Heterogeneous catalysts for halide-free carbonylation of dimethyl ether

G.G. Volkova *, L.M. Plyasova, A.N. Salanov, G.N. Kustova, T.M. Yurieva, and V.A. Likholobov

Boreskov Institute of Catalysis, Pr. Akademika Lavrentieva 5, Novosibirsk 630090, Russia

Received 14 August 2001; accepted 21 February 2002

Acidic cesium salts of 12-tungstophosphoric acid promoted with rhodium, $Rh/Cs_xH_{3-x}PW_{12}O_{40}$ ($1.5 \leq x \leq 2$ and $Rh \geq 0.1\%$), were shown to be novel and effective catalysts for halide-free carbonylation of dimethyl ether (DME) to methyl acetate. The catalysts were characterized by chemical analysis, nitrogen adsorption, XRD, SEM, TGA-DTA and IR spectroscopy. Their behavior may be explained by assuming that (1) activation of the C–O bond in the DME molecule and formation of a metal–alkyl bond occurs in the presence of the strong acid sites and (2) these strong acid sites act in conjunction with Rh carbonyl complexes, which are responsible for CO insertion and acetate formation.

KEY WORDS: rhodium; cesium salts of polyoxotungstate; halide-free carbonylation; dimethyl ether; methyl acetate.

1. Introduction

Acetic acid is an important industrial chemical which is manufactured on a large scale. The main route to acetic acid is through the carbonylation of methanol in the Monsanto process, which uses a homogeneous rhodium catalyst and halide promoter, typically methyl iodide [1]. The halide is highly corrosive and requires the use of a special alloy. Moreover, halides are poisons for many types of catalysts, so that their use may limit the further chemistry which can be performed after the carbonylation step.

Catalysts suggested for the iodide-free carbonylation are based on the acid form of various types of zeolites (mordenite, Y, H-ZSM-5) [2–5] or on rhodium, or iridium salts of tungstophosphoric heteropoly acid supported on silica [6]. The latter show good selectivity but very low activity. Therefore, design of a heterogeneous catalyst for halide-free carbonylation reaction is an urgent problem.

Heteropolycompounds have been used successfully for catalyzing acidic as well as oxidation reactions [7–14]. The most interesting compounds for acidic reaction would be acidic cesium salts of $H_3PW_{12}O_{40}$ [15–28]. $Cs_xH_{3-x}PW_{12}O_{40}$ were claimed to exhibit high activity in gas phase reactions [15–23], liquid phase [22–27] and even in solid phase reaction such as pinacol rearrangement at room temperature [28]. The high activity of Cs 2.0–Cs 2.5 salts was attributed to a large surface area ($40–150\,m^2g^{-1}$) and high surface protonic acidity [18,19,27].

Studies at the Boreskov Institute of Catalysis have shown that acidic cesium salts of 12-tungstophosphoric acid promoted with rhodium revealed high activity in the iodide-free carbonylation of dimethyl ether (DME) to methyl acetate (MA) [29]:

$$CH_3{-}O{-}CH_3 + CO \rightarrow CH_3{-}CO{-}O{-}CH_3$$

DME is more favorable for carbonylation than methanol from the economic viewpoint because it can be produced from syn-gas more effectively [30].

This paper presents the preparation, performance and physical characterization of $Rh/Cs_xH_{3-x}PW_{12}O_{40}$ catalysts.

2. Experimental

Cesium salts of 12-tungstophosphoric acid promoted with rhodium were prepared by dropwise addition of stoichiometric amounts of a 0.1 M aqueous solution of cesium nitrate to a mixture of 0.1 M solutions of $H_3PW_{12}O_{40}$ and rhodium chloride to the required ratio. The resulting suspension was kept under vigorous stirring for 24 h and then was evaporated at 353–373 K to the solid.

The samples were characterized by chemical analysis, nitrogen adsorption, XRD patterns (Siemens diffractometer D-500 and Cu K_α radiation), SEM observation (Bs-350, TESLA apparatus) and TGA-DTA (Derivatograph Q-1500D). The IR spectra were recorded with a Bomem M-102 FTIR spectrometer.

