

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}PW₁₂O₄₀ efficiently catalysed *n*-butane isomerization at 300 °C under a low H₂ pressure (0.05 atm); the activity was comparable to or higher than that of Pt-H-ZSM-5 or Pt-SO₄²⁻/ZrO₂, 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-Al₂O₃ 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-SO₄²⁻/ZrO₂ 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}PW₁₂O₄₀ on silica catalysed the isomerization of hexane.⁶ Recently, we have found that an acidic Cs salt of H₃PW₁₂O₄₀, namely Cs_{2.5}H_{0.5}PW₁₂O₄₀, 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}PW₁₂O₄₀ for the skeletal isomerization of *n*-butane.

The catalysts were prepared as follows. An aqueous solution of Pt(NH₃)₄Cl₂ (0.08 mol dm⁻³) was added dropwise to an aqueous solution of H₃PW₁₂O₄₀ (0.06 mol dm⁻³), followed by the addition of an aqueous solution of Cs₂CO₃ (0.08 mol dm⁻³) at 50 °C. The resulting suspension was evaporated at 50 °C to solid. The molar ratio of Pt²⁺: Cs⁺: PW₁₂O₄₀³⁻ 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}PW₁₂O₄₀. The surface area was determined by BET method using N₂ to be 112 m² g⁻¹. 1.5% m/m

Pd-Cs_{2.5}H_{0.5}PW₁₂O₄₀ (100 m² g⁻¹) was obtained from Pd(NO₃)₂ in the same way. For reference, 1% m/m Pt-H-ZSM-5, which was prepared from Pt(NH₃)₄Cl₂ and H-ZSM-5 (Na-ZSM-5, Tosoh corporation), and 1% m/m Pt-SO₄²⁻/ZrO₂ prepared according to the literature⁴ 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 H₂, and N₂ balance. Total flow rates were 10–20 cm³ min⁻¹. Prior to the reaction, Pt- or Pd-Cs_{2.5}H_{0.5}PW₁₂O₄₀ (0.5–2 g) was pretreated in a flow of O₂, and then in a flow of N₂ each for 1 h at 300 °C. Pt-SO₄²⁻/ZrO₂ and Pt-H-ZSM-5 were pretreated in the following sequence of gas flows, O₂ (1 h) – H₂ (1 h) – N₂ (1 h) at 370 °C for Pt-SO₄²⁻ 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 C₁–C₅) and SE-30 (for C₅–C₇) 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}PW₁₂O₄₀ were 39%, 35% and 34% at 1, 3 and 5 h, respectively, in the presence of 0.5 atm of H₂.

As shown in Table 1 at 0.5 atm of H₂, 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 H₂

Catalyst ^a	Conv. (%)	Selectivity (mol%) ^c						
		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}PW₁₂O₄₀. ^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}PW₁₂O₄₀ were comparable to those of Pt-H-ZSM-5 and Pt-SO₄²⁻/ZrO₂. The activity of Pt-SO₄²⁻/ZrO₂ 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}PW₁₂O₄₀ showed very high selectivities (94–96%) to isobutane as compared with Pt-SO₄²⁻/ZrO₂ (47%) and Pt-H-ZSM-5 (34%). The selectivities at similar conversion levels (about 30%) were about 70 and 54% for Pt-SO₄²⁻/ZrO₂ and Pt-H-ZSM-5, respectively.

The activity and selectivity under 0.05 atm of H₂ are also shown in Table 1. It was found that Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀ also gave high activity (6.2 × 10⁻⁸ mol g⁻¹ s⁻¹), which is comparable to that under 0.5 atm of H₂, and high selectivity (88%). On the other hand, the activity of Pt-SO₄²⁻/ZrO₂ was very low (1.2 × 10⁻⁸ mol g⁻¹ s⁻¹), which is about 1/10 that under 0.5 atm of H₂. A similar large effect of hydrogen

pressure for Pt-SO₄²⁻/ZrO₂ has been reported.^{4,5} Pt-H-ZSM-5 was still highly active at the low H₂ pressure, but the selectivity was low. Therefore, it is demonstrated that Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀ is a prominent catalyst for the skeletal isomerization of *n*-butane, especially under low pressure of H₂.

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}PW₁₂O₄₀ 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}PW₁₂O₄₀ 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 formation⁵ or to form protons as catalytic sites.^{4,6}

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