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Framework of ruthenium-containing nickel hydrotalcite-type material: preparation, characterisation, and its catalytic application†

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The framework ruthenium-containing nickel (NiRu) hydrotalcite (HT)-type materials were prepared by a co-precipitation method for the first time in this study. Fourier-transform infrared spectroscopy and X-ray diffraction analysis revealed the formation of a layered hydrotalcite-type phase. DRUV-Vis and X-ray photoelectron spectroscopic studies revealed the presence of nickel in the +2 and +3 oxidation states along with the presence of ruthenium as Ru³⁺ ions. Temperature-programmed desorption studies of the NiRu-HT-type materials indicated a two-stage reduction with a decrease in T_{max} , supporting the presence of Ni²⁺ and Ru³⁺ in the framework of hydrotalcite. The obtained NiRu-HT-type materials proved to be promising catalysts for the reduction of aromatic nitro compounds in the presence of hydrazine as a hydrogen source under ambient conditions. The NiRu-HT-type material demonstrated enhanced activity and selectivity during the reduction of nitrobenzene and its derivatives due to the synergistic effect of nickel and ruthenium ions.

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Introduction

Anionic clays or hydrotalcite (HT)-like layered mixed hydroxides are natural or synthetic materials that are extensively used as adsorbents, ion-exchangers, ceramic precursors, flame retardants, stabilisers, corrosion inhibitors, and electrode materials and are employed in catalysis and pharmaceutical applications.^{1,2} These crystalline materials consist of positively charged two-dimensional sheets with water and exchangeable charge-balancing anions in the interlayer region. The general formula of the materials is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A_{x/n}^n) \cdot mH_2O$, where M²⁺ and M³⁺ respectively represent divalent and trivalent cations, A is the interlayer anion with charge n , and x is the fraction of trivalent cations.³ The structure of HT-like compounds is similar to that of layered brucite, where Mg²⁺/Al³⁺ ions are located on octahedral (O_h) co-ordination sites and share edges to form infinite sheets. The infinite sheets are stacked on each

other to form a positively charged framework, and the electrical neutrality is maintained by anions located in the interlayer domains containing water molecules.^{4,5} HT materials have also proved to be promising catalysts in a wide range of organic reactions, such as reduction, oxidation, alkylation, condensation, hydroxylation, transesterification, isomerisation, epoxidation, hydro-isomerisation, and reforming.³⁻⁵ These materials have advantages such as improved activity, selectivity, less waste production, and easy recovery of products. These materials can be used either in the as-synthesised form or in the form of mixed metal oxides derived after calcination.^{1-4,6-14} These types of layered HT materials possess inherent basicity and have redox properties, which are derived from the elemental composition of the octahedral layers of the materials. Catalytic properties of HTs can be modified by introducing varying divalent and trivalent cations such as Zn²⁺, Ni²⁺, Mn²⁺, Co²⁺, Fe²⁺, Cr³⁺, Fe³⁺, Mn³⁺, Co³⁺, and Ga³⁺ into the framework. Moreover, the properties can be modified by introducing anions like halides, carbonates, nitrates, sulphates, silicates, organic anions, anionic complexes, or anionic polymers in the interlayer region.¹⁵⁻²²

In recent decades, the transition-metal-based HT-like system has gained increasing interest among researchers because of its enormous applications in the field of reforming, fine chemicals, and redox processes.³⁻⁵ A nickel-based material is one among the most widely used transition metal and has a strong ability to form a bimetallic system with other trivalent metal ions. Nickel-based HT was developed because it is easily available, low-cost alternative to noble metal catalysts, has electronic properties

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† Electronic supplementary information (ESI) available: Fig. S1 wide scan XPS spectra of (a) α -Ni(OH)₂, and (b) NiRu-0.2; Table S1 nitrobenzene reduction using a series of nickel based hydrotalcite; Scheme S1 representative reaction pathway of nitrobenzene reduction on nickel based hydrotalcite. See DOI: 10.1039/c8ra03506g

