There are characteristic types of kinetic curves of the reactions of liquid-phase hydrogenation of various functional groups (Fig.-1). In the case of the high reactivity of reaction intermediates, a hydrogenation mechanism is observed (Fig.-1a). For liquid-phase hydrogenation reactions of substituted nitrobenzenes over nickel catalysts curves of type Fig.-1a and b are the most characteristic. The condensation mechanism of hydrogenation is characterized by extreme dependences of the observed kinetic parameters at high concentrations of the starting materials (Fig.-1b). The kinetic curve in Fig.-1c is a reduction process by the hydrogenation mechanism, accompanied by partial oxidation of the catalyst surface. In this review, the main focus is on the discussion of nickel and iron-containing catalysts.

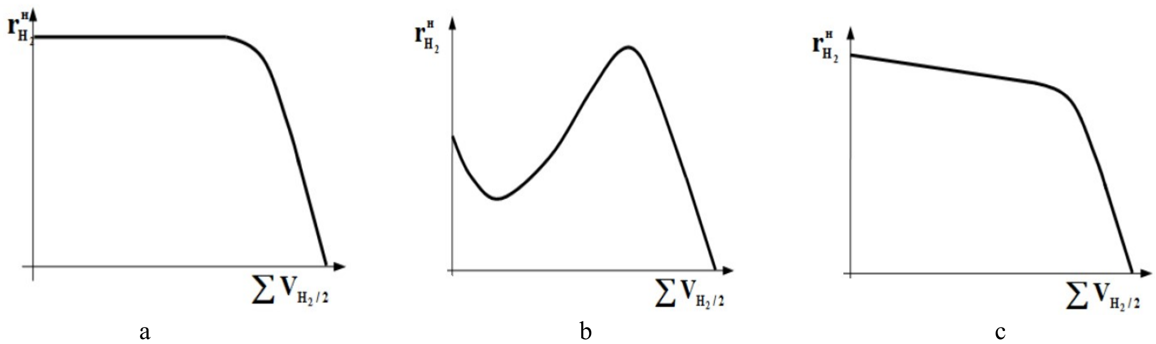
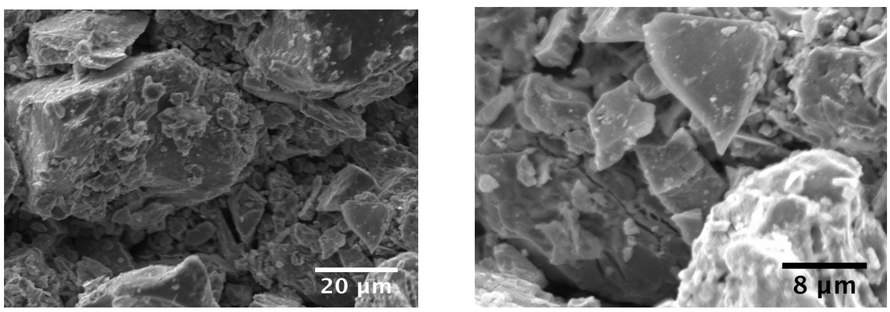


Fig.-1: Characteristic Dependences of Absorption Rates on the Amount of reacted Hydrogen in Liquid-phase Hydrogenation Reactions: a - Hydrogenation Mechanism; b - Condensation Mechanism; c - Hydrogenation Mechanism with Catalyst Deactivation

Catalysts on the Base of Nickel

Most studies of the reduction of nitro compounds, as shown by the analysis of patents and literature data, are carried out using nickel catalysts.[1,10,15,20,21-26] The most common catalyst for the reduction of various objects, including nitro compounds, is Raney nickel. Skeletal nickel catalyst was developed by M. Raney in 1924-1925. It is obtained by leaching aluminum from aluminum-nickel alloys with different contents of these metals. With increasing nickel content in the initial alloy, the size of the crystals and the rate of leaching decrease. Nickel and copper catalytic systems are much more common and effective catalysts in industrial processes than catalyst systems based on noble metals.[4,26,27] The advantages of skeletal catalysts are determined by the metal base and are in their mechanical strength, improved heat transfer, relatively low cost. The main technological disadvantages in the use of skeletal catalysts are reduced to the necessity of processing synthesis waste, possible deactivation of the catalyst both during its operation and during reactor loading, and its pyrophoricity.[28,29]

Fig.-2a shows an enlarged SEM image of a Raney nickel in which small cracks within 1-100 nm wide are observed inside the crystals, due to which the surface area increases.[25] Figure-2b demonstrates the SEM of a skeletal nickel hydrogenation catalyst with well-fixed crystals 1-50 m in size.



a b

Fig.-2: Raney Nickel SEM Images: a-Enlarged SEM Image; b- Nickel Hydrogenation Catalyst[25]