Transition Met Chem (2011) 36:269–274
DOI 10.1007/s11243-011-9465-3

Fabrication of highly active Sn/W mixed transition-metal oxides as solid acid catalysts

Zhiwang Yang · Lengyuan Niu · Zhenhong Ma · Hengchang Ma · Ziqiang Lei

Received: 20 November 2010 / Accepted: 24 January 2011 / Published online: 8 March 2011

Abstract Catalytically active Sn/W mixed transition-metal oxides were prepared by calcination of the corresponding Sn/W hydroxide precursors at different temperatures. The obtained mixed oxides were characterized by physicochemical and spectroscopic methods. With variation of the molar ratios of Sn/W, the prepared Sn/W mixed oxide catalysts had different reaction activities. Thus, the Sn/W-2-800 oxide acted as an effective heterogeneous catalyst for the Baeyer–Villiger oxidation of ketones and the Friedel–Crafts reaction. Many ketones, as well as benzyl alcohol and acetic anhydride, were transformed into the corresponding products with high conversion and selectivity. The catalysts can be easily separated from the reaction mixtures and can be reused for at least five cycles without significant loss of activity.

Introduction

Traditionally, inorganic acids such as H_2SO_4 and H_3PO_4, and Lewis acids such as $AlCl_3$, $ZnBr_2$, $FeCl_3$, and BF_3 etherate have been used to promote acid-catalyzed reactions. Although these catalytic processes are generally simple and efficient, several problems have been encountered. First, selective transformations of the substrates are often difficult; by-products are often obtained, resulting in the need for product separation and the waste of solvent. Second, such homogeneous catalysts cannot be recycled. Hence, these systems will potentially cause environmental problems. Therefore, the discovery of environmentally benign catalysts is a very important area of current research. In principle, heterogeneous solid acids can overcome these problems.

Many solid acids are mineral oxides, such as sulfated zirconia [1–3], Cs-exchanged heteropoly acids [4], acidic polymers [5, 6], and zeolites [7], which contain both Lewis and Brønsted acid sites. These materials have been used in the isomerization of alkanes and other petrochemical processes such as alkylation of aromatics and hydrocarbon cracking reactions [8]. As important solid acids, transition-metal oxides are currently attracting considerable attention due to their unique properties and broad range of potential applications. During the last decades, monometallic oxides such as MgO [9–11], SnO_2 [12–14], WO_3 [12, 14], ZrO_2 [12, 14, 15], TiO_2 [12, 14, 16], Al_2O_3 [17], Nb_2O_5 [12, 14, 18], Ta_2O_5 [12, 14, 19], and bimetallic oxides such as Nb–Ta oxides [12, 14, 20, 21], Mg–Ta oxides [21, 22], Nb-W oxides [23], Sn/W oxides [24], Zr-W oxides [25, 26], and WO_3-TiO_2 [27] have all been studied. The transition-metal centers in the inorganic frameworks of porous structures also possess variable oxidation states and empty *d*-orbitals, which allow electron transfer to occur between the reactants and active sites during the catalytic process [28].

In this paper, we report the synthesis of Sn/W mixed oxides and their application in some acid-catalyzed reactions including Baeyer–Villiger oxidation and the Friedel–Crafts reaction. A series of Sn/W oxides were synthesized through coprecipitation and calcination methods. The obtained Sn/W oxides, especially for the oxide of Sn/W-2-800, exhibit the advantages of high conversion, high selectivity, and recyclability in these reactions.

Z. Yang · L. Niu · Z. Ma · H. Ma · Z. Lei
Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, China

Z. Yang · L. Niu · Z. Ma · H. Ma · Z. Lei (✉)
Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China
e-mail: leizq@nwnu.edu.cn

Experimental

$SnCl_4 \cdot 5H_2O$ and $Na_2WO_4 \cdot 2H_2O$ were obtained from Shanghai Zhongtai Chemical Co. 2-Adamantanone (98%), 2-methylcyclohexanone (95%), 4-methylcyclohexanone (98%), and 4-*tert*-butylcyclohexanone (98%) were purchased from Meryer Chemical Co. Ltd., Shenzhen. Cyclopentanone (99%), cyclohexanone (98%), anisole, acetic anhydride, and benzyl alcohol were obtained from Tianjin Guangfu Fine Chemical Technology Co. Ltd. Other solvents were all obtained from commercial sources and were used as received without further purification.