DME carbonylation reaction was carried out in a flow reactor with gas chromatography analysis on line. Reaction conditions: CO/DME ratio = 10/1, GHSV = $3000\,h^{-1}$, pressure 10 bar, temperature 473–523 K. Prior

---

* To whom correspondence should be addressed.
E-mail: g.g.volkova@catalysis.nsk.su

1011-372X/02/0600-0175/0 © 2002 Plenum Publishing Corporation

to reaction, samples were reduced at 473 K in a stream of 2%H_2–He for 2 h.

3. Results and discussion

The chemical compositions of the samples, given in table 1, show that the desired cesium salts were obtained from the preparation process. Table 1 also shows the BET surface areas for the samples after heating to 573 K. As anticipated from previous work [15–28], the addition of cesium increased the surface area significantly. We have shown that increasing the cesium content from Cs 1 to Cs 2.5 increased the surface area from 37 to 216 m^2/g. The same tendency was observed by Essayem *et al.* [19,22] and Bardin and Davis [21].

From the powder X-ray diffraction patterns (figure 1), the typical BCC structure of $H_3PW_{12}O_{40}$ and the cesium salts (Cs 1–Cs 2.5) of the heteropolyacid is clearly indicated [31]. In the as-prepared form without heat treatment, Cs 1, Cs 1.5 and Cs 2 formed two crystalline phases, possibly derived from the precipitation of the Cs phase with pure acid phase trapped in the crystal structure or in the micropores of the system. Acid phase was not observed in Cs 2.5 sample. However, the peaks of Cs 2.5 are broad and asymmetric, which means that the presence of the microcrystalline cubic $H_3PW_{12}O_{40}$ phase cannot be ruled out. Addition of rhodium up to 2.5% causes no change in the X-ray patterns of cesium salts.

The thermograms of the various acidic cesium salts with rhodium were similar to those already reported for $Cs_xH_{3-x}PW_{12}O_{40}$ compounds [19]. SEM observations presented in figure 2 show that the Cs 1 and Cs 2 samples are composed of elementary particles (10–30 nm) which are agglomerated in large-shaped particles (100–1000 nm) with a spongy aspect. Such a morphology was already described by Misono and coworkers [26,27] for Cs salts of $H_3PW_{12}O_{40}$.

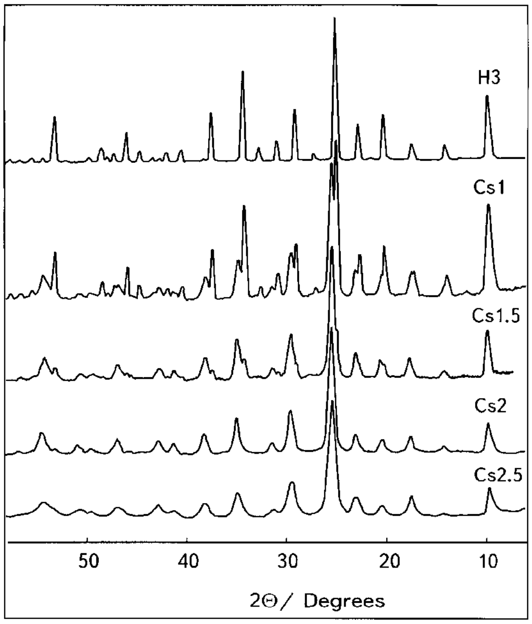

Figure 1. X-ray diffraction patterns of the $H_3PW_{12}O_{40}$ and acidic Cs salts.

Results of the DME carbonylation reaction over the Cs 1–Cs 2.5 samples are presented in table 1. It can be seen that the best catalyst revealed activity to MA = 190 g l^{-1} h^{-1}, that is, one order of magnitude higher than rhodium salts of the same acid supported on silica in the iodide-free carbonylation of the DME to methyl acetate [6]. Activity dramatically changes with cesium content. Cs 1.5 and Cs 2 are the most active catalysts; the activity of Cs 1 and C 2.5 is 3–5 times less. At the same time, the amount of rhodium slightly affected catalyst activity at constant Cs content; it is reduced by 35% at very low concentration of rhodium (0.1%).

