

# Direct methane conversion to methanol by ionic liquid-dissolved platinum catalysts†

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**Ternary systems of inorganic Pt salts and oxides, ionic liquids and concentrated sulfuric acid are effective at catalyzing the direct, selective oxidation of methane to methanol and appear to be more water tolerant than the Catalytica reaction.**

Homogeneous catalysis using transition metal complexes for the direct conversion of natural gas to liquid products under mild conditions (such as  $T < 300\text{ }^{\circ}\text{C}$ ) has attracted considerable interest since the 1970s due to their scientific and industrial significance.<sup>1–3</sup> Shilov chemistry in aqueous solution was the earliest reported catalytic system, in which Pt(II) (added to the reaction as  $\text{PtCl}_4^{2-}$ ) was the catalyst and Pt(IV) (in the form of  $\text{PtCl}_6^{2-}$ ) was a stoichiometric oxidant to oxidize methane to methanol and chloromethane.<sup>2</sup> More recently, the Catalytica catalyst ((bpy)m) $\text{PtCl}_2$  in oleum has been found to be highly efficient and highly selective, with up to 72% yields of methanol (in the form of methylbisulfate that can be hydrolyzed later).<sup>3</sup> Though the Catalytica system appears to be the one most suited to practical applications in terms of conversion and selectivity, the catalyst is unfortunately deactivated by the water and methanol that are produced *in situ* during the reaction.<sup>4</sup>

We demonstrate here a versatile method to prepare highly active ternary systems that involve ionic liquids (ILs), inorganic Pt compounds and sulfuric acid (98% and below). Ionic liquids are promising “green” media for organic synthesis due to their low volatility and good thermal stability;<sup>5</sup> however, their potential in other applications has not been fully recognized. Many inorganic platinum compounds, such as  $\text{PtCl}_2$  or  $\text{PtO}_2$ , are rarely used in homogeneous catalysis because they are insoluble in typical organic or aqueous solutions, and even in concentrated acids, although some of them have been used as heterogeneous catalysts.<sup>6</sup> Another platinum salt,  $\text{PtCl}_4$ , and the reagents of Shilov chemistry,  $\text{K}_2\text{PtCl}_4$  and  $\text{H}_2\text{PtCl}_6$ , are soluble in water but are not compatible with concentrated sulfuric acid. We found that all five of these Pt compounds could be readily dissolved in a variety of ILs upon heating, and were subsequently soluble in concentrated sulfuric acid, forming a homogeneous solution.<sup>7</sup> Suitable ILs found so far include imidazolium, pyridinium, pyrazolium and triazolium-based examples, with chloride ( $\text{Cl}^-$ ) or bisulfate ( $\text{HSO}_4^-$ ) as the anion (Table 1). The initial dissolution of inorganic Pt compounds into ILs was presumably through  $\text{Cl}^-$  or  $\text{HSO}_4^-$  coordination.<sup>8</sup> Studies of the detailed dissolution mechanism for binary systems of Pt/IL

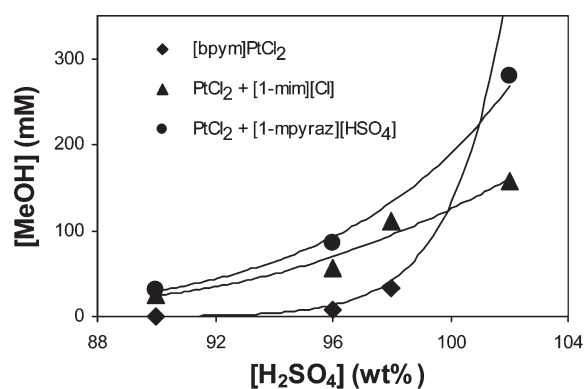
**Table 1** Catalytic oxidation of methane to methanol in 96%  $\text{H}_2\text{SO}_4^a$

Entry	Catalyst	Ionic liquid <sup>b</sup>	$T/^\circ\text{C}$	$\text{CH}_3\text{OH}/\text{mM}^c$	TON
1	(bpy)m) $\text{PtCl}_2$		220	31	0.6
2	(bpy)m) $\text{PtCl}_2$	[im][Cl]	220	26	0.5
3	$\text{PtCl}_2$	[1-mim][Cl]	220	173	3.5
4	$\text{PtCl}_2$	[im][Cl]	220	100	2.0
5	$\text{PtCl}_2$	[mmim][ $\text{HSO}_4$ ]	220	73	1.5
6	$\text{K}_2\text{PtCl}_4$	[1-mim][Cl]	220	105	2.1
7	$\text{PtCl}_4$	[1-mim][Cl]	220	89	1.8
8	$\text{PtO}_2$	[im][Cl]	220	52	1.0
9	$\text{PtO}_2$	[1-mim][ $\text{HSO}_4$ ]	220	0	0
10	$\text{H}_2\text{PtCl}_6$	[1-mim][Cl]	220	157	3.1
11	$\text{PtCl}_2$	[pyrid][ $\text{HSO}_4$ ]	220	1	~0
12	$\text{PtCl}_2$	[pyraz][ $\text{HSO}_4$ ]	200	42	0.8
13	$\text{PtCl}_2$	[1-mpyraz][ $\text{HSO}_4$ ]	200	79	1.6
14	$\text{PtCl}_2$	[mmpyraz][ $\text{HSO}_4$ ]	200	94	1.9
15	$\text{PtCl}_2$	[triaz][ $\text{HSO}_4$ ]	200	0	0

