RASĀYAN J. Chem.

Vol. 14 | No. 3 |1795-1802 | July - September | 2021

Hydrogenation can be stopped at intermediate stages.^{21,22}Thus, the reduction of nitrobenzene to Pd / C in an alkaline medium leads to the formation of hydrazobenzene in a yield of 93-97% and purity of 99.5 -99.7%. Hydrogenation of o-mononitrotoluene in an alcohol medium with a Pd catalyst at 30-150°C in the presence of bases leads to the formation of hydrazotoluene. Similarly, o-hydrazotoluene is obtained in a yield of more than 80% in the presence of sodium hydroxide and quinone. The presence of alkali contributes to the acceleration and selectivity of the reaction, and quinone inhibits further reduction; the dielectric constant of the solvent exerts a strong influence on the process. When nitro compounds are reduced by hydrogen with Pt/C or Pd/S/Se/C catalysts in the methylmorpholine medium at 28-30°C, the process stops at the hydroxylamine stage (in the reduction of o-nitrotoluene, the content of o-tolyl hydroxylamine in the reaction product reaches 96%). As a solvent, methylpiperidine and dimethyl sulfoxide are also used.^{17,22,23} Platinum and palladium catalysts deposited on coal showed high activity and stability in the reduction of nitrobenzene, nitroanilines, p- and o-nitrophenols and other nitro compounds with various substituents.¹⁷⁻²²

Palladium Catalysts with Additives of Rare-earth Elements

Recently, to improve the processes of organic and inorganic synthesis, catalysts based on rare-earth elements (REE) are increasingly being used by different scientific schools. The catalyst sub-industry consumes about 25% of all REE. The transition metals of the lanthanum group, as well as scandium and yttrium, are used in various fields of modern technology: in radio electronics, instrument making, nuclear technology, mechanical engineering, the chemical industry, and metallurgy. The REE market has been developing significantly in recent years; the world demand for REE is regularly increasing.²⁴The content of rare earth elements in the earth's crust is high and represents a significant material base in various industries. Rare earth elements are used as an active phase, a promoting additive, and their oxides as a carrier.²⁵⁻²⁷

Rare earth elements can be added to increase the activity and stability of Pd and Pt catalysts in the hydrogenation of nitro compounds.²⁸⁻³⁴Thus, it was revealed that the specific catalytic activity of Pd catalysts promoted with REE in the hydrogenation reactions of nitro compounds is 2 orders of magnitude higher than on Pd/Al₂O₃. Within the group of lanthanides, the highest specific activity was found to be characteristic of the central elements (Eu, Ga, Tb).

Rare-earth elements are used as an active phase, promoting additives, and their oxides are used as a carrier.^{12,17,26} It is pointed out that one of the directions of use of rare and platinum metals is associated with the development of catalysts for various purposes.

Hydrogenation of nitrobenzene on 1% Pd deposited on rare earth element oxides Ce, Pr, Nd, Sm, Eu, Cd, Tb, Dy, Ho, Tm, Yb, Lu was studied and compared with Pd/Al_2O_3 .³¹ It was shown that Eu_2O_3 , Yb_2O_3 , and Tb_2O_3 were the most active carriers of all oxides. The activity of catalysts on REE oxides exceeds that of Al_2O_3 by 1.2-4 times. The authors explain the high activity of these catalysts by the influence of REE oxides on the formation of active centers of palladium catalysts.

The efficiency of catalytic systems based on 5% Pd - 5% OREE (where OREE are oxides of rare earth metals - lanthanum, europium, gadolinium, and terbium) for hydrogenation of p - nitrotoluene to p-toluidine was studied. The authors have applied α -Al₂O₃ and 6% γ -Al₂O₃ / α -Al₂O₃ as carriers. It was found that the addition of OREE to 6% γ -Al₂O₃/ α -Al₂O₃ causes a decrease in the specific surface area of the support, and the addition of OREE to α -Al₂O₃ increases the surface area. It should be noted that the addition of terbium oxide for both types of carriers showed the best results. Thus, in the case of the α -Al₂O₃ support, the increase in the specific surface area turned out to be the largest: from the initial value of 0.20 m²/g, with the addition of terbium oxide, the specific surface area increased to 3.96 m²/g. If a 6% γ -Al₂O₃ / α -Al₂O₃ support was used, then the decrease in the specific surface area was the smallest in comparison with other modifying additives (12.51 m²/g), with the initial value of the specific surface area in the case of using other modifying additives was more than 10 m² / g.³²⁻³⁴ The authors concluded that the promotion of the initial aluminum oxide carrier by adding OREE leads to a significant increase in the rate of hydrogen absorption in the hydrogenation reaction. According to the conclusions of some scientists, a significant influence of the modifier on the activity of