetone | 5        | 70        |
| 4     | Benzyl ethane           | Benzylacetone | 1        | 95        |
| 5     | Diphenyl ethane         | Diphenylacetone | 3        | 97        |
| 6     | 1-Methylindene         | 1-Methylindane | 10       | 92        |
| 7     | Benzylic alcohol        | Benzylic acid | 8        | 74        |
| 8     | Acetophenone            | Acetophenone | 7        | 48        |

The reactions were run with substrate (1 mmol), NHPI (0.1 mmol), and catalyst (10 mg) under O2 (5–7 mL min⁻¹) at 75 °C in AcOH (0.3 mL). The products were identified by comparison with authentic sample retention times of GC analysis and NMR spectra. The selectivities of products were >99% based on GC analysis.

Figure 9. Recycling of the catalytic system for the oxidation of 1-phenylethanol and ethylbenzene using the Mo(VI)–V(V) bimetallic nanocomplex, according to procedures mentioned in the Experimental Section.
alcohol, an alcohol containing a C==C double bond, and 4-(methylsulfanyl)benzyl alcohol, carrying an oxidative sensitive sulfur atom, were subjected to the oxidation procedure. The related carbonyl compounds were produced in both cases, and the olefin moiety and sulfide group remained intact (Table 1, entries 11 and 12). In addition, heterocyclic alcohol, such as furan-2-ylmethanol, was a good substrate in this transformation and afforded the corresponding aldehyde in 48% yield (Table 1, entry 13). It should be mentioned that attempts to oxidize saturated aliphatic alcohols under different conditions failed.

The promising results obtained in the oxidation of benzylic alcohols impelled us to evaluate the potential of the title bimetallic nanocomplex for the selective oxidation of benzylic hydrocarbons. The result obtained from the oxidation of ethyl benzene (Figure 10). Quite the same spectra were observed, from the reaction of both 1-phenylethanol and ethylbenzene (Figure 10). Quite the same spectra were observed, by recording the FTIR spectra of the used catalyst recovered (<1 ppm). The stability of the catalyst was also documented. The hot solution showed no Mo or V within the limit of detection analysis of the product mixtures after centrifugation of the reaction was the only examination. The leaching of Mo and V from the catalyst was excluded by AAS analysis of filtrates. The analysis of the product mixtures after centrifugation of the hot solution showed no Mo or V within the limit of detection (<1 ppm). The stability of the catalyst was also documented by recording the FTIR spectra of the used catalyst recovered from the reaction of both 1-phenylethanol and ethylbenzene (Figure 10).

Table 3. Comparison of Oxidative Activity of Mo(VI)–V(V) Bimetallic Nanocomplex with Other Mo and V Based Catalysts in Oxidation of 1-Phenylethanol and Ethylbenzene

| entry | catalyst | catalyst (mol % or g) | conditions | time (h) | yield (%) | ref |
|--------|----------|-----------------------|------------|----------|-----------|-----|
| 1-phenylethanol | Mo(VI)–V(V) | 0.013 g | EtOH/NHPI/O2/75 °C | 2 | 100 | this work |
| 2 | (Mo2V2O8) | 0.01 g | EtOAc/NHPI/O2/70 °C | 2.5 | 85 | 57 |
| 3 | [Pd–V]–[PMo2O9]4L | 0.62 | DMSO/O2/130 °C | 12 | 94.9 | 63 |
| 4 | VO(acac)2 | 5 | [bmin]PF6/DABCO/O2/80 °C | 12 | 29 | 64 |
| 5 | FeVO4 | 2 | MeCN/H2O2/80 °C | 12 | 72 | 65 |
| 6 | VOSO4 | 0.006 g | H2O/MgSO4/O2/90 °C | 20 | 22 | 66 |
| 7 | V2O5/AC | 0.1 g | toluene/O2/95 °C | 8 | 97 | 67 |
| 8 | MoO3–pyridine | 3.2 | HOAc/IBA/O2/50 °C | 1 | 95 | 68 |
| 9 | polyaniline–Mo(acac)3 | 0.022 | toluene/O2/100 °C | 18 | 89 | 69 |
| 10 | H2PV2O7O9 | 1 | acetone/TEMPO/O2/100 °C | 6 | 98 | 70 |
| 11 | MoO3(acac)–NAP–MgO | 0.07 g | toluene/O2/110 °C | 21 | 84 | 71 |
| ethylbenzene | Mo(VI)–V(V) | 0.01 g | AcOH/NHPI/O2/75 °C | 1 | 100 | this work |
| 13 | (Mo2V2O8) | 0.05 | EtOAc/O2/NHPI/70 °C | 3 | 89 | 57 |
| 14 | CpMo(CO)x(C6Ph) | 1 | MeCN/TBHP/80 °C | 20 | 88 | 72 |
| 15 | [MoO3L(EtOH)]/Y | 0.02 | MeCN/TBHP/80 °C | 5 | 25 | 73 |
| 16 | VO4O2 | 0.002 | PhCN/NHPI/O2/90 °C | 12 | 69 | 75 |
| 17 | [V2O5(OEt)(ashz), μ-OEt]2 | 0.1 | PCA/MeCN/H2O2/50 °C | 2.5 | 16.4 | 76 |
| 18 | VO(acac)2–LiCl | 0.5 | MeCN/NHPI/O2/75 °C | 20 | 79 | 77 |
| 19 | CPS–[VO(SAAM)]2 | 0.1 | O2/110 °C | 14 | 98 | 74 |
demonstrating that the catalyst preserved its integrity during the oxidation reaction.

