

NOTE

Oxidative Dehydrogenation of Isobutane to Isobutene: Dawson-Type Heteropolyoxoanions as Stable and Selective Heterogeneous Catalysts

The design of new catalysts, especially those of known composition and structure, constitutes one of the key challenges in catalysis today. Heteropolyoxometalates are unique among metal–oxygen compounds in that they possess a molecular-type structure of discrete and thus well-defined composition; heteropolyoxometalates can, therefore, be rationally designed, synthesized, and characterized for use in catalysis (1). Their reactivity and selectivity can, in turn, be fine tuned, for example, by modifying their composition by incorporating alkali or transition metal ions. A relevant example is the conversion of the well-known Wells–Dawson $P_2W_{18}O_{62}^{6-}$ compound to the $P_2W_{17}MO_{61}^{n-}$ ($M = Fe, Mn, Co, Cu$) polyoxoanions (2, 3) (Fig. 1).

While Keggin-type polyoxometalates have been widely studied as homogeneous and heterogeneous catalysts for the oxidation of organic substrates (1, 4–6), with particular attention to the activation of paraffinic hydrocarbons (7–10), the use of Wells–Dawson-type polyoxoanions as oxidation catalysts has been limited to homogeneous, liquid-phase applications: (1,5-COD)Ir· $P_2W_{15}Nb_3O_{62}^{8-}$ has been used for oxidative reactions with O_2 in the liquid phase (11), and the same $P_2W_{17}MO_{61}^{n-}$ polyoxoanions have been examined for their homogeneous catalytic oxidation of cyclohexene using oxidants such as $(PhIO)_x$ (12). On the contrary, no example concerning the use of Wells–Dawson-type polyoxoanions has been previously reported in the scientific or patent literature of heterogeneous catalysis.

In addition, there is no prior report of polyoxoanions as catalysts for the selective oxidative dehydrogenation of isobutane to isobutene. The oxidative activation of paraffins is a current challenge in catalysis aimed at the employment of new types of low cost, widely available, raw materials for the petrochemical industry. Among light paraffins, isobutane is one of the currently most interesting targets due to the increasing market for isobutene, to be used as a raw material for the synthesis of oxidation products (such as methacrylic acid, currently produced via the highly environmental unfriendly acetone–cyanhydrin route), or MTBE, an octane booster for reformulated gasolines. Oxidative dehydrogenation of isobutane to isobutene may constitute a valid alternative to the capital- and energy-intensive

dehydrogenation, provided active and selective catalysts are developed (5, 13, 14).

Herein we report the solid-state catalytic reactivity of Dawson-type heteropolycompounds $K_xP_2W_{17}MO_{62-y} \cdot nH_2O$ (with $y = 0$ when $M = W$ and $y = 1$ when $M = Fe, Mn, Co, Cu$), which represent a good example of stable and efficient catalysts for the oxydehydrogenation of isobutane.

The $K_xP_2W_{17}MO_{62-y} \cdot nH_2O$ compounds were synthesized as detailed elsewhere (3). Their identity and purity were confirmed by solid-state IR spectroscopy, thermogravimetric analysis, solution ^{31}P NMR spectroscopy, and elemental analysis, as detailed in Table 1. Their surface areas, as measured by N_2 adsorption, were in the range 1–3 m^2/g . The thermal stability of $K_xP_2W_{17}MO_{62-y} \cdot nH_2O$ polyoxoanions under oxidizing conditions up to 500°C (the maximum temperature used in catalytic tests) was checked by FT-IR spectroscopy, X-ray powder diffraction, and thermogravimetric analysis (DTA/TG). In all cases, the Wells–Dawson polyoxoanions proved stable in air up to 500°C, regardless of the nature of the substituting metal M in the heteropolyanion skeleton. Figure 2 shows for comparison the FT-IR spectra of the precursor $K_6P_2W_{18}O_{62} \cdot nH_2O$ and of the iron-substituted $K_7P_2W_{17}FeO_{61} \cdot nH_2O$ as synthesized and after treatment at 500°C for 2 h. The IR bands typical of the P=O (ca. 1090 and 1020 cm^{-1}), W=O (ca. 780 cm^{-1}), and W–O–W (ca. 910 and 950 cm^{-1}) vibrations are observed. No major modifications of the IR pattern are observed after treatment in an oxidizing atmosphere up to 500°C, indicating that the polyoxoanion structure remains intact and that substitution of a W atom with a transition metal does not modify the stability of the polyanion framework, at least under the conditions employed by us (i.e., treatment in air at temperature <500°C). This is also confirmed by DTA/TG in which only an exothermic peak is observed at around 150°C, corresponding to the elimination of water.