GC analysis was carried out on a Shimadzu GC-2010 gas chromatography instrument equipped with a 15 m × 0.53 mm × 1.50 μm RTX-1 capillary column. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 plus instrument in $CDCl_3$ using TMS as internal standard. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance instrument using CuKα radiation ($k = 1.5406$ Å). FT/IR spectra were recorded on a Nicolet Nexus 670 Fourier transform infrared spectrometer using KBr tablets. The SEM images were taken on a Hitachi S-4800 scanning electron microscope. BET results as well as the Nitrogen adsorption–desorption isotherms were recorded at 77 K on a Quantachrome Autosorb-3B instrument.

Catalyst preparation

The Sn/W oxides were synthesized according to the literature [24]. In typical synthesis, 2.5 mmol of $Na_2WO_4 \cdot 2H_2O$ (dissolved in 5 mL of deionized water) and *a* mmol of $SnCl_4 \cdot 5H_2O$ ($a = 2.5$, 5, 10 or 20) were mixed and stirred for 1 h at room temperature, and then 20 mL of deionized water was added. After stirring for 24 h at room temperature, the resulting white precipitate was filtered off and washed with deionized water until no chloride ion was detected. The precipitate was dried in vacuum to afford hydroxide precursors with different molar ratios of Sn/W. Different Sn/W oxide catalysts were prepared by calcining the corresponding hydroxide at different temperatures (ranging from 400 to 1,000 °C) in a muffle furnace for 3 h under air. The as-prepared products are denoted as Sn/W-*x*-T ($x = a/2.5$, representing the different molar ratios of Sn/W in the products).

General procedures for the catalytic reactions

Oxidation of ketones was carried out in a 10-mL flask by stirring a mixture of 0.1 mmol of the ketone required, 3 mL of 1, 2-dichloroethane, 0.3 mmol of 30% H_2O_2, and 6 mg of Sn/W- *x* -T at 75 °C for 10 h. Friedel–Crafts reaction of anisole was performed by stirring a mixture of 20 mg of catalyst, 10 mmol of anisole and 1 mmol of benzyl alcohol or 1 mmol of acetic anhydride at 100 °C for 3–5 h. All the products in these reactions were determined by GC analysis. Some of the products from the Baeyer–Villiger oxidations were purified by silica gel column chromatography with hexane/ethyl acetate (10:1) as eluent. The products of alkylation were first separated by silica gel column chromatography with petroleum ether as eluent and then further purified by silica gel column chromatography with CCl_4 as eluent, similar to the first step.

Product separation and identification

The products were purified by a silica gel column chromatography with hexane/ethyl acetate (10:1) or petroleum ether as eluent. NMR data are given below.

Product **1b**: ^1H NMR: δ 4.489 (1H), 3.076 (1H), 2.114 (2H), 2.004 (2H), 1.957 (1H), 1.921 (2H), 1.856 (2H), 1.739 (2H), 1.280 (1H). ^{13}C NMR: δ 178.960, 73.136, 41.151, 35.862, 35.679, 33.713, 30.863, 29.628, 25.856, 25.650.

Product **2b**: ^1H NMR: δ 4.282 (2H), 2.49 (2H), 1.798 (4H). ^{13}C NMR: δ 171.339, 69.331, 29.636, 22.091, 18.875.

Product **3b**: ^1H NMR: δ 4.235 (2H), 2.643 (2H), 1.867 (2H), 1.795 (4H). ^{13}C NMR: δ 171.339, 69.331, 29.636, 22.091, 18.875.

Product **4b**: ^1H NMR: δ 4.449 (1H), 2.653 (2H), 1.930 (4H), 1.627 (2H), 1.352 (3H). ^{13}C NMR: δ 175.60, 76.80, 36.21, 35.00, 28.28, 22.88, 22.57.