Table 3 shows the merit of this operational protocol in comparison with those previously reported methods, in terms of catalyst loading, yield, and especially conditions used in the aerobic oxidation of 1-phenylethanol and ethylbenzene as model substrates. Therefore, the title methodology is environmentally benign because of using oxygen as an ideal oxidant, reusing of an active catalyst, and finally green reaction media.

3. CONCLUSIONS

In summary, we have designed a new heterobimetallic organosilicon Schiff base nanocomplex containing Mo and V, both of which are biologically significant transition metals. The Mo(VI)–V(V) bimetallic nanocomplex was found to be an efficient heterogeneous catalyst for aerobic oxidation of benzylic alcohols and benzylic hydrocarbons in the presence of NHPI. The presented catalytic oxidation systems showed remarkable selectivities. The intriguing features of this catalytic system are the use of oxygen as a green oxidant, safe reaction media, reusability, and recyclability of the catalyst, which render the catalyst amenable to use in industrial applications. The catalytic system inspired by the presented method is expected to provide a new strategy toward more sustainable transformations, which is currently ongoing in our laboratory.

4. EXPERIMENTAL SECTION

4.1. Preparation of the Mo(VI)–V(V) Bimetallic Nanocomplex. To a solution of HL (1 mmol) in ethanol (10 mL), a mixture of Mo(acac)₃ (0.5 mmol) and VO(acac)₂ (0.5 mmol) in ethanol (10 mL) was gradually added over a period of 30 min at 60 °C under ultrasonic agitation (59 KHz). Then, the as-obtained mixture was kept for 3 h under this condition. Afterward, the precipitated product was centrifuged and washed with ethanol repeatedly. Finally, the Mo(VI)–V(V) bimetallic nanocomplex was obtained after drying for 12 h at 100 °C in a vacuum oven (dark green powder, 75% yield).

4.2. General Procedure for Aerobic Oxidation of Benzylic Alcohols. To a mixture of 1-phenylethanol (1 mmol) and Mo(VI)–V(V) bimetallic nanocomplex (13 mg) in ethanol (0.5 mL) was added NHPI (0.06 mmol), and the reaction mixture was stirred at 75 °C under an O₂ stream (5–7 mL/min) for the required time. The reaction progress was monitored by GC, and the yields of the products were determined by GC and NMR analyses.

4.3. General Procedure for Aerobic Oxidation of Benzylic Hydrocarbons. To a mixture of ethyl benzene (1 mmol) and Mo(VI)–V(V) bimetallic nanocomplex (10 mg) in acetic acid (0.3 mL) was added NHPI (0.1 mmol), and the reaction mixture was stirred at 75 °C under an O₂ stream (5–7 mL/min) for the required time. The reaction progress was monitored by GC, and the yields of the products were determined by GC and NMR analyses.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02832.

Experimental details of the preparation of organosilicon aldehyde and Schiff base ligand and the optimization of oxidation of benzylic hydrocarbons (PDF)

AUTHOR INFORMATION

Corresponding Authors

E-mail: mjaafarpour@birjand.ac.ir. Tel: +98 561 2502516. Fax: +98 561 2502515 (M.J.). E-mail: rezaeifard@birjand.ac.ir; rezaeifard@gmail.com (A.R.).

ORCID

Maasoumeh Jafarpour: 0000-0002-9946-5013

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Support for this work by the Research Council of the University of Birjand is highly appreciated.