The catalytic activity of $K_xP_2W_{17}MO_{62-y}$ polyoxoanions for the gas-phase oxidation of isobutane using O_2 was examined using a flow reactor operating at atmospheric pressure and with a feed of 26 mol% isobutane, 13% oxygen, 12% water, and the balance helium; details of the apparatus have

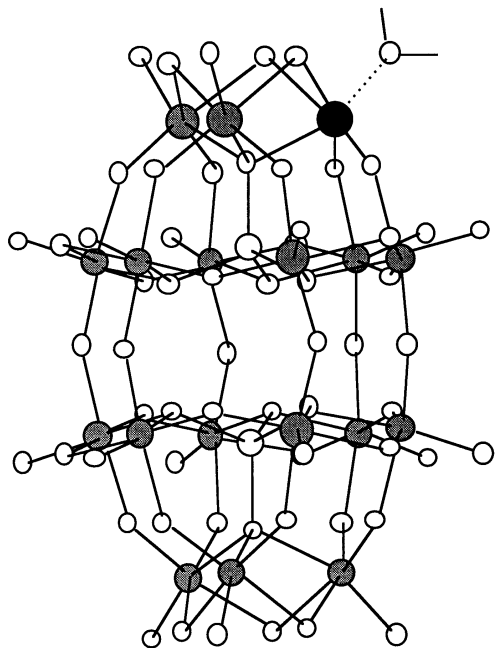


FIG. 1. The structure of $K_7P_2W_{17}(M \cdot OH_2)O_{61}$ derived from the classic Wells–Dawson heteropolyoxoanion, $P_2W_{18}O_{62}^{6-}$, by replacing an apical “[$W^{VI} = O^{4+}$]” unit by a [$M^{II/III} \cdot OH_2$] unit ($M = Mn, Fe, Cu, Co$; shown as the upper right, most dark, solid circle with its H_2O ligand). The two central PO_4^{3-} tetrahedra serve as a template for the 18 surrounding MO_6 edge- and corner-sharing octahedra.

been given elsewhere (10). Carbon balance was always in the range 95–110%. Data were collected under steady-state conditions at several reaction temperatures in the range 380 to 450°C and are reported in Table 2. Before reactivity tests, compounds were calcined at 450°C for 3 h.

A notable finding is that isobutene is formed with good selectivity for all the polyoxoanion catalysts tested; insertion of oxygen into the isobutene yields only traces of methacrylic acid or methacrolein (traces of acetic acid are also formed).

Figure 3 plots the effect of the residence time on the catalytic performance. The isobutane conversion was increased on increasing the residence time, whereas the selectivity to isobutene was only slightly decreased; this suggests that isobutene is stable under these conditions, and that consecutive reactions of oxidative degradation are relatively unimportant. In other previously studied paraffin oxydehydrogenations, the selectivity for paraffins with more than two carbon atoms (specifically propane, isobutane, and *n*-butane) typically diminishes rapidly with increasing conversion, accomplished by increasing either the temperature or the residence time (15–18).

Reaction rate studies, performed at low conversion, demonstrate that the present Wells–Dawson polyoxoanion catalysts are as active as the best catalysts reported in the literature, but at considerably lower temperatures, as shown in Table 3, with the exception of the V/Mg/O system (18, 21), whose high surface area contributes to its high activity. However, if we compare the specific activity referred to unit surface area, the greater activity of the polyoxoanion $K_7P_2W_{17}FeO_{61}$ is clearly evidenced.