Essayem *et al.* [19,20,22] and Bardin and Davis [21] have shown that Cs 2 salt of 12-tungstophosphoric acid revealed excellent catalytic performance in skeletal

Table 1
Chemical composition, surface area and performance of $Rh/Cs_xH_{3-x}PW_{12}$ catalysts in halide-free DME carbonylation at 473 K and 10 bar after 120 min on stream

Samples	Cs/P[a]	S BET (m^2 g^{-1})	Rate of methyl acetate formation		Selectivity (%)
			g l^{-1} h^{-1}	10^{-8} mol g^{-1} s^{-1}	
1%Rh/Cs 1	1.0	37	60	15	91
1%Rh/Cs 1.5	1.4	57	180	45	94
1%Rh/Cs 2.0	2.0	103	170	43	95
1%Rh/Cs 2.5	2.5	216	35	9	96
0.1%Rh/Cs 2.0	1.9	96	120	30	95
0.5%Rh/Cs 2.0	2.1	100	190	47	96
2.5%Rh/Cs 2.0	2.0	92	175	44	93
Cs 2.0	1.9	90	40	10	92

[a] Atomic ratio of cesium to phosphorus.

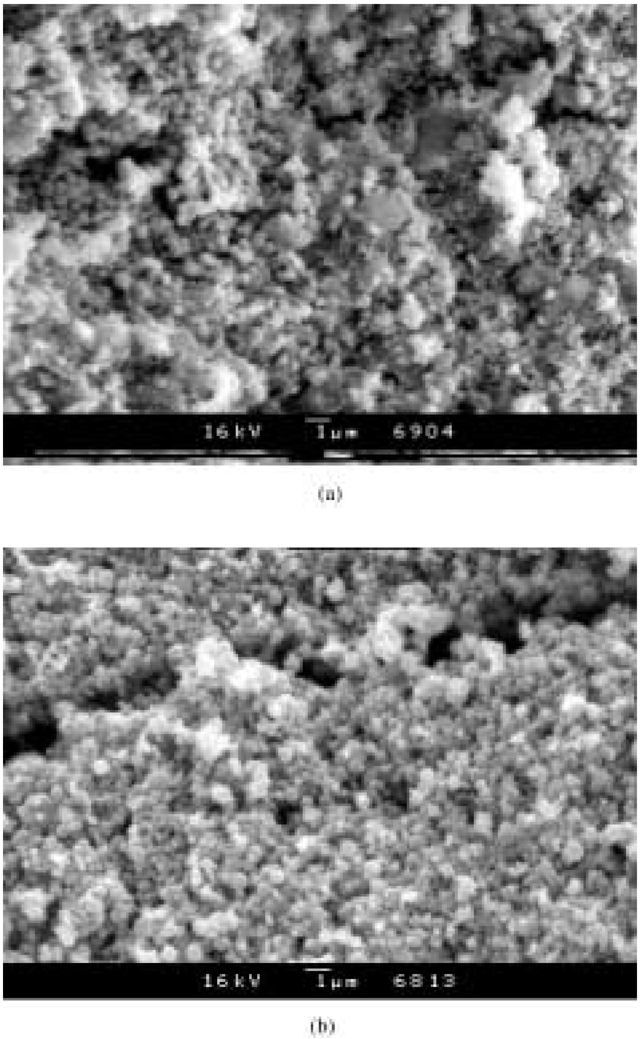

Figure 2. SEM photographs of (a) 1%Rh/$Cs_1H_2PW_{12}O_{40}$ and (b) 1%Rh/$Cs_2HPW_{12}O_{40}$.