REFERENCES

(1) VanLoon, G. W.; Duffy, S. J. Environmental Chemistry: a Global Perspective; Oxford University: Oxford, U.K., 2017.
(2) Anastas, P. T.; Eghbali, N. Green chemistry: principles and practice. Chem. Soc. Rev. 2010, 39, 301–312.
(3) Anastas, P. T.; Kirchhoff, M. M. Origins, current status, and future challenges of green chemistry. Acc. Chem. Res. 2002, 35, 686–694.
(4) Long, X.; Wang, Z.; Xiao, S.; An, Y.; Yang, S. Transition metal based layered double hydroxides tailored for energy conversion and storage. Mater. Today 2016, 19, 213–226.
(5) Khan, M. S.; Haque, A.; Al-Sulti, M. K.; Raithby, P. R. Recent advances in the application of group-10 transition metal based catalysts in C-H activation and functionalization. J. Organomet. Chem. 2015, 793, 114–133.
(6) Yuan, C.; Wu, H. B.; Xie, Y.; Lou, X. W. D. Mixed transition-metal oxides: design, synthesis, and energy-related applications. Angew. Chem., Int. Ed. 2014, 53, 1488–1504.
(7) Que, L., Jr.; Tolman, W. B. Biologically inspired oxidation catalysis. Nature 2008, 455, 333.
(8) Largeron, M.; Fleury, M.-B. A biologically inspired CuI/Topaquinone-like Co-catalytic system for the highly atom-economical aerobic oxidation of primary amines to imines. Angew. Chem. 2012, 124, 5505–5508.
(9) Kainzka, K.; Miyamura, H.; Kobayashi, S. Remarkable effect of bimetallic nanocluster catalysts for aerobic oxidation of alcohols: combining metals changes the activities and the reaction pathways to aldehydes/carboxylic acids or esters. J. Am. Chem. Soc. 2010, 132, 15096–15098.
(10) Shibasaki, M.; Yamamoto, Y. Multimetallic Catalysts in Organic Synthesis; Wiley: Weinheim, Germany, 2006.
(11) Bratko, I.; Gómez, M. Polymeric complexes linked to a single-frame ligand: cooperative effects in catalysis. Dalton Trans. 2013, 42, 10664–10681.
(12) Shibasaki, M.; Kanai, M.; Matsuura, S.; Kumagai, N. Recent progress in asymmetric bifunctional catalysis using multimetallic systems. Acc. Chem. Res. 2009, 42, 1117–1127.
(13) Sankar, M.; Dimitratos, N.; Miedziak, P. J.; Wels, P. P.; Kiely, C. J.; Hutchings, G. J. Designing bimetallic catalysts for a green and sustainable future. Chem. Soc. Rev. 2012, 41, 8099–8139.
(14) Kaub, C.; Lebedkin, S.; Li, A.; Kruppa, S. V.; Strebert, P. H.; Kappes, M. M.; Riehn, C.; Roesky, P. W. Bimetallic d₁₀-metal complexes of a bipyrindine substituted N-heterocyclic carbene. Chem. Eur. J. 2018, 24, 6094–6104.
(15) Dang-Bao, T.; Pla, D.; Favier, I.; Gómez, M. Bimetallic nanoparticles in alternative solvents for catalytic purposes. Catalysts 2017, 7, 207.
(16) Mahato, M.; Dey, D.; Pal, S.; Saha, S.; Ghosh, A.; Harms, K.; Nayek, H. P. Syntheses, structures, optical properties and biological activities of bimetallic complexes. RSC Adv. 2014, 4, 64725–64730.
(17) Chen, B.; Li, F.; Huang, Z.; Yuan, G. Carbon-coated Cu-Co bimetallic nanoparticles as selective and recyclable catalysts for production of biofuel 2, 5-dimethylfuran. Appl. Catal. B 2017, 200, 192–199.

(18) Wang, D.; Li, Y. Bimetallic nanocrystals: liquid phase synthesis and catalytic applications. Adv. Mater. 2011, 23, 1044–1060.

(19) Lopez-Valbuena, J. M.; Escudero-Adan, E. C.; Benet-Buchholz, J.; Freixa, Z.; van Leeuwen, P. W. N. M. An approach to bimetallic catalysts by ligand design. Dalton Trans. 2010, 39, 8560–8574.

(20) Ly, B. K.; Minh, D. P.; Pinel, C.; Besson, M.; Tapin, B.; Epron, F.; Espeel, C. Effect of addition of Rm in bimetallic Pd-Re/TiO2 catalysts upon the selective aqueous-phase hydrogenation of succinic acid to 1, 4-butanediol. Top. Catal. 2012, 55, 466–473.

(21) Park, J.; Hong, S. Cooperative bimetallic catalysis in asymmetric transformations. Chem. Soc. Rev. 2012, 41, 6931–6943.