Stability under the isobutane oxydehydrogenation reaction conditions has also been tested. All the catalysts turned out to be stable even after 100 h of reaction as tested by IR, by XRD, and by solution ^{31}P NMR (the latter obtained by dissolving the catalyst recovered from the reaction). The lack of detectable deactivation confirms that, at least at 450°C, no major modifications occur in the catalysts

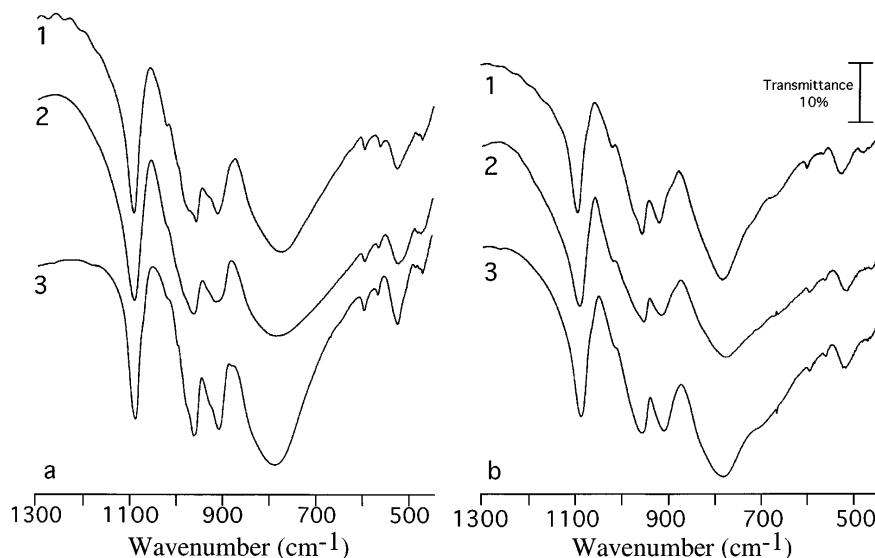


FIG. 2. FT-IR spectra of $K_6P_2W_{18}O_{62} \cdot 10H_2O$ (a) and of $K_7P_2W_{17}FeO_{61} \cdot 13H_2O$ (b) as synthesized (1), after calcination at 500°C for 3 h (2), and after catalytic reaction (3).

TABLE 1
Elemental Analysis and IR and ^{31}P NMR Spectroscopic Data for $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 10\text{H}_2\text{O}$
and Its Transition Metal Substituted Derivatives

Catalyst	Elemental analysis, calc (found)	IR bands, cm^{-1} (KBr disc)	^{31}P NMR, ^a ppm
$\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 10\text{H}_2\text{O}$	K 4.91 (4.93); P 1.29 (1.29); W 69.26 (69.18); O 24.11 (25.0); H 0.41 (0.47); H_2O 3.8 (3.7) ^b	778, 911, 957, 1020, 1091	-12.3
$\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61} \cdot 13\text{H}_2\text{O}$	K 8.16 (8.54); P 1.29 (1.29); W 65.27 (64.9); O 24.72 (25.11), H 0.54 (0.56); H_2O 4.9 (4.8) ^b	727, 792, 919, 941, 1013, 1053, 1085	-6.8, -13.6
$\text{K}_7\text{P}_2\text{W}_{17}\text{FeO}_{61} \cdot 14\text{H}_2\text{O}$	K 5.76 (5.76); W 65.87 (65.5); Fe 1.18 (1.19); H_2O 5.3 (5.3) ^b	779, 913, 946, 1015, 1090	-12.4 ^c
$\text{K}_7\text{P}_2\text{W}_{17}\text{MnO}_{61} \cdot 12\text{H}_2\text{O}$	K 5.79 (5.72); W 66.13 (65.7); Mn 1.16 (1.13); H_2O 4.9 (5.1) ^b	780, 918, 950, 1016, 1089	-11.4 ^c
$\text{K}_8\text{P}_2\text{W}_{17}\text{CoO}_{61} \cdot 15\text{H}_2\text{O}$	K 6.51 (6.09); W 65.04 (64.6); Co 1.22 (1.23); H_2O 5.6 (5.5) ^b	712, 801, 915, 944, 1013, 1056, 1084	-22.4 ^c
$\text{K}_8\text{P}_2\text{W}_{17}\text{CuO}_{61} \cdot 14\text{H}_2\text{O}$	K 6.53 (6.31); W 65.22 (64.9); Cu 1.32 (1.29); H_2O 5.3 (5.3) ^b	701, 790, 917, 944, 1016, 1061, 1084	-12.4 ^c

