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# Decomposition of Pt-intercalated hydrotalcite-like nanocomposites to produce micro/mesoporous catalysts

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**Platinum intercalated into a hydrotalcite-like solid, $Mg_{0.74}Al_{0.26}(OH)_2(NO_3)_{0.26}$, was found to catalytically reduce interlayer nitrate ($NO_3^-$) to $N_2/N_2O$ so as to give rise to a large surface area micro/mesoporous structure at lower temperature of *ca.* 300 °C, compared to 500 °C required for the decomposition of the pristine hydrotalcite phase.**

A series of hydrotalcite (HT)-like compounds have been extensively studied as precursors of highly-dispersed supported noble metal catalysts for a wide applications, including *n*-hexane aromatization, steam reforming, $CO_2$ reforming, methane partial oxidation, NO*x* storage and reduction and so on.[1,2] In these studies, the noble metals are introduced by coprecipitation to form mixed HT precipitates, or by incipient wet impregnation onto calcined HT.[3,4] However, an alternative method utilizes anion-exchange and subsequent thermal decomposition. In the present paper, we have synthesized a porous Pt-intercalated HT from an anion ($PtCl_6^{2-}$)-exchanged phase. The deposition of Pt in the gallery space explores a novel route, which is based upon catalytic conversion of interlayer nitrate species to $N_2/N_2O$, to yield a micro/mesoporous material at low temperatures.

The HT phase with the composition of $Mg_{0.74}Al_{0.26}(OH)_2(NO_3)_{0.26}$ was prepared by a conventional coprecipitation method.[5] A solution containing $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ was added dropwise to aqueous ammonia (0.5 M) with vigorous stirring. The resulting precipitates were collected by centrifugal separation and washed thoroughly with deionized water, followed by drying overnight *in vacuo* at room temperature. As-prepared HT was then exchanged in an aqueous solution of $K_2PtCl_6$ at room temperature for 24 h to give a $PtCl_6$-HT composite (Pt/Al = 0.015). Finally, the composite was activated in a stream of 5% $H_2$/He at elevated temperatures (200–600 °C) for 5 h prior to characterization.

Fig. 1 exhibits the change of XRD patterns of pristine HT as well as $PtCl_6$-exchanged HT (Pt-HT) after heating at elevated temperatures in the stream of $H_2$/He. The peaks observed for the pristine sample can be indexed as (003), (006), (012), and (113) reflections, which can be attributed to a HT phase with the basal spacing of 0.89 nm. The so-called hydrotalcite phase is related to brucite, $Mg(OH)_2$, by replacing $Mg^{2+}$ by $Al^{3+}$ in edge-sharing Mg–O octahedral sheets of a layered structure. The XRD pattern was negligibly affected after exchange by $PtCl_6^{2-}$ with a loading which corresponds only to *ca.* 3% of the anion-exchange capacity, although the layered HT structure of these samples was decomposed similarly at > 300 °C to form an MgO-like phase with very low crystallinity. In the lower temperature range, however, their interlayer structure was found to be quite different, *i.e.*, the positions of (00*l*) peaks of the Pt-HT shifted to higher $2\theta$ at elevated temperatures, whereas those of pristine HT remained constant. The shift of the (00*l*) peak corresponds to the decreasing interlayer spacing from 0.880 (as prepared) to 0.692 nm (300 °C). In addition, a drastic color change of Pt-HT from pale yellow to gray occurred at *ca.* 200 °C, suggesting the deposition of Pt metal particles in the interlayer.

To clarify such different basal spacing observed in the course of heating, gas evolution from the precursors was analyzed by using mass spectroscopy as shown in Fig. 2. When the pristine HT was heated in 10% $H_2$/He, the water molecules escaped from the interlayer at 100–200 °C, but this leads to no change of the interlayer distance as is shown in Fig. 1. At higher temperatures ( > 350 °C), significant amounts of $NO/N_2O$ were evolved with simultaneous collapse of the layered HT structure, which should be coincident with total dehydration. Pt-HT placed in flowing 10% $H_2$/He exhibited a completely different result; there is no detectable NO, but significant amount of $N_2$ at ≥200 °C with simultaneous consumption of $H_2$. The absence of NO evolution as well as the completion of desorption at lower temperatures compared to the pristine HT clearly demonstrate that Pt deposits catalyzed the reduction of $NO_3^-$ species in the interlayer to evolve $N_2$. In this measurement, chlorine species from $PtCl_6^{2-}$ could not be detected because of the low content ($Cl/NO_3$ = 0.06), but the XRF analysis of solids showed that chlorine was gradually eliminated in the range 200–500 °C.