Product **5b**: ^1H NMR: δ 4.188 (2H), 2.630 (2H), 1.912 (2H), 1.862 (1H), 1.498 (1H), 1.343 (1H), 1.002 (3H). ^{13}C NMR: δ 175.995, 67.984, 37.097, 35.116, 33.081, 30.634, 22.008.

Product **6b**: ^1H NMR: δ 4.335 (1H), 4.158 (1H), 2.585 (1H), 2.569 (1H), 2.085 (2H), 1.527 (1H), 1.369 (2H), 0.898 (9H). ^{13}C NMR: δ 176.285, 68.579, 50.667, 33.386, 32.936, 30.261, 27.472, 27.373, 27.304, 23.669.

Para-benzylanisole: ^1H NMR: δ 7.256 (2H), 7.182 (3H), 7.092 (2H), 6.831 (2H), 3.922 (2H), 3.770 (3H). ^{13}C NMR: δ 157.888, 141.549, 133.219, 129.828, 128.776, 128.395, 125.941, 113.817, 55.219, 40.984.

Ortho-benzylanisole: ^1H NMR: δ 7.214 (6H), 7.065 (1H), 6.869 (2H), 3.971 (2H), 3.807 (2H). ^{13}C NMR: δ 157.279, 140.977, 130.270, 129.607, 128.929, 128.220, 127.367, 125.736, 120.416, 110.326, 55.303, 35.809.

Results and discussion

FTIR spectra and XRD patterns and SEM images

The FTIR spectra of the Sn/W oxides are shown in Fig. 1, and the peak at 954 cm^{-1} is attributed to the W=O stretching vibration. The W–O–W band at 740–890 cm^{-1} and Sn–O–Sn band at 610–700 cm^{-1} were also observed for all of the samples, suggesting the presence of polytungstate species. As shown in Fig. 2, the XRD patterns of the Sn/W hydroxide showed broad signals as also observed for SnO_2, suggesting that a SnO_2-like phase was formed, and the polytungstate species were highly dispersed on SnO_2 and/or incorporated into the SnO_2 frameworks [24]. Temperature is a major factor that affects the crystal form of the oxides. Thus, XRD patterns similar to those of the hydroxide precursor were obtained for the oxides prepared at low calcination temperatures (<800 °C). On increasing the temperature to 800 °C, signals of triclinic WO_3 phase were observed in the products. On increasing the Sn content and keeping the temperature at 800 °C, similar patterns to Sn/W-2-800 were detected. Finally, most of the tungstate species are converted into WO_3 crystallites at 1,000 °C.

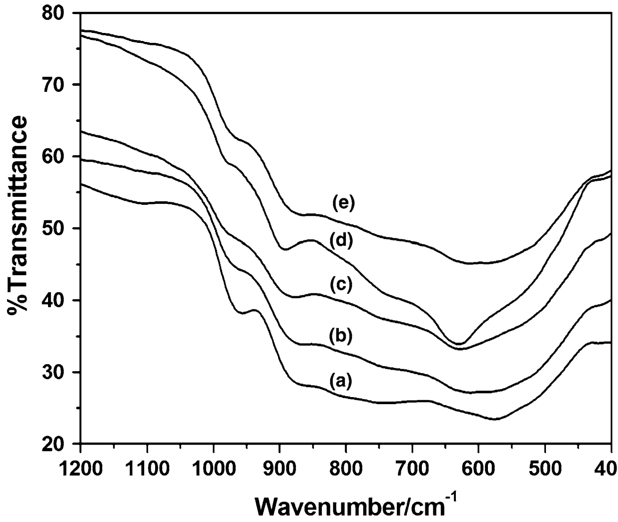


Fig. 1 FT-IR spectra for **a** Sn/W-2 hydroxide, **b** Sn/W-2-400, **c** Sn/W-2-600, **d** Sn/W-2-800, **e** Sn/W-2-1000 oxides