<sup>a</sup> Reaction conditions: 0.05 mmol Pt species + 0.3 mmol IL + 1 mL 96%  $\text{H}_2\text{SO}_4$  + 3.4 MPa  $\text{CH}_4$  in a 69 mL reactor at the chosen temperature for 2.5 h. <sup>b</sup> IL: im = imidazolium; 1-mim = 1-methylimidazolium; mmim = 1,3-dimethylimidazolium; pyrid = pyridinium; pyraz = pyrazolium; 1-mpyraz = 1-methylpyrazolium; mmpyraz = 1,2-dimethylpyrazolium; triaz = 1,2,4-triazolium. <sup>c</sup> The methanol concentration was determined by  $^1\text{H}$  NMR from the sum of the free or protonated methanol and the ester ( $\text{CH}_3\text{OSO}_3\text{H}$ ).

and ternary systems of Pt/IL/ $\text{H}_2\text{SO}_4$  are ongoing. A prepared ternary solution with [Pt] = 50 mM and methane gas ( $\sim 3.4$  MPa) were introduced into a high pressure reactor and reactions carried out at 180–220  $^{\circ}\text{C}$  for 2.5 h.†

Analyses by  $^1\text{H}$  NMR and GC-MS on the crude reaction solutions showed that the only liquid products derived from methane, if any, were methanol and methylbisulfate ( $\text{CH}_3\text{OSO}_3\text{H}$ ),



**Fig. 1** Methanol yield as a function of  $\text{H}_2\text{SO}_4$  concentration (reaction conditions: 200  $^{\circ}\text{C}$ , 2.5 h). The methanol concentration from the Catalytica reaction in 2% oleum was 600 mM and is not indicated on the plot.

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**Table 2** Effects of water concentration in different catalyst systems on methane C–H activation and oxidation to methanol

Entry	System	Activation at 150 °C <sup>a</sup>		Oxidation at 200 °C <sup>b</sup>	
		[CH <sub>x</sub> D <sub>4-x</sub> ]/mmol	TON	[CH <sub>3</sub> OH]/mmol	TON
1	(bpym)PtCl <sub>2</sub> + 2% water	0.367	7.35	0.047	0.94
2	(bpym)PtCl <sub>2</sub> + 6% water	0.276	5.51	0.016	0.31
3	PtCl <sub>2</sub> + [1-mim][HSO <sub>4</sub> ] + 2% water	0.480	9.60	0.065	1.31
4	PtCl <sub>2</sub> + [1-mim][HSO <sub>4</sub> ] + 6% water	0.420	8.39	0.037	0.73

<sup>a</sup> H/D exchange occurred between CH<sub>4</sub> and deuterated liquid media D<sub>2</sub>SO<sub>4</sub>, D<sub>2</sub>O and [1-mim-*d*<sub>4</sub>][DSO<sub>4</sub>]. TONs were determined from the gas analysis of methane isotopomers by GC-MS. Reaction conditions: 0.05 mmol Pt(II) + 0.3 mmol IL + 1 mL D<sub>2</sub>SO<sub>4</sub> + 3.4 MPa CH<sub>4</sub> in a 15 mL reactor; 150 °C, 2.0 h. <sup>b</sup> Tests were performed using non-deuterated liquid media. The reaction conditions were the same as those in Table 1.

which is similar to the Catalytica system.<sup>3</sup> The data in Table 1 show that all Pt species (PtCl<sub>2</sub>, PtCl<sub>4</sub>, PtO<sub>2</sub>, K<sub>2</sub>PtCl<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub>) could exhibit significant catalytic activity depending on the nature of the IL used. In the case of PtCl<sub>2</sub> + [1-mim][Cl] in 96% H<sub>2</sub>SO<sub>4</sub> (Table 1, entry 3) a methanol concentration of 0.17 M was demonstrated, which was about 5 times higher than that for (bpym)PtCl<sub>2</sub> (Table 1, entry 1). As a sharp contrast to the imidazolium- and pyrazolium-based IL systems, the pyridinium-based (Table 1, entry 11) and triazolium-based (Table 1, entry 15) IL systems exhibited either negligible or no measurable activity. The reason for this striking difference is not as yet well understood. Furthermore, comparison between Table 1, entries 8 and 9 suggests that having at least one chlorine coordinated to Pt might be essential in the catalysis. This is consistent with a previous theoretical study of the Catalytica system,<sup>4b</sup> which revealed that chlorine participated in the most active catalysis state.