^a Spectra were recorded on a Bruker AC200/F in 1 : 1 $\text{H}_2\text{O} : \text{D}_2\text{O}$ at 20°C and are referenced externally to 85% H_3PO_4 . The Li^+ salt is used to increase the solubility of the anion.

^b H_2O weight loss observed by TGA.

^c P(2) resonance.

TABLE 2
Oxidation of Isobutane with Dawson-Type Polyanions^a

Catalyst	Temp., °C	E_a^d	Conversion % ^b		Selectivity % ^c			
			i-C ₄	O ₂	i-C ₄ -ene	Propylene	CO + CO ₂	Others
$\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}$	383	29.1	3.3	11	64	3	22	11
	427		15.4 (15.5) ^e	61(62)	55(55)	7(6)	29(29)	9(10)
$\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$	387	31.9	2.8	8	77	3	16	4
	431		16.3	57	62	8	22	7
$\text{K}_7\text{P}_2\text{W}_{17}\text{FeO}_{61}$	383	25.7	4.1	10	76	3	14	7
	427		17.4 (17) ^e	68(66)	61(61)	7(7)	20(19)	12(13)
$\text{K}_7\text{P}_2\text{W}_{17}\text{MnO}_{61}$	383	30.0	2.1	7	79	3	18	—
	426		10.9	43	65	6	25	4
$\text{K}_8\text{P}_2\text{W}_{17}\text{CoO}_{61}$	382	37.8	1.9	7	77	1	22	—
	424		14.3	63	66	7	23	4
$\text{K}_8\text{P}_2\text{W}_{17}\text{CuO}_{61}$	382	31.7	2.9	9	78	3	19	—
	426		17.2	70	61	8	26	5

^a Reaction conditions: residence time, 3.6 s. Feed composition; isobutane, 26 mol%; oxygen, 13%; water, 12%; balance, He.

^b Conversion: moles of i-C₄ (or O₂) reacted per mole of i-C₄ (or O₂) fed. Oxygen is the limiting reagent.

^c Others: methacrylic acid, methacrolein, and acetic acid.

^d Activation energy (kcal/mol) for isobutene formation.

^e Data were taken after 10 h time-on-stream; in parentheses are reported data collected after 4 days time-on-stream. Small variations in catalytic performance were observed during the first 2 h, after which the performance was stable during the time required for catalytic tests (at least 300 h).

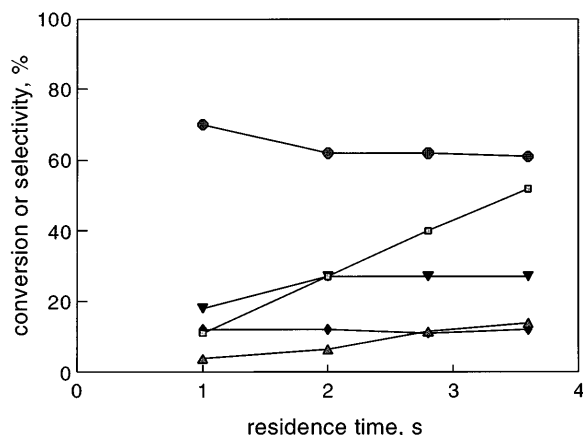


FIG. 3. Isobutane oxidation with $K_7P_2W_{17}FeO_{61}$. Conversion of isobutane (▲), and of oxygen (◻), and selectivity to isobutene (●), carbon oxides (▼), and others (◆) (others are propylene, methacrylic acid, methacrolein, and acetic acid). Temperature, 415°C; other conditions as those described in Table 2.

during 100 h of use. A visual observation of the catalyst after reaction reveals that the operating catalyst is in a reduced, W^V -containing, deep blue-black, structurally intact “heteropoly-blue” form of the type $H_xK_6P_2W_{18-x}^VI W_x^VO_{62}$ (22–24). This is consistent with the literature which indicates that formation of 1–2 electron-reduced “heteropoly-blues” causes remarkably little change in the structure of a heteropolycompound (25). The formation of heteropoly-blues is also probably a factor in enhancing the polyoxoanion’s thermal stability.