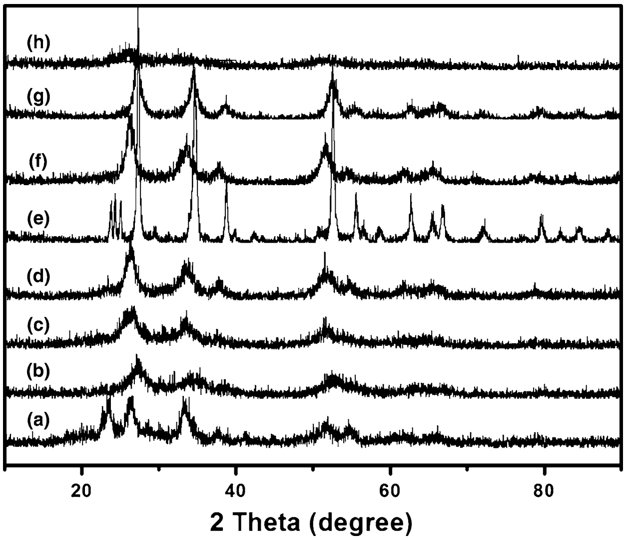


Fig. 2 XRD patterns for **a** Sn/W-1-800, **b** Sn/W-2-400, **c** Sn/W-2-600, **d** Sn/W-2-800, **e** Sn/W-2-1000, **f** Sn/W-4-800, **g** Sn/W-8-800, **h** Sn/W-2 hydroxide

The crystal morphologies of the Sn/W oxides and Sn/W-2 hydroxide were investigated by scanning electron microscopy (SEM). As shown by the representative SEM images (Fig. 3), the samples of Sn/W-2 hydroxide consisted of lump-shaped particles with diameters of about 40 μm (Fig. 3a), while the corresponding Sn/W oxides consisted of smaller corallite-type uniform crystal powders (Fig. 3b–g). The particle diameters of the Sn/W oxides tend to become smaller with increasing calcining temperatures. When the temperature was raised to 1,000 °C, the particles were aggregated and the framework was collapsed (Fig. 3b–d). On the other hand, the images also reveal that the particles are inclined to aggregate when a high content of Sn component was present in the oxides (Figs. 3f, g).

N_2 adsorption–desorption experiments

The pore properties of all samples were characterized by nitrogen adsorption–desorption methods. Table 1 shows the specific surface areas and pore properties of the synthesized materials. The surface areas were estimated using the Brunauer–Emmett–Teller (BET) method, and pore volumes were obtained by the Barrett–Joyner–Halenda (BJH) method. Different results were observed for Sn/W mixed oxides obtained at different calcination temperatures. The data clearly showed that the surface area gradually decreased from 137 to 13 m^2/g as the calcining temperature increased from 400 to 1,000 °C, while the pore volumes increased drastically due to the formation of void spaces between particles and the increasing pore size.

Figure 4 displays the N_2 adsorption–desorption isotherms of the Sn/W oxides. The nitrogen adsorption isotherms of the three oxides obtained at different calcination temperatures from 400 to 800 °C are of classical type IV, mesoporous materials, according to the IUPAC classification [29]. However, for Sn/W-2-1000, high calcination temperature resulted in a collapse of the framework leading to the formation of an amorphous structure without any long-range order.