In many other applications, the most widely used ILs are those with long alkyl chains, *e.g.*, 1-butyl-3-methylimidazolium ([bmim]).<sup>5</sup> However, in methane oxidation, it has been found that alkyl chains longer than –CH<sub>3</sub> would be oxidized quickly by Pt catalysis in concentrated H<sub>2</sub>SO<sub>4</sub>. This is understandable as methane is more inert than any longer alkyl group. We have actually observed intermediate oxygenated products due to partial oxidation of an ethyl group in an IL, 1-ethyl-3-methylimidazolium chloride ([emim][Cl]). Thus, only no-methyl, 1-methyl or dimethyl, imidazolium or pyrazolium ILs were used in the methane oxidation tests (Table 1). To eliminate the suspicion that the products might be coming from the methyl substituent on the IL ring, control experiments using <sup>13</sup>C-enriched methane for a system of PtCl<sub>2</sub> + [1-mim][HSO<sub>4</sub>] were carried out under similar conditions. Subsequent analyses by GC-MS and <sup>1</sup>H NMR confirmed that the produced methylbisulfate was indeed <sup>13</sup>CH<sub>3</sub>OSO<sub>3</sub>H.

The stability of an IL's ring structure could itself be a challenge under the harsh catalytic conditions, since they are also hydrocarbons. Slight decomposition of the imidazolium ring was observed after the reaction had been run for a few hours, as monitored by the products due to deep oxidation, CO<sub>2</sub> and NH<sub>4</sub><sup>+</sup>. The formation of extra CO<sub>2</sub> complicated the calculation of the selectivity of methane-to-methanol conversion. We subsequently developed the pyrazolium-based ILs (Table 1), in which the ring structure proved to be stable against oxidation in the presence of Pt catalysts in concentrated sulfuric acid within the duration of our tests. Selectivity in these ternary systems was then found to be comparable to the Catalytica reaction under similar conditions.

Because of the desired use of a dilute sulfuric acid solution in practice, the effect of water concentration on the reactivity of

Pt/IL/H<sub>2</sub>SO<sub>4</sub> ternary systems was studied. Methane oxidation to methanol in concentrated H<sub>2</sub>SO<sub>4</sub> by the Catalytica catalyst can be written as: CH<sub>4</sub> + 2H<sub>2</sub>SO<sub>4</sub> → CH<sub>3</sub>OSO<sub>3</sub>H + 2H<sub>2</sub>O + SO<sub>2</sub> in which water is generated *in situ* during the reaction. The reactivity of (bpym)PtCl<sub>2</sub> was found to be extremely sensitive to even small amounts of water. Quantum chemistry computations suggest that the water complex [(Hbpym)PtCl(H<sub>2</sub>O)]<sup>2+</sup> is about 30 kJ mol<sup>-1</sup> more thermodynamically stable than the starting active Pt complex [(Hbpym)PtCl(HSO<sub>4</sub>)]<sup>2+</sup>, which is the so-called ground state effect for C–H activation.<sup>4</sup> Experimentally demonstrated in Fig. 1, the catalytic activity dropped sharply when the sulfuric acid was diluted from the oleum to below 100%. This leads to uneconomical catalysis rates and high separation costs for the methanol.<sup>4a</sup> As a comparison, the Pt/IL/H<sub>2</sub>SO<sub>4</sub> systems at lower H<sub>2</sub>SO<sub>4</sub> concentration (90 to 100%) exhibited higher methanol yields than the Catalytica system and hence were more water-tolerant.

This trend was further examined through methane C–H bond activation tests *via* H/D exchange between the regular CH<sub>4</sub> and deuterated reaction media at 150 °C. The data are summarized in Table 2. At this temperature, the Catalytica system catalyzed extensive H/D exchange while producing no measurable amount of methanol.<sup>3</sup> Table 2, entries 1–4 indicate that ternary systems of Pt/IL/H<sub>2</sub>SO<sub>4</sub> are more active than the Catalytica reaction, both in the C–H activation and oxidation steps, prompting a different mechanistic interpretation.

In summary, the ILs in the homogeneous catalysis of methane to methanol conversion not only acted as a dissolution media for those otherwise insoluble Pt salts/oxide, but also played a key role in promoting Pt reactivity, possibly through coordination and/or intermolecular interactions. The versatile method described here could also be used in other chemical reactions.

## Notes and references

‡ Methane oxidation in 1 mL of these ternary solutions was conducted in a 69 mL cylindrical stainless steel reactor (outside diameter = 1 inch) with a glass liner inside. Mild stirring was provided *via* a magnetic stirring bar.

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