Kinetic data reveal a surprisingly small influence of the nature of the substituted metal, $M = Fe, Mn, Co, Cu, \text{ or } W$, on the $K_xP_2W_{17}MO_{62}$ activity (Table 2), with the Fe system, $K_7P_2W_{17}FeO_{61}$ being most active but only by a factor of 1.2 (at 383°C) vs the parent $K_6P_2W_{18}O_{62}$. This would seem

to demand that $W-O-W$ or $W=O$ are kinetically competent, C–H bond activation active sites in at least the unsubstituted parent compound $K_6P_2W_{18}O_{62}$, a situation reminiscent of what has been reported for heteropolytungstate photocatalysis of RH reactions involving H^\bullet abstractions by $W-O-W$ or $W=O$ active sites (25). The $K_7P_2W_{17}FeO_{61}$ system possesses additional possible active sites, including $Fe-O-W$ and adsorbed oxygen species, $Fe-OO^\bullet$ or $Fe-O^\bullet$. In addition, dehydrated, oxygen-deficient polyoxoanions, such as $K_xP_2W_{17}MO_{62-y}$, with $W(V)^\bullet$ active sites are also quite plausible (26). Additional structure–reactivity studies will be required to distinguish these possibilities, but such studies are possible because of the discrete, structurally well-defined and readily modifiable nature of the present, polyoxoanion catalysts.

In conclusion, the custom-made, Dawson-type polyoxoanion catalysts described herein have good catalytic activity and selectivity in comparison to previous catalysts for the selective oxidative dehydrogenation of isobutane. Of special importance is the finding that the Dawson-type polyoxoanion catalysts are stable in the reaction environment, and thus that their well-defined structure can lead to the mechanistic information (27) needed for the rational design of even better catalysts.

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REFERENCES

- Misono, M., *Catal. Rev. Sci. Eng.* **29**, 269 (1987).
- Finke, R. G., in “Polyoxometalates: From Platonic Solids to Antiretroviral Activity” (M. T. Pope and A. Müller, Eds.), p. 267. Kluwer Academic, Dordrecht, 1993.

TABLE 3

Comparison of the Best Catalysts Described in the Literature for the Oxydehydrogenation of Isobutane to Isobutene

Catalyst	Ref.	$T(^{\circ}C)$	$t(s)^a$	i-C ₄ /O ₂ /inert gas/ H ₂ O ^b	i-C ₄ conv. (%)	sel ^c (%)	Rate ^d	Rate ^e
Ni ₂ P ₂ O ₇	17	550	11	75/5/20/0	10.8	83	16	1.3
Zn ₂ P ₂ O ₇	17	550	11	75/5/20/0	8.1	70	11	2.8
Mg ₂ P ₂ O ₇	17	550	11	75/5/20/0	6.4	60	7	1.3
Mg ₃ V ₂ O ₈ /MgO	18, 21	500	0.045 ^f	4/8/88/0	8.0	64	135	2.6
Ferrisilicate	19	450	0.06 ^f	4.3/4.3/91.3/0	1.6	40	11	0.03
Y ₂ O ₃ /CeF ₃	20	480	0.6	50/50/0/0	12.0	75	na	na
K ₇ P ₂ W ₁₇ FeO ₆₁	This work	427	3.6	26/13/49/12	17.4	61	10	4.9

^a t , residence time.

^b Relative percentage of isobutane, oxygen, inert gas, and water in feedstock.

^c Selectivity to isobutene.

^d Rate of isobutene formation ($\mu\text{mol/g} \cdot \text{min}$).

^e Rate of isobutene formation ($\mu\text{mol/m}^2 \cdot \text{min}$) based on the reported surface area of each catalyst.