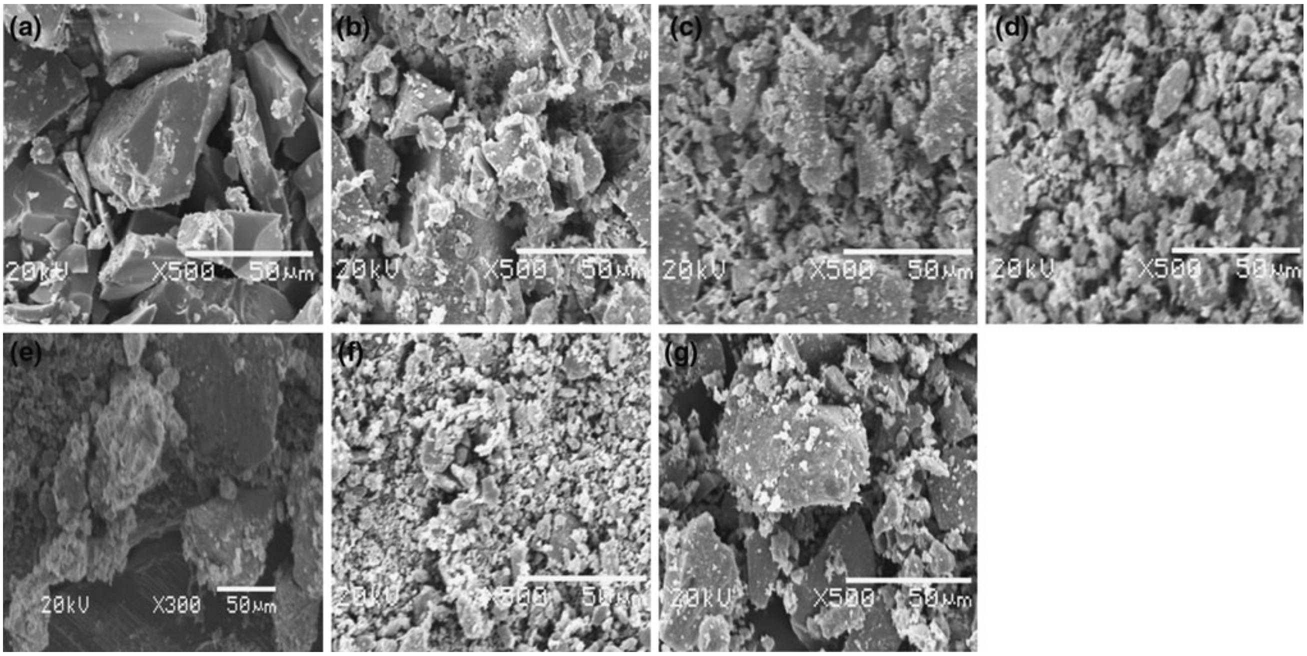


Fig. 3 SEM images for **a** Sn/W-2 hydroxide, **b** Sn/W-2-400, **c** Sn/W-2-600, **d** Sn/W-2-800, **e** Sn/W-2-1000, **f** Sn/W-4-800, **g** Sn/W-8-800

Table 1 Properties of the as-prepared Sn/W mixed transition-metal oxides

Sample	Surface area (m^2/g)	Pore size (nm)	Pore volume (mL/g)
Sn/W-2-400	137	1.54	0.048
Sn/W-2-600	84	1.92	0.114
Sn/W-2-800	63	3.25	0.205
Sn/W-2-1000	13	16.7	0.228

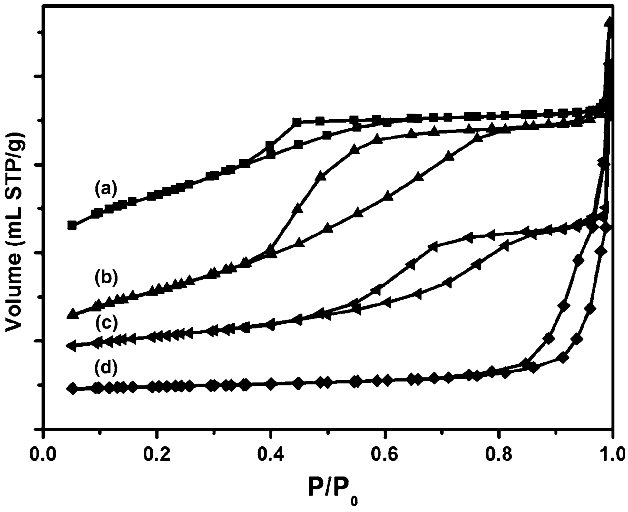


Fig. 4 N_2 adsorption–desorption isotherms of **a** Sn/W-2-400, **b** Sn/W-2-600, **c** Sn/W-2-800, **d** Sn/W-2-1000

