Isomerization of *n*-Butane over Bifunctional Platinum-heteropoly Compounds in the Presence of Hydrogen

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Bifunctional Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ efficiently catalysed *n*-butane isomerization at 300 °C under a low H_2 pressure (0.05 atm); the activity was comparable to or higher than that of Pt-H-ZSM-5 or Pt-SO_4^{2-}/ZrO_2, and the selectivity was higher than that of either of the other two catalysts.

Skeletal isomerization of *n*-butane has attracted much attention, since isobutane is a probable feedstock for synthesis of methyl *tert*-butyl ether, a high-octane vehicle fuel additive.[1] Pt/Cl-Al_2O_3 has been utilized commercially in *n*-butane isomerization in the presence of hydrogen. Owing to its sensitivity to water, addition of a small amount of organic chloride is required in the feed gas.[2] Pt-SO_4^{2-}/ZrO_2 has been reported to be active for the isomerization of pentane or butane in the presence of hydrogen.[3-5] Ono *et al.* reported that $Pd_{x/2}H_{3-x}PW_{12}O_{40}$ on silica catalysed the isomerization of hexane.[6] Recently, we have found that an acidic Cs salt of $H_3PW_{12}O_{40}$, namely $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, is remarkably active in acid-catalysed reactions.[7-9] This high activity is due to its strong acidity and the large quantity of surface protons.[9] Here, we report a prominent catalytic performance of the bifunctional Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for the skeletal isomerization of *n*-butane.

The catalysts were prepared as follows. An aqueous solution of $Pt(NH_3)_4Cl_2$ (0.08 mol dm^{-3}) was added dropwise to an aqueous solution of $H_3PW_{12}O_{40}$ (0.06 mol dm^{-3}), followed by the addition of an aqueous solution of Cs_2CO_3 (0.08 mol dm^{-3}) at 50 °C. The resulting suspension was evaporated at 50 °C to solid. The molar ratio of Pt^{2+}: Cs^+: $PW_{12}O_{40}^{3-}$ is 0.25 : 2.5 : 1, where the amount of Pt corresponds to 1.5% m/m. Hereafter this is formally denoted by 1.5% m/m Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$. The surface area was determined by BET method using N_2 to be 112 m^2 g^{-1}. 1.5% m/m Pd-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (100 m^2 g^{-1}) was obtained from $Pd(NO_3)_2$ in the same way. For reference, 1% m/m Pt-H-ZSM-5, which was prepared from $Pt(NH_3)_4Cl_2$ and H-ZSM-5 (Na-ZSM-5, Tosoh corporation), and 1% m/m Pt-SO_4^{2-}/ZrO_2 prepared according to the literature[4] were used.

The reaction was performed in a flow reactor (Pyrex tube, 8 mm internal diameter) at 300 °C under atmospheric pressure. The feed gas consisted of 0.05 atm (5 vol %) of *n*-butane, 0.05 or 0.5 atm of H_2, and N_2 balance. Total flow rates were 10–20 cm^3 min^{-1}. Prior to the reaction, Pt- or Pd-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (0.5–2 g) was pretreated in a flow of O_2, and then in a flow of N_2 each for 1 h at 300 °C. Pt-SO_4^{2-}/ZrO_2 and Pt-H-ZSM-5 were pretreated in the following sequence of gas flows, O_2 (1 h) – H_2 (1 h) – N_2 (1 h) at 370 °C for Pt-SO_4^{2-} and 450 °C for Pt-H-ZSM-5, respectively. These are the pretreatments recommended in the literature.[4,5,10,11] The gases at the outlet of the reactor were analysed by gas chromatography (FID) with VZ-10 (for C_1–C_5) and SE-30 (for C_5–C_7) columns.

The reaction rate and the selectivity for conversion to isobutane are summarized in Table 1, where the data were collected after *ca.* 5 h of reaction, when nearly stationary rates were obtained for all catalysts. The changes in the conversion with time were small for all catalysts; *e.g.* the conversions over 1.5% m/m Pd-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ were 39%, 35% and 34% at 1, 3 and 5 h, respectively, in the presence of 0.5 atm of H_2.