^f W/F (weight catalyst/total flow rate), in $\text{g} \cdot \text{s/ml}$.

3. Lyon, D. K., Miller, W. K., Novet, T., Domaille, P. J., Evitt, E., Johnson, D. C., and Finke, R. G., *J. Am. Chem. Soc.* **113**, 7209 (1991).
4. Ono, Y., in "Perspectives in Catalysis" (J. M. Thomas and K. I. Zama-raev, Eds.), p. 431. Blackwell Sci., Oxford, 1992.
5. Cavani, F., and Trifirò, F., in "Catalysis," Vol. 11, p. 246. Royal Chem. Soc., Cambridge, 1994.
6. Kozhevnikov, I. V., and Matveev, K. I., *Appl. Catal.* **5**, 135 (1983).
7. Lyons, J. E., Ellis, P. E., Myers, H. K., Slud, G., and Langdale, W. A., U.S. Patent 4,803,187, 1989, assigned to Sun Refining and Marketing Co.
8. Centi, G., and Trifirò, F., in "Catalytic Science and Technology" (S. Yoshida, N. Takezawa, and T. Ono, Eds.), Vol. 1, p. 225. Kodansha, Tokyo, 1991.
9. Ahmed, S., and Moffat, J. B., *J. Catal.* **118**, 281 (1989).
10. Cavani, F., Etienne, E., Favaro, M., Galli, A., Trifirò, F., and Hecquet, G., *Catal. Lett.* **32**, 215 (1995).
11. Mizuno, N., Lyon, D. K., and Finke, R. G., *J. Catal.* **128**, 84 (1991).
12. Mansuy, D., Bartoli, J. F., Battioni, P., Lyon, D. K., and Finke, R. G., *J. Am. Chem. Soc.* **113**, 7222 (1991), and references therein.
13. Kung, H. H., *Adv. Catal.* **40**, 1 (1994).
14. Cavani, F., and Trifirò, F., *Catal. Today* **24**, 307 (1995).
15. Bellussi, G., Centi, G., Perathoner, S., and Trifirò, F., in "Catalytic Selective Oxidation" (S. T. Oyama and J. W. Hightower, Eds.), ACS Symposium Series 523, p. 1242. Am. Chem. Soc., Washington, DC, 1992.
16. Chaar, M. A., Patel, D., and Kung, H. H., *J. Catal.* **109**, 463 (1988).
17. Takita, Y., Kurosaki, K., Mizuhara, Y., and Ishihara, T., *Chem. Lett.* 335 (1993).
18. Michalakos, P. M., Kung, M. C., Jahan, I., and Kung, H. H., *J. Catal.* **140**, 226 (1993).
19. Uddin, M. A., Komatsu, T., and Yashima, T., *J. Catal.* **150**, 441 (1994).
20. Zhang, W., Tang, D. L., Zhou, X. P., Wan, H. L., and Tsai, K. R., *J. Chem. Soc. Chem. Commun.* 771 (1994).
21. Patel, D., Kung, M. C., and Kung, H. H., in "Proceedings 9th, International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 4, p. 1554. Chem. Institute of Canada, Ottawa, 1988.
22. Papaconstantinou, E., *Chem. Soc. Rev.* **18**, 1 (1989).
23. Fox, M. A., Cardona, R., and Gillard, E., *J. Am. Chem. Soc.* **109**, 6347 (1987).
24. Renneke, R. F., and Hill, C. L., *J. Am. Chem. Soc.* **110**, 5461 (1988).
25. Casana-Pastor, N., Gomez-Romero, P., Jameson, G. B., and Baker, L. C. W., *J. Am. Chem. Soc.* **113**, 5658 (1991).
26. Kawafune, I., and Matsubayashi, G., *Inorg. Chim. Acta* **33**, 188 (1991).
27. For the insightful use of polyoxoanions to establish the dominant active site in methanol oxidative dehydrogenation see Sorensen, C. M., and Weber, R. S., *J. Catal.* **142**, 1 (1993). See also Racine, B. N., Sorensen, C. M., and Weber, R. S., *J. Catal.* **142**, 735 (1993).

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