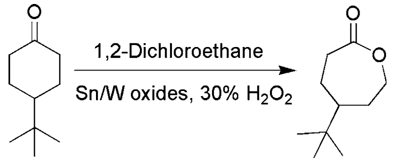
Application as catalysts for Baeyer–Villiger oxidations

The catalytic properties of all the synthesized Sn/W oxides were first tested for the Baeyer–Villiger oxidation of 4-*tert*-butylcyclohexanone, with the results listed in Table 2. Variation of the Sn and W content resulted in remarkably different conversions of the substrate. Of all the oxides, the series of Sn/W-2 type possessed the highest catalytic activity under an identical calcining temperature. A maximum conversion of 81% was reached for the oxide of Sn/W-2-800. These results indicate that the structure of the oxides plays an important role in the oxidation.

We then went on to explore the Baeyer–Villiger oxidation of 4-*tert*-butylcyclohexanone catalyzed by different amounts of Sn/W-2-800. As shown in Table 3, the conversion of 4-*tert*-butylcyclohexanone is accelerated with increasing amounts of catalyst, and the highest conversion was obtained when 6 mg of Sn/W-2-800 was used. Therefore, the optimum catalyst amount used in the Baeyer–Villiger oxidation system was fixed at 6 mg for further experiments.

According to the above results, the Sn/W-2-800 oxide bears the highest catalytic activity in Baeyer–Villiger oxidation, so it was selected and was applied for the oxidation of other ketones with a range of different structures. As shown in Table 4, several of the cyclic ketones, including 2-adamantanone, cyclopentanone, cyclohexanone, and its derivatives, were oxidized to the corresponding lactones with high conversion and selectivity. The results also suggest that the reactivity of different

Table 2 Baeyer–Villiger oxidation of 4-*tert*-butylcyclohexanone with various Sn/W oxides catalysts

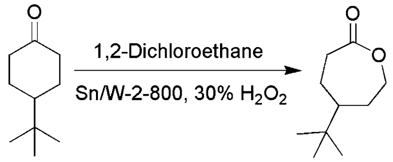


Entry	Catalysts	Conversion (%)[a]	Selectivity (%)[a]
1	Sn/W-1-400	19	100
2	Sn/W-2-400	26	79
3	Sn/W-4-400	13	100
4	Sn/W-8-400	15	100
5	Sn/W-1-600	46	92
6	Sn/W-2-600	73	89
7	Sn/W-4-600	23	81
8	Sn/W-8-600	12	100
9	Sn/W-1-800	51	100
10	Sn/W-2-800	81	100
11	Sn/W-4-800	19	100
12	Sn/W-8-800	14	100
13	Sn/W-1-1000	10	100
14	Sn/W-2-1000	16	63
15	Sn/W-4-1000	5	100
16	Sn/W-8-1000	6	100
17	Sn/W-2 hydroxide	0	0
18	None	0	0

Reaction conditions: 4-*tert*-butylcyclohexanone 0.1 mmol, catalyst 6 mg, 30%H_2O_2 3.0 eq., 1,2-dichloroethane 3 mL, 10 h, 75 °C

[a] Conversion and selectivity were determined by GC analysis

Table 3 Baeyer–Villiger oxidation of 4-*tert*-butylcyclohexanone catalyzed by different amounts of Sn/W-2-800

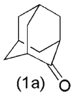
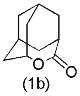
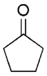
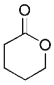
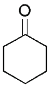
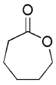
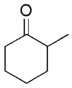
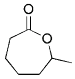
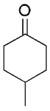
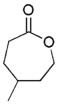
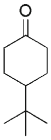
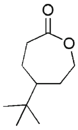


Entry	Catalyst (mg)	Conversion (%)[a]	Selectivity (%)[a]
1	2.0	61	99
2	4.0	72	99
3	6.0	81	100
4	8.0	80	98

Reaction conditions: 4-*tert*-butylcyclohexanone 0.1 mmol, 30% H_2O_2 3.0 eq., 1,2-dichloroethane 3 mL, 10 h, 75 °C

