Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Molecular NO_2 induced $K_2Ti_2O_5$–$K_2Ti_6O_{13}$ structure switching in dry gas phase: lattice potassium reactivity

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1. XRD data

To determine the mechanism of NO_2 adsorption and de-sorption processes, $K_2Ti_2O_5$ was first exposed to 700 ppm NO_2 and 5% O_2 at 550 °C for a given time, then analyzed by XRD, as shown in Fig. S1. With increasing NO_2 adsorption time, the structure of $K_2Ti_2O_5$ gradually transformed to $K_2Ti_6O_{13}$. After adsorption for 6 h, the main peak at 11.4° is much weaker and broader than that of $K_2Ti_6O_{13}$ synthesized by the solid state method, indicating that the particle of $K_2Ti_6O_{13}$ formed by NO_2 adsorption is very small. Two peaks at 23.6° and 46.6° gradually appeared, which indicate that KNO_3 (PDF 05-0377) was formed by NO_2 adsorption. After regenerating the NO_2-adsorbed $K_2Ti_2O_5$ by TPR with 3.5% H_2, all characteristic peaks of KNO_3 disappeared; consequently, the same XRD pattern as that of fresh $K_2Ti_2O_5$ was attained, indicating that the formed $K_2Ti_6O_{13}$ transformed back to $K_2Ti_2O_5$ by releasing the adsorbed NO_x species.

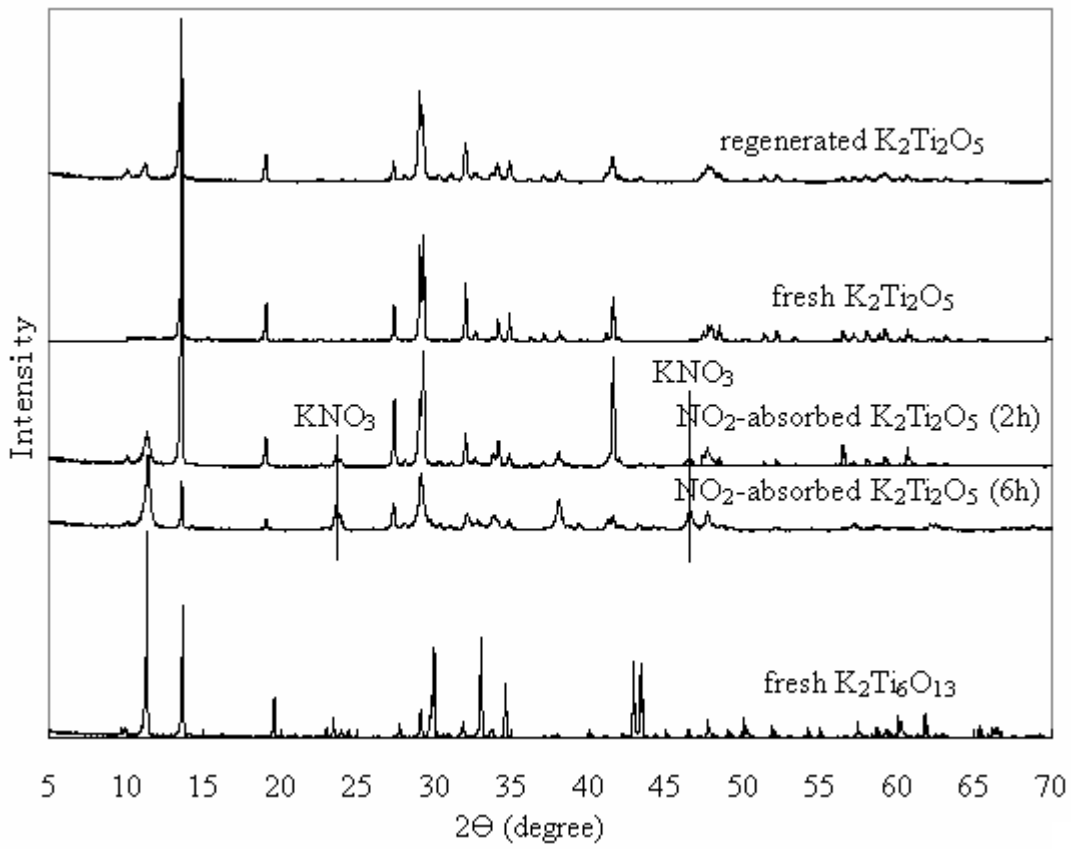

Fig. S1. XRD patterns of fresh $K_2Ti_2O_5$, NO_2-adsorbed $K_2Ti_2O_5$ (2 h), NO_2-adsorbed $K_2Ti_2O_5$ (6 h), fresh $K_2Ti_6O_{13}$, and regenerated $K_2Ti_2O_5$. Adsorption conditions: 0.6 g catalyst, 700 ppm NO_2, 5% O_2 with He balanced, 200 ml/min, 550 ^oC. Regeneration condition: temperature programmed reduction (25–750 °C, 5 ^oC/min), 3.5% H_2 with He balanced, 100 ml/min.

2. Extended discussions

Nowadays, the acidic gases removal and conversion such as NO_x storage, CO_2 capture, SO_2 capture are critical environmental issues. However, people are mainly using alkali metal oxides or carbonates as adsorbents which are not thermally stable. In the present work, we revealed that the lattice K in $K_2Ti_2O_5$ is still active for NO_2 adsorption at certain temperatures and the NO_2 adsorption and de-sorption could

induce a structure switching of $K_2Ti_2O_5$-$K_2Ti_6O_{13}$. We proved that the reactivity of lattice alkali ions depends not only on the ion itself, but also on the crystal structure (e.g. the coordination number). We expect that the lattice ions have much higher thermal stability. We believe this new finding might be further extended to other layered compounds, and also other acidic gases (CO_2, SO_2, etc). This suggests us to search novel alternative adsorbents from layered compounds and even perovskite materials.

What's more, we observed that the synthesized $K_2Ti_6O_{13}$ from NO_2 adsorption on $K_2Ti_2O_5$ is nano-size, which might be a new "top-down" method for synthesis of nanomaterials. We also think our report will contribute a lot to the fundamental understanding of the behaviour of lattice ions in layered structures.