(22) Mankad, N. P. Selectivity effects in bimetallic catalysis. Chem. Eur. J. 2016, 22, 5882–5892.

(23) Singh, A. K.; Xu, Q. Synergistic catalysis over bimetallic alloy nanoparticles. ChemCatChem 2013, 5, 652–676.

(24) Liu, X.; Wang, D.; Li, Y. Synthesis and catalytic properties of bimetallic nanomaterials with various architectures. Nano Today 2012, 7, 448–466.

(25) Huang, T.; Huang, W.; Huang, J.; Ji, P. Methane reforming reaction with carbon dioxide over SBA-15 supported Ni-Mo bimetallic catalysts. Fuel Process. Technol. 2011, 92, 1868–1875.

(26) Trinh, Q. H.; Lee, S. B.; Mok, Y. S. Removal of ethylene from air stream by adsorption and plasma-catalytic oxidation using silver-based bimetallic catalysts supported on zeolite. J. Hazard. Mater. 2015, 285, 525–531.

(27) Wong, M. S.; Alvarez, J. J. F.; Fang, Y.; Akcin, N.; Ntut, M. O.; Miller, J. T.; Heck, K. N. Cleaner water using bimetallic nanoparticle catalysts. J. Chem. Biolotechnol. 2009, 84, 158–166.

(28) Shiraiishi, Y.; Sakamoto, H.; Sugano, Y.; Ichikawa, S.; Hirai, T. Pt-Cu bimetallic alloy nanoparticles supported on anatase TiO2: highly active catalysts for aerobic oxidation driven by visible light. ACS Nano 2013, 7, 9287–9297.

(29) Wang, D.; Villa, A.; Spontoni, P.; Su, D. S.; Prati, L. In situ formation of Au-Pd bimetallic active sites promoting the physically mixed monometallic catalysts in the liquid-phase oxidation of alcohols. Chem. Eur. J. 2010, 16, 10007–10103.

(30) Kurbah, S. D.; Asthana, M.; Syiemlieh, I.; Lal, R. A. Peroxidative aerobic oxidation of alcohols catalyzed by heterobinuclear vanadium (V) complexes using H2O2 as terminal oxidizing agents. Appl. Organomet. Chem. 2018, 32, No. e4299.

(31) Pérez-Temprano, M. H.; Casares, J. A.; Espinet, P. Bimetallic catalysis using transition and group 11 metals: an emerging tool for C-C coupling and other reactions. Chem. Eur. J. 2012, 18, 1864–1884.

(32) Gholeinejad, M.; Bahrami, M.; Na, N. Synthesis and catalytic properties of FeCo bimetallic catalysts by ligand design. RSC Adv. 2015, 5, 45649–45660.

(33) Jafarpour, M.; Rezaeifard, A.; Feizpour, F.; Asakura, H.; Tanaka, T.; Nishio, M. Insight into effect of microstructure on the selectivity of hydrogenation reaction over supported Au-Pt bimetallic catalysts. J. Catal. 2014, 314, 1574–1583.

(34) Smith, I. G.; Gribakin, J. C.; Gutauskas, A. C.; Gray, D. L.; Domski, G. J. Synthesis, characterization, and catalytic behavior of mono- and bimetallic ruthenium(II) and iridium(III) complexes supported by pyridine-functionalized N-heterocyclic carbene ligands. Inorg. Chem. Commun. 2017, 81, 27–32.

(35) Xu, C.; Du, Y.; Li, C.; Yang, J.; Yang, G. Insight into effect of acid/base nature of supports on selectivity of glycerol oxidation over supported Au-Pt bimetallic catalysts. Appl. Catal. B 2015, 164, 334–343.

(36) Cavani, F. Catalytic selective oxidation: The forefront in the challenge for a more sustainable chemical industry. Catal. Today 2010, 157, 8–15.
(59) Mathew, M.; Carty, A. J.; Palenik, G. J. Unusual complex containing vanadyl groups. Crystal structure of N, N'-propylenebis (salicylaldiminate) oxovanadium (IV). J. Am. Chem. Soc. 1970, 92, 3197–3198.

(60) Botar, B.; Kögerler, P.; Hill, C. L. \([(\text{Mo}-\text{Mo})_{2}(\text{H}_{2}\text{O})_{3}(\text{SO}_{4})_{3})_{12}(\text{VO})_{40}(\text{H}_{2}\text{O})_{30}]^{36-}\): A molecular quantum spin icosidodecahedron. Chem. Commun. 2005, 3138–3140.