[a] Conversion and selectivity were determined by GC analysis

Table 4 Baeyer–Villiger oxidation of ketones catalyzed by Sn/W-2-800

Entry	Substrate	Conversion (%) [a]	Selectivity (%) [a]	Product
1	 (1a)	100	100	 (1b)
2	 (2a)	72	100	 (2b)
3	 (3a)	88	87	 (3b)
4	 (4a)	65	82	 (4b)
5	 (5a)	97	84	 (5b)
6	 (6a)	81	100	 (6b)

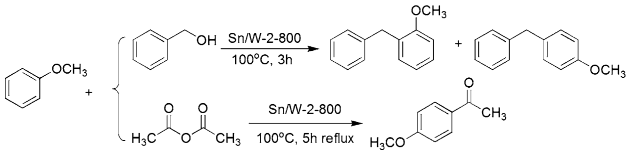
Reaction conditions: substrate 0.1 mmol, catalyst 6 mg, 30%H_2O_2 3.0 eq., 1,2-dichloroethane 3 mL, 10 h, 75 °C

[a] Conversion and selectivity were determined by GC analysis

ketones depends on the ring size and the migratory ability of the substituent group. Ketones with a highly strained ring, such as 2-adamantanone, show the highest conversion among the investigated series under identical conditions. On the other hand, ketones that possess a substituent near the carbonyl group, such as 2-methyl-cyclohexanone, always show lower reactivity in the oxidation. This is because Baeyer–Villiger oxidation is a two-step reaction: nucleophilic addition of an oxidant to give the so-called Criegee adduct is followed by rearrangement to the ester or lactone [30, 31]. A substituent neighboring the carbonyl bond hinders the formation of the Criegee adduct. However, as for 4-methylcyclohexanone and 4-*tert*-butylcyclohexanone, promising conversions (97 and 81%, respectively) were obtained because of the long distance between the alkyl and carbonyl group.

Application as catalysts for Friedel–Crafts reactions

The high catalytic performance of the Sn/W-2-800 oxide was further demonstrated as a heterogeneous catalyst for the Friedel–Crafts reaction of anisole with benzyl alcohol or acetic anhydride. Anisole was efficiently converted into the corresponding benzylanisole in excellent yields



Scheme 1 Friedel–Crafts reaction of anisole catalyzed by Sn/W-2-800

Table 5 Recycling properties of Sn/W-2-800 in the Baeyer–Villiger oxidation of 2-adamantanone

Entry	1	2	3	4	5
Conversion (%)[a]	100	100	99	97	93
Selectivity (%)[a]	100	99	99	99	97

Reaction conditions: 2-adamantanone 0.1 mmol, catalyst 6 mg, 30% H_2O_2 2.0 eq., 1,2-dichloroethane 3 mL, 10 h, 75 °C

[a] Conversion and selectivity were determined by GC analysis

(>99%) in the presence of Sn/W-2-800; both *ortho*- and *para*-benzylanisole were formed in the reaction. A slight selectivity for *para*-benzylanisole (53%) over *ortho*-benzylanisole (47%) was observed, and no *meta*-product was detected. For the acylation of anisole, the conversion of acetic anhydride was 37% after 5 h. It is noteworthy that *para*-methoxyacetophenone was exclusively obtained and no *ortho*-product was formed (Scheme 1). All these results suggest that the prepared Sn/W mixed oxides are promising solid acid catalysts for Friedel–Crafts reactions.

To investigate the recycling properties of the catalyst, the Sn/W-2-800 oxide was filtered from the reaction mixture, thoroughly washed with the solvent used in the oxidation, dried at 100 °C for 24 h, and then subjected to another catalytic oxidation cycle with 2-adamantanone as substrate (Table 5). We found that the catalyst can be recycled at least five times without significant decline in catalytic activity.

Conclusion

A series of Sn/W oxides were synthesized through a simple coprecipitation and calcination approach. These metal oxides showed promising catalytic activities for some acid-catalyzed reactions, including Baeyer–Villiger oxidation and Friedel–Crafts reaction. The catalysts possess the advantages of high conversion, high selectivity, and recyclability, especially for the oxides of Sn/W-2-800, and can be used as a good substitute for some traditional homogeneous catalysts.

