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Ammonium fluoride mediated mechanochemical synthesis of A_2MF_6 (A=K, Rb; M=Pd, Mn, Ni) along with their catalytic role in environmental remediation

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Bond breaking and bond making triggered by stress are usually referred to as mechanochemical reactions. To highlight the power of mechanochemistry to oxidize metal ions leading to the discovery of newer phases, ammonium fluoride mediated synthesis of A_2MF_6 (A=Rb, K; M=Pd, Mn, Ni) has been carried out. Stability of high oxidation state of transition elements using mechanochemical approach has been demonstrated. Grinding reactions of ammonium fluoride with metal (II) acetate and further cation exchange with AF (A=Rb, K) were closely monitored *ex-situ* characterizations such as high resolution powder x-ray diffraction (PXRD), Fourier-transform infrared spectroscopy (FT-IR) and Raman spectroscopy measurements. For the reaction involving AF (A=Rb, K), A_2MF_6 possessing K_2PtCl_6 type structure was confirmed from the Rietveld refinement of PXRD pattern, high-resolution transmission electron microscopy (HR-TEM) and selected-area electron diffraction (SAED) measurements. Elemental composition and oxidation state of palladium in Rb_2PdF_6 were examined using x-ray photoelectron spectroscopy (XPS) analysis. Ligand to metal charge transfer and d-d transitions of Pd(IV) were present in the UV-visible diffuse reflectance spectrum of Rb_2PdF_6 with a band gap of 2.67 eV estimated using the Kubelka–Munk function. Other than ligand-to-metal charge-transfer (LMCT), they also show a broad band in visible region for d-d transitions. Its role as a photocatalyst to degrade the aqueous dye solutions (MB, RhB, Rh6G and MG) under UV-visible radiation has been evaluated along with their kinetic studies. The reduction of Pd(IV) to Pd(0) by $NaBH_4$ has been favourably used for the efficient and rapid conversion of highly carcinogenic, toxic, mutagenic Cr^{6+} to less toxic Cr^{3+} . Application of Mn^{4+} in K_2MnF_6 as red phosphors has been demonstrated by using PL spectroscopy.

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