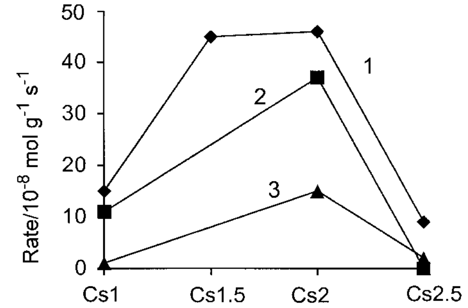

Figure 3. Direct comparison of the rates of (1) methyl acetate formation, (2) isopentane formation [21] and (3) isobutane formation [19] *versus* cesium content.

isomerization of alkanes (C4, C5 and C6) and the Cs 2.5 sample was not active in butane and pentane isomerization. It is known that the first step in methanol carbonylation reaction is activation of the C–I bond ($E = 240\,kJ\,mol^{-1}$) in methyl iodide. In the absence of CH_3I it is necessary to activate the C–O bond ($E = 350\,kJ\,mol^{-1}$) in methanol or in DME. The energy of the C–C bond in *n*-alkanes ($E = 344\,kJ\,mol^{-1}$) is closely matched with the energy of the C–O bond in methanol and DME. It may be suggested that DME carbonylation in the absence of an iodide promoter requires the presence of very strong acid sites which are similar to those for skeletal isomerization of *n*-paraffins, and activation of C–O (methanol, DME) and C–C (*n*-alkanes) occurs at the same acid sites which are presented in the Cs 1.5 and Cs 2 samples.

If polar molecules such as alcohols, ethers, H_2O and NH_3 are dissolved in solid HPA, the latter can exhibit pseudoliquid phase behavior, so the rate of "bulk-type" reaction may be more than 100 times higher [32] than the rate of "surface-type" reaction typical for non-polar molecules (butane or pentane) that do not dissolve in HPA. Dimethyl ether and methyl acetate are polar molecules and "bulk-type" reaction may be observed. In fact, the reaction rate of DME carbonylation does not differ much from those for butane or pentane isomerization [19,21] (figure 3), which means that DME carbonylation is mainly a "surface-type" reaction, and the solubility of reactants or products in the solid phase of catalysts does not play an important role in this reaction.

Thus, unique properties of acidic Cs salts of $H_3PW_{12}O_{40}$ are exhibited in a carbonylation reaction, and these catalysts make it possible to activate the C–O bond in DME instead of activation of the C–I bond in methyl iodide. The high activity of Rh/$Cs_xH_{3-x}PW_{12}O_{40}$ is caused not only by the high surface area of the samples, but also Cs 2 ($100\,m^2\,g^{-1}$) is five times more active than C 2.5 ($216\,m^2\,g^{-1}$) or Rh concentration. This can be attributed to the high surface acidity of Cs salts and/or to certain structural and textural properties that require further detailed investigations.

The infrared spectra (figure 4) in the range 1200–400 cm^{-1} for acidic cesium salts before and after reaction exhibited the same characteristic absorption bands due to the vibrations of the $PW_{12}O_{40}^{3-}$ anions, also described by Rocchiccioli-Deltcheff [33]. The post-reaction FTIR spectroscopy shows in the range 1200–2400 cm^{-1} additional bands at 1200–1600 cm^{-1} and at 2000–2200 cm^{-1}. The bands at 1417, 1450 and 1555 cm^{-1} are often observed for acetate groups [34], the bands at 1278 and 1326 cm^{-1} were assigned to DME vibrations [35] and the very weak band at 2070 cm^{-1} may be attributed to the traces of Rh carbonyl complexes [36–38]. It was shown by numerous researchers that Rh carbonyl clusters and carbonyl ions are formed at appreciable pressures of CO in zeolites and on the surface of SiO_2 [36–40]. No study of such carbonyl complexes in heteropolyacids or in their salts is known to us, but it seems probable that Rh carbonyl clusters are formed at the surface of $Cs_xH_{3-x}PW_{12}O_{40}$ catalysts at high pressure of CO (10 bar) and these Rh carbonyl