Acknowledgments The research was financially supported by NSFC (20774074), Gansu provincial Natural Science Foundation of China (3ZS061-A25-018), and Scientific Research Fund of NWNU (NWNU-KJCXGC-03-56). We also thank Key Laboratory of Eco-Environment-Related Polymer Materials (Northwest Normal University), Ministry of Education, for financial support.

References

1. Arata K, Matsuhashi H, Hino M (2003) Catal Today 81:17
2. Yue C, Trudeau ML, Antonelli DM (2006) Chem Commun 18:1918
3. Epifanio A, Navarra MA, Weise FC, Mecheri B, Farrington J, Licoccia S, Greenbaum S (2006) Chem Mater 22:813
4. Okuhara T (2002) Chem Rev 102:3641
5. Harmer MA, Sun Q (2001) Appl Catal A 221:45
6. Xing R, Liu N, Liu YM, Wu HH, Jiang YW, Chen L, He MY, Wu P (2007) Adv Funct Mater 17:2455
7. Corma A (1995) Adv Mater 7:137
8. Rao YX, Trudeau M, Antonelli D (2006) J Am Chem Soc 128:13996
9. Roggenbuck J, Tiemann M (2005) J Am Chem Soc 127:1096
10. Llamas R, Ruiz JR (2007) Appl Catal B 72:18
11. Li JX, Dai WL, Fan KN (2008) J Phys Chem C 112:17657
12. Yang P, Zhao D, Margolese DI, Chmelka BF, Stucky GD (1998) Nature 396:152
13. Severin KG, Abdel-Fattah TM, Pinnavaia TJ (1998) Chem Commun 14:1471
14. Yang P, Zhao D, Margolese DI, Chmelka BG, Stucky GD (1999) Chem Mater 11:2813
15. Wong MS, Ying JY (1998) Chem Mater 10:2067
16. Shiraishi Y, Saito N, Hirai T (2005) J Am Chem Soc 127:12820
17. Kuemmel M, Grosso D, Boissiere C, Smarsly B, Brezesinski T, Albouy PA, Amenitsch H, Sanchez C (2005) Angew Chem Int Ed 44:4589
18. Nakajima K, Fukui T, Kato H, Kitano M, Kondo JN, Hayashi S, Hara M (2010) Chem Mater 22:3332
19. Noda Y, Lee B, Domen K, Kondo JN (2008) Chem Mater 20:5361
20. Katou T, Lee B, Lu D, Kondo JN, Hara M, Domen K (2003) Angew Chem Int Ed 42:2382
21. Bayot DA, Devillers MM (2004) Chem Mater 16:5401
22. Kondo JN, Uchida M, Nakajima K, Lu D, Hara M, Domen K (2004) Chem Mater 16:4304
23. Tagusagawa C, Takagaki A, Iguchi A, Takanabe K, Kondo JN, Ebitani K, Hayashi S, Tatsumi T, Domen K (2009) Angew Chem 121:1
24. Ogasawara Y, Uchida S, Yamaguchi K, Mizuno N (2009) Chem Eur J 15:4343
25. Shiju NR, AnilKumar M, Hoelderich WF, Brown DR (2009) J Phys Chem C 113:7735
26. Song YQ, Kang CL, Feng YL, Liu F, Zhou XL, Wang JA, Xu LY (2009) Catal Today 148:63
27. Bondarchuk O, Huang X, Kim J, Kay BD, Wang LS, White JM, Dohnalek Z (2006) Angew Chem Int Ed 45:4786
28. Rao YX, Kang JJ, Antonelli D (2008) J Am Chem Soc 130:394
29. Sing KSW, Everett DH, Haul RAW, Moscow L, Pinerotti RA, Rouquerol J, Siemieniewska T (1985) Pure Appl Chem 57:603
30. Criegee R (1948) Liebigs Ann Chem 560:127
31. Renz M, Meunier B (1999) Eur J Org Chem 4:737