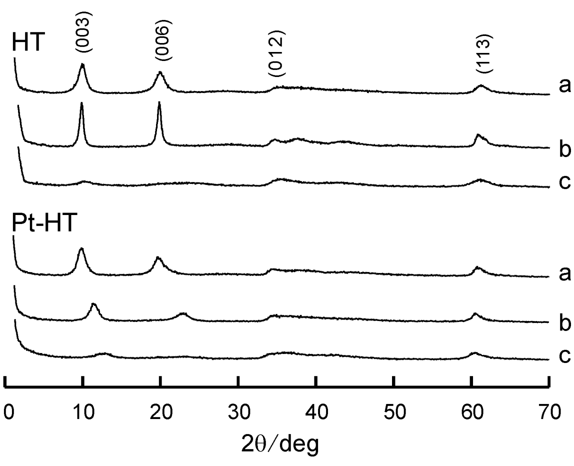

**Fig. 1** Powder XRD patterns of HT and Pt-HT after heating in a flowing 5% $H_2$/He. (a) as precipitated, (b) 200 °C, (c) 300 °C.

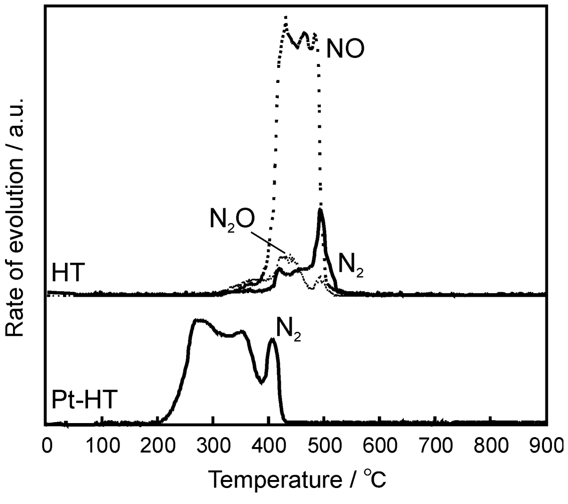

**Fig. 2** Temperature programmed gas evolution from pristine as well as Pt-HT in a flow of 10% $H_2$/He. Heating rate: 10 °C $min^{-1}$.

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The BET surface area of Pt-HT and HT after heating was measured from $N_2$ isotherms at 77 K (Table 1). The initial HT as well as Pt-HT precipitates were actually non-porous solids with very small surface areas ($< 5$ m$^2$ g$^{-1}$). After decomposition of the pristine HT phase at $\geq$400 °C, the surface area increased significantly to a maximum ($> 100$ m$^2$ g$^{-1}$) at 500–600 °C. For Pt-HT samples, on the other hand, it should be noted that a significant increase in the surface area was observed at lower temperatures at $\geq$300 °C, giving rise to the maximum (228 m$^2$ g$^{-1}$) at 600 °C. From simple comparison with XRD results (Fig. 1), it is clear that the major increase in surface area of pristine HT occurs when the layered structure is decomposed. By contrast, the formation of large surface area Pt-HT was accompanied by removal of $NO_3^-$ from the interlayer gallery space, which preserved the porous layered structure at 300 °C. This implies that the deposition of Pt particles occurs inside the interlayer space, which yields open pores between adjacent layers. The amorphous nature of these samples after calcination at $> 300$ °C may be rationalized by assuming that heterogeneous shrinkage of the pillars ($NO_3^-$ and $PtCl_6^{2-}$) at higher temperatures may destroy Bragg reflections.

