

used as a carrier for the preparation of supported catalysts, as well as independent catalytically active particles. In most cases, the precipitation method is used to obtain magnetite.⁴¹

The selective reduction of various nitroarenes having functional groups (halogen, olefin, carboxylic acid, amines, heterocyclic fragments, ketone, nitrile, hydroxy, ester) to corresponding aniline derivatives by transferring hydrogen on an iron-containing catalyst is described.⁴² A fairly easy method of preparation of iron pyrite (FeS_2) nanocrystals with the application of nano-needle iron oxyhydroxide as a precursor was proposed. For the preparation of the catalyst, $\beta\text{-FeOOH}$ nanorods were applied as an iron precursor. The authors synthesized pyrite nanomaterial, which demonstrated good efficiency in the process of hydrogenation of nitroarenes to anilines. The yields of amines ranged from 67 to 99% at 100% selectivity. The supported catalysts of 8% $\text{Fe}_2\text{O}_3/\text{C}$ for selective reduction of nitrobenzene were prepared.⁴³ Hydrazine hydrate was used as a source of hydrogen. When carrying out the reactions under mild conditions (atmospheric pressure and 60°C), during the reaction time of 90 minutes, 100% selectivity of aniline formation at 95% nitrobenzene conversion was obtained.

The combination of two types of metals in catalysts can lead to the formation of solid solutions of Fe-Me (Me - Ni, Pd, Pt, Ru) and, as a result, to a change in the catalytic properties of monometallic iron-containing catalysts.^{44,45} The Ru catalyst with a 15% iron addition deposited on carbon and tested in the liquid-phase hydrogenation of nitro compounds was synthesized.⁴⁶ The Ru-Fe/C catalyst obtained by stepwise impregnation, in comparison with the Ru/C monometallic catalyst, exhibits higher catalytic activity, selectivity and high stability (up to 140 hours of the experiment) in liquid-phase hydrogenation of ortho-chloronitrobenzene (o-CNB) to ortho-chloraniline (o-CAN). The conversion of ortho-chloronitrobenzene (o-CNB) to the corresponding amine was 99.7%, the selectivity on the o-CAN production was 98.7%. Figure-4 shows the XPS spectrum of a freshly prepared Ru-Fe/C catalyst. The energy level of Ru $3d_{3/2}$, close to C^{1s} (about 284 eV) was not observed.^{47,48} The presence of elementary Ru on the surface of the carrier is established, which corresponds to the binding energy of Ru $3d_{5/2}$ (BE) of 280.6 eV, and relative to the standard peak of Ru (281 eV) negatively shifted by 0.4 eV. The energy level of Fe $2p_{3/2}$ in the Ru-Fe/C catalyst (BE value is 711.1 eV) indicates that the Fe element in the sample exists in the form of Fe_3O_4 , and its BE value is positively shifted by 0.6 eV relative to the standard peak Fe_3O_4 (710.5 eV). This may be because Fe_3O_4 with electron-donating properties transfers some electrons to metallic Ru, transforming Fe_3O_4 in the Ru-Fe/C catalyst into an electron acceptor state, thereby enhancing the electron-enriched Ru state.

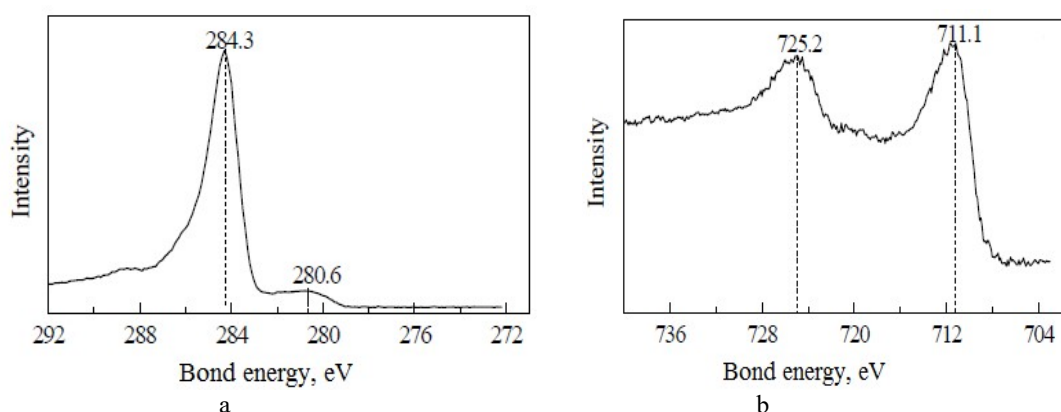


Fig.-4: XPS Spectra: (a) Ru 3d, (b) Fe 2p in Ru-Fe/C Catalyst⁴⁶

It was shown that the addition of Pd to a supported monometallic Fe sample reduces the temperature of reduction of iron oxide phases by hydrogen to 400°C and the formation of a $\text{Pd}_x\text{Fe}_{1-x}$ solid solution.^{44,49} The ratio of metals in Fe-Pd catalysts has a significant effect on the reducing ability of the samples. The Mössbauer spectroscopy of the 2Fe-2Pd sample (wt.%) indicates the presence of metallic $\alpha\text{-Fe}$, an alloy of Pd_xFe and Fe^{2+} in the sample, reduced at 400°C . With an increase in the Fe:Pd molar ratio to 5:1, the content of metallic iron particles increases. At the same time, when this ratio is 1:1, the amount of the Pd_xFe alloy increases, while the number of Pd^+ centers decreases sharply.⁴⁹