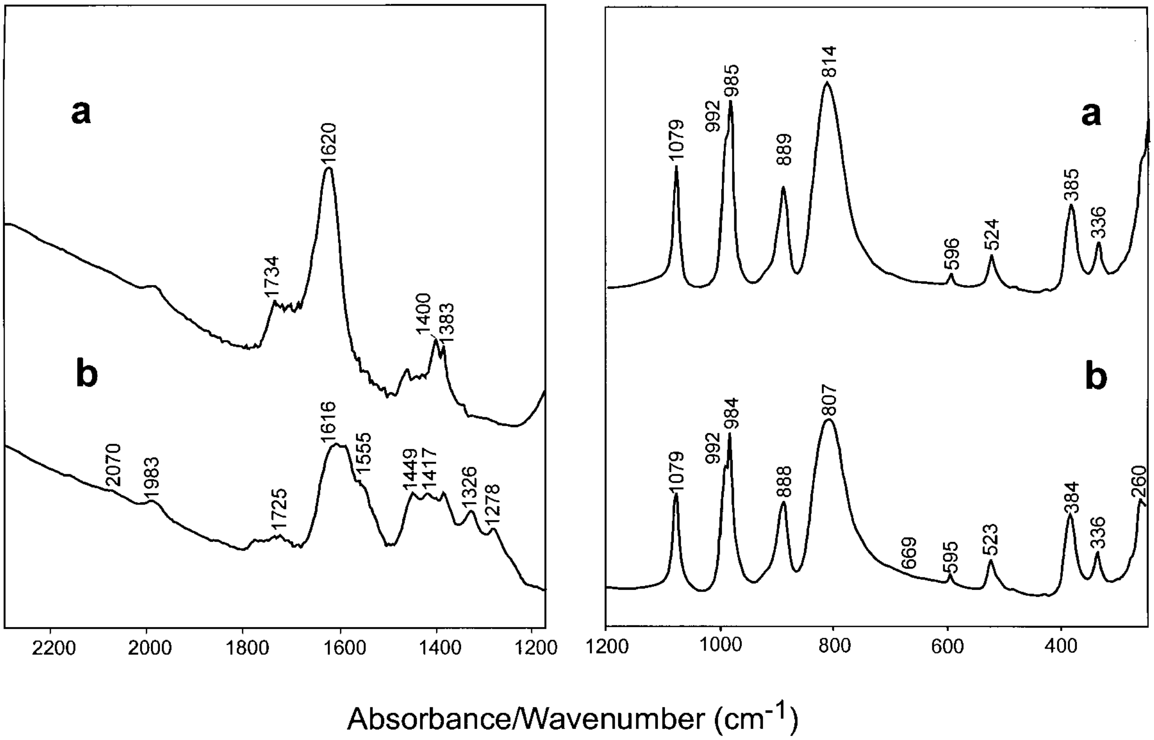

Figure 4. FTIR spectra of the 1%Rh/$Cs_2HPW_{12}O_{40}$ (a) before and (b) after DME carbonylation reaction.

clusters are instrumental for the CO insertion into metal alkyl bonds and the formation of acetate groups, as was suggested for zeolites [38–40].

4. Conclusions

It was shown that Rh/$Cs_xH_{3-x}PW_{12}O_{40}$ with $1.5 \le x \le 2$ and $Rh \ge 0.1\%$ are novel and effective catalysts for halide-free carbonylation of DME to methyl acetate. Their behavior can be rationalized qualitatively by assuming that (1) activation of the C–O bond in the DME molecule and formation of a metal–alkyl bond occurs in the presence of the strong acid sites and (2) these acid sites act in conjunction with Rh carbonyl complexes, which are responsible for CO insertion and acetates formation.

References

[1] M.J. Howard, M.D. Jones, M.S. Roberts and S.A. Taylor, Catal. Today 18 (1993) 325.

[2] B. Ellis, M.J. Howard, R.W. Joyner, K.N. Reddy, M.B. Padley and W.J. Smith, Stud. Surf. Sci. Catal. 101 (1996) 771.

[3] W.J. Smith, European Patent 0 596 632 (1993).

[4] US Patent 4,612,387 (1987).

[5] German Patent DE 36 06 169 A1 (1988).

[6] W.R. Wegman, European Patent 0 353 722 (1989).

[7] T. Okuhara, N. Mizuno and M. Misono, Adv. Catal. 41 (1996) 113.