(61) Li, Y.; Fu, X.; Gong, B.; Zou, X.; Tu, X.; Chen, J. Synthesis of novel immobilized tridentate Schiff base dioxomolybdenum (VI) complexes as efficient and reusable catalysts for epoxidation of unfunctionalized olefins. J. Mol. Catal. A: Chem. 2010, 322, 55–62.

(62) Bukhtiyarov, V. I. XPS and SIMS characterization. Catal. Today 2000, 56, 403–413.

(63) Huang, X.; Zhang, X.; Zhang, D.; Yang, S.; Feng, X.; Li, J.; Lin, Z.; Cao, J.; Pan, R.; Chi, Y.; et al. Binary Pd-polyoxometalates and isolation of a ternary Pd-V-polyoxomolybdate active species for selective aerobic oxidation of alcohols. Chem. Eur. J. 2014, 20, 2557–2564.

(64) Jiang, N.; Ragauskas, A. J. Vanadium-catalyzed selective aerobic alcohol oxidation in ionic liquid [bmim] PF6. Tetrahedron Lett. 2007, 48, 273–276.

(65) Heydari, A.; Sheykhan, M.; Sadeghi, M.; Radfar, I. Nanorods of FeVO4: An efficient heterogeneous catalyst for chemoselective oxidation of benzylc alcohols. Inorg. Nano-Met. Chem. 2017, 47, 248–255.

(66) Marui, K.; Higashiura, Y.; Kodama, S.; Hashidate, S.; Nomoto, A.; Yano, S.; Ueshima, M.; Ogawa, A. Vanadium-catalyzed green oxidation of benzylc alcohols in water under air atmosphere. Tetrahedron 2014, 70, 2431–2438.

(67) Tang, Q.; Chen, Y.; Yang, Y. Understanding the nature of vanadium species supported on activated carbon and its catalytic properties in the aerobic oxidation of aromatic alcohols. J. Mol. Catal. A: Chem. 2010, 315, 43–50.

(68) Malakooti, R.; Feghhi, A. MoOx-pyridine organic-inorganic hybrid wires as a reusable and highly selective catalyst for the oxidation of alcohols: a comparison study between reaction-controlled phase-transfer catalysis and heterogeneous catalysis. New J. Chem. 2017, 41, 3405–3413.

(69) Velusamy, S.; Ahamed, M.; Punniyamurthy, T. Novel polyaniline-supported molybdenum-catalyzed aerobic oxidation of alcohols to carbonyl compounds. Org. Lett. 2004, 6, 4821–4824.

(70) Ben-Daniel, R.; Alsters, P.; Neumann, R. Sensitive aerobic oxidation of alcohols with a combination of a polyoxometalate and nitroxyl radical as catalysts. J. Org. Chem. 2001, 66, 8650–8653.

(71) Kantam, M. L.; Yadav, J.; Laha, S.; Sreedhar, B.; Bhargava, S. Nanocrystalline magnesium oxide-stabilized molybdenum: an efficient heterogeneous catalyst for the aerobic oxidation of alcohols to carbonyl compounds. Adv. Synth. Catal. 2008, 350, 2575–2582.

(72) Khomane, S. B.; Doke, D. S.; Dongare, M. K.; Halligudi, S. B.; Umbarkar, S. B. Efficient oxidation of ethyl benzene using in situ generated molybdenum acetylde oxo-peroxo complex as recyclable catalyst. Appl. Catal., A 2017, 531, 45–51.

(73) Ghorbanloo, M.; Alamooti, A. M. Encapsulation of molybdenum (VI) complex with thiazole-hydrazone ligand in zeolite Y: an efficient reusable catalyst for oxidation of primary alcohols and hydrocarbons. J. Porous Mater. 2017, 24, 769–777.

(74) Gao, B.; Li, Y.; Shi, N. Oxovanadium (IV) Schiff base complex immobilized on CPS microspheres as heterogeneous catalyst for aerobic selective oxidation of ethyl benzene to acetophenone. React. Funct. Polym. 2013, 73, 1573–1579.

(75) Qin, J.; Fu, Z.; Liu, Y.; He, X.; Zhang, D.; Wu, W.; Wang, Y.; Gong, X.; Deng, X.; Wu, H.; Zou, Y.; Yu, N.; Yin, D. Aerobic oxidation of ethylbenzene Co-catalyzed by N-hydroxyphthalimide and oxobis (8-quinolinolato) vanadium (IV) complexes. Chin. J. Catal. 2011, 32, 1342–1348.

(76) Sutradhar, M.; Kirillova, M. V.; Caires da Silva, M. F. C.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. A hexanuclear mixed-valence oxovanadium (IV,V) complex as a highly efficient alkane oxidation catalyst. Inorg. Chem. 2012, 51, 11229–11231.