As shown in Table 1 at 0.5 atm of H_2, the rates for the

Table 1 Activity and selectivity for skeletal isomerization of *n*-butane over metal-promoted catalysts at 300 °C in the presence of H_2

			Selectivity (mol%)[c]					
Catalyst[a]	Conv. (%)	Rate[b]	i-C4	C1	C2	C3	C4=	C5
In the presence of 0.5 atm of H_2								
Pt-Cs 2.5	25[d]	7.9	93.9	1.4	2.4	1.8	0	0.5
Pd-Cs 2.5	34[d]	10.9	95.6	0.5	0.5	2.0	0	1.4
Pt-SO_4^{2-}/ZrO_2	65[d]	10.4	47.3	6.0	11.6	30.3	0	4.8
Pt-H-ZSM-5	51[e]	12.0	34.0	18.8	24.9	21.4	0	0.9
In the presence of 0.05 atm of H_2								
Pt-Cs 2.5	20.5[d]	6.2	88.3	0.3	0.5	5.8	0.7	4.4
Pd-Cs 2.5	12.9[d]	3.4	78.4	0.3	0.4	11.3	1.8	7.8
Pt-SO_4^{2-}/ZrO_2	4.8[d]	1.2	72.6	1.0	2.3	16.6	0	7.5
Pt-H-ZSM-5	70.4[e]	8.8	16.4	3.9	6.5	66.8	0	6.4

[a] Cs 2.5 indicates $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. [b] The rate for isobutane formation: 10^{-8} mol g^{-1} s^{-1}. [c] i-C4, C1, C2, C3, C4=, and C5 indicate isobutane, methane, ethane, propane, butenes, and pentanes. [d] M/F = 41 g h mol^{-1}. [e] M/F = 18 g h mol^{-1}, where M is the catalyst mass and F is the total flow rate.

formation of isobutane over Pt- and Pd-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ were comparable to those of Pt-H-ZSM-5 and Pt-SO_4^{2-}/ZrO_2. The activity of Pt-SO_4^{2-}/ZrO_2 was 10 × 10^{-8} mol g^{-1} s^{-1}, which is consistent with the result of Sommer *et al.*[5] It is remarkable that Pt- and Pd-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed very high selectivities (94–96%) to isobutane as compared with Pt-SO_4^{2-}/ZrO_2 (47%) and Pt-H-ZSM-5 (34%). The selectivities at similar conversion levels (about 30%) were about 70 and 54% for Pt-SO_4^{2-}/ZrO_2 and Pt-H-ZSM-5, respectively.

The activity and selectivity under 0.05 atm of H_2 are also shown in Table 1. It was found that Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ also gave high activity (6.2 × 10^{-8} mol g^{-1} s^{-1}), which is comparable to that under 0.5 atm of H_2, and high selectivity (88%). On the other hand, the activity of Pt-SO_4^{2-}/ZrO_2 was very low (1.2 × 10^{-8} mol g^{-1} s^{-1}), which is about 1/10 that under 0.5 atm of H_2. A similar large effect of hydrogen pressure for Pt-SO_4^{2-}/ZrO_2 has been reported.[4,5] Pt-H-ZSM-5 was still highly active at the low H_2 pressure, but the selectivity was low. Therefore, it is demonstrated that Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is a prominent catalyst for the skeletal isomerization of *n*-butane, especially under low pressure of H_2.

In order to confirm the Keggin structure of the heteropoly compound, IR spectra were recorded before and after the reaction. Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ gave four characteristic peaks at 1080 ν(P-O), 985 ν(W=O), 983 and 812 cm^{-1} ν(W-O-W)[12] and no change in the IR spectra was observed after the reaction. This shows that the structure of heteropoly compound Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was retained during the reaction. Thus, the strong acidity of the heteropoly compound is probably responsible for the high catalytic performance, together with the effect of hydrogen spillover from Pt to suppress the coke formation[5] or to form protons as catalytic sites.[4,6]

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