[8] I.V. Kozhevnikov, Catal. Rev.-Sci. Eng. 37(2) (1995) 311.

[9] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.

[10] S. Shikata, S. Nakata, T. Okuhara and M. Misono, J. Catal. 166 (1997) 263.

[11] F. Cavani, Catal. Today 41 (1998) 73.

[12] M.A. Parent and J.B. Moffat, Chem. Lett. 60 (1999) 191, and references therein.

[13] B.B. Bardin and R.J. Davis, Appl. Catal. 185 (1999) 283.

[14] J. Yang, D. Lee, J. Lee, J. Hyun and K. Lee, Appl. Catal. 194–195 (2000) 123.

[15] Y. Liu, G. Koyano, K. Na and M. Misono, Appl. Catal. 166 (1998) L263.

[16] Y. Liu, K. Na and M. Misono, J. Mol. Catal. 141 (1999) 145.

[17] Y. Liu, G. Koyano and M. Misono, Topics Catal. 11/12 (2000) 239.

[18] M. Guisnet, Ph. Bichon, N.S. Gnep and N. Essayem, Topics Catal. 11/12 (2000) 247.

[19] N. Essayem, G. Coudurier, M. Fournier and J.C. Vedrine, Catal. Lett. 34 (1995) 223.

[20] S. Quelen, C. Travers, M. Delage and N. Essayem, Europacat-IV, Abstracts (1999) p. 28.

[21] B.B. Bardin and R.J. Davis, Topics Catal. 6 (1998) 77.

[22] N. Essayem, S. Kieger, G. Coudurier and J.C. Vedrine, Stud. Surf. Sci. Catal. 101 (1996) 591.

[23] T. Okuhara and T. Nakato, Catalysis Surveys from Japan 2 (1998) 31.

[24] T. Okuhara, T. Nishimura, H. Watanabe and M. Misono, J. Mol. Catal. 74 (1992) 247.

[25] M. Kimura, T. Nakato and T. Okuhara, Appl. Catal. 165 (1997) 227.

[26] G. Koyano, K. Ueno and M. Misono, Appl. Catal. 181 (1999) 267.

[27] T. Okuhara, T. Nishimura and M. Misono, Stud. Surf. Sci. Catal. 101 (1996) 581.

[28] T. Nakato, Y. Toyoshi, M. Kimura and T.Okuhara, Catal. Today 52 (1999) 23.

[29] G.G. Volkova, L.E. Pindyurina, L.S. Egorova, T.M. Yurieva and V.A. Likholobov, Russian Patent 2170724 (2001).

[30] T. Shikada, Y. Ohno, T. Ogawa, M. Ono, M. Mizuguchi, K. Tomura and K. Fugimoto, Stud. Surf. Sci. Catal. 119 (1998) 515.

[31] G.M. Brown, M.R. Noe-Spirlet, W.R. Busing and H.A. Levy, Acta Cryst. B33 (1977) 1038.

[32] M. Misono, Catal. Rev.-Sci. Eng. 30 (1987) 269.

[33] C. Rocchiccioli-Deltcheff, M. Fournier, R. Frank and R. Thouvenot, Inorg. Chem. 22 (1983) 207.

[34] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds* (New York, 1962), p. 270.

[35] R. Schlogl, in: *Handbook of Heterogeneous Catalysis*, Vol. 1, eds. G. Ertl, H. Knozinger and J. Weitkamp (VCH, Weinheim: 1997) ch 2.1.9, p. 138–191 (p. 174).

[36] W.A. Weber and B.C. Gates, J. Catal. 180 (1998) 207.

[37] H. Kusama, K.K. Bando, K. Okabe and H. Arakawa, Appl. Catal. 205 (2001) 285.

[38] B. Xu and W.M.H. Sachtler, J. Catal. 180 (1998) 194.

[39] W.M.H. Sachtler and Y.-Y. Huang, Appl. Catal. 191 (2000) 35.

[40] B. Xu, K. Sun, Q. Zhu and W.M.H. Sachtler, Catal. Today 63 (2000) 453.