Fig. 3a shows the $N_2$ adsorption–desorption isotherms for HT and Pt-HT after heating at 600 °C. These are very similar to a type IV isotherm defined in the IUPAC classification,[6] indicating the presence of some mesopores. However, a different $N_2$ uptake near zero relative pressure ($p_0/p$) clearly demonstrates that the larger surface area of Pt-HT compared to pristine HT results from micropores. The shape of hysteresis is different according to whether Pt is intercalated or not. The pristine HT after calcination showed a type H3-like loop that does not level off near the saturation vapor pressure, which reveals a high degree of textural mesoporosity indicative of aggregates of plate like particles forming slit-like pores. On the other hand, the loop for Pt-HT is rather similar to an intermediate between types H1 and H2.[7] The corresponding pore size distributions which are calculated using BJH methods are shown in Fig. 3b. The BJH pore size distribution of Pt-HT gave a sharp peak centered at *ca.* 2 nm, whereas that of pristine HT was rather broad with pore radii ranging from 1 to 5 nm. These results suggest that the Pt-HT phase possesses more uniform pore structure relative to the pristine HT after heating in a $H_2$ flow.

The CO chemisorption measurement was conducted to estimate the Pt particle size. The amount of adsorption decreased with increasing reduction temperature and became constant at $\geq$500 °C. As was evident from the residual chlorine content, however, the size of the Pt particles after reduction at $\leq$400 °C cannot be estimated due to the incomplete reduction of $PtCl_6^{2-}$ species. After reduction at $\leq$500 °C, the diameter of the Pt particles seems to be around 2 nm. This is almost equal to the position of the peak in the pore size distribution (Fig. 3b). It must be noted that the present ion-exchange route can stabilize such small Pt particles in the micro/mesoporous matrix, which is useful for many industrial catalytic processes. In particular, highly dispersed and stabilized Pt in a porous solid with the controlled basicity of the present system would be useful for low temperature NO–$H_2$–$O_2$ reactions.[8]

**Table 1** BET surface area of pristine HT and Pt-HT after heating at elevated temperatures

| BET Surface area/m$^2$ g$^{-1}$ | | | | | | |
|---|---|---|---|---|---|---|
| | 200 °C | 300 °C | 400 °C | 500 °C | 600 °C | 700 °C |
| HT | < 5 | 5 | 82 | 119 | 136 | 31 |
| Pt-HT | 11 | 193 | 210 | 202 | 228 | 68 |

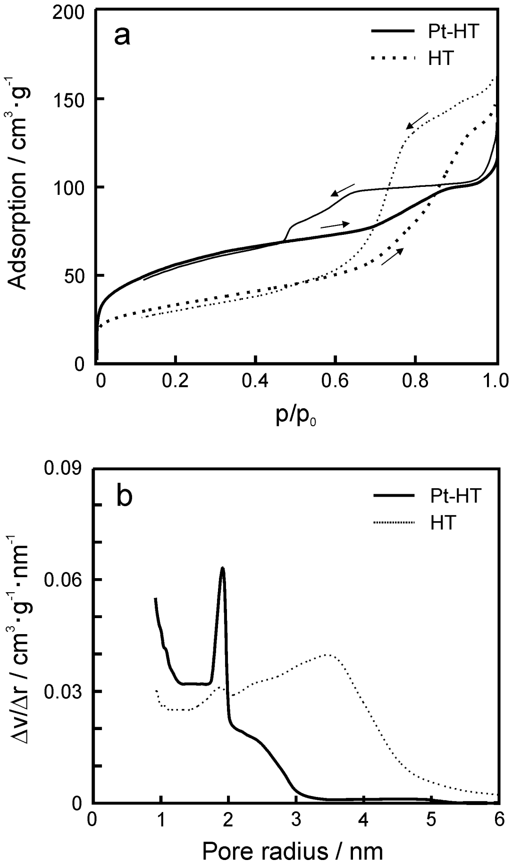

**Fig. 3** (a) $N_2$ adsorption isotherms at 77 K and (b) pore size distributions of pristine and Pt-HTs after calcination at 600 °C. Pore specific volume at $p/p_0 = 0.99$ is 0.298 cm$^3$ g$^{-1}$ (HT) and 0.164 cm$^3$ g$^{-1}$ (Pt-HT).

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