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C_2 -Symmetric diamines and their derivatives as promising organocatalysts for asymmetric synthesis

1077

S.G.Zlotin, S.V.Kochetkov

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The review is devoted to the application of C_2 -symmetric diamines and their derivatives as organocatalysts for asymmetric reactions (aldol, Michael, Mannich, Diels-Alder, desymmetrization, allylation, etc.). Amino acid derivatives, di- and polyamides (sulfamides), bisureas, bisthioureas, bisamidines and bisguanidines are considered. Substantial attention is given to the effect of the catalyst structure on the mechanism of catalytic action. Examples of the use of such catalysts in the enantioselective synthesis of chiral biologically active compounds are given. Bibliography — 181 references.

Development of approaches to a conjugated carbohydrate vaccine of the third generation against *Streptococcus pneumoniae*: the search for optimal oligosaccharide ligands

1100

M.L.Gening, E.A.Kurbatova, Yu.E.Tsvetkov, N.E.Nifantiev

The application of synthetic oligosaccharides related to fragments of *Streptococcus pneumoniae* capsular polysaccharides for the design of conjugated pneumococcal vaccines of the third generation is reviewed. Particular attention is paid to features of the chemical structure of oligosaccharides that induce the protective immune response in the application of synthetic glycoconjugate vaccines based on oligosaccharide ligands and carrier proteins. Bibliography 101 references.

Ligand-protected gold clusters: structure, synthesis and applications

1114

D.A.Pichugina, a N.E.Kuz'menko, a A.F.Shestakov b

The modern views on the structure and properties of atomic gold clusters protected by thiols, selenols and phosphine and phenylacetylene ligands are analyzed. In terms of the superatom concept, the 'divide and protect' concept and the structure rule, the cluster stability and composition are determined by the clusters core structure, the type of ligand and the number of common valence electrons. The strategies and challenges of selective synthesis of gold clusters in solution and on the surface of inorganic composites are discussed, in particular, based on the interaction of Au_n with RS, RSe, PhC≡C and Hal ligands or with functional groups of the proteins, on the cluster stabilization in the cavities of α -, β and γ -cyclodextrins $(Au_{15} \text{ and } Au_{25})$ and anchorage on the support surface $(Au_{25}/SiO_2, Au_{20}/C, Au_{10}/FeO_x)$. Among the methods used to elucidate the cluster structure, the attention is focused on theoretical approaches using the density functional theory. The structures of some synthesized clusters based on X-ray diffraction and DFT data are presented. A probable mechanism of the formation of the SR(AuSR), staple motif in the cluster shell is proposed. The structure and properties of bimetallic $M_x A u_n L_m$ clusters (M = Pd, Pt, Ag, Cu) are discussed. The Pd or Pt atom tends to occupy the position at the cluster centre, while Ag and Cu atoms form bimetallic compounds in which the heteroatom is located on the core surface or is a part of the staple motif. The optical properties, fluorescence and luminescence of ligand-protected gold clusters are caused by quantum effects of the core atoms and atoms of the oligomeric SR(AuSR), fragments of the shell. The known homogeneous and heterogeneous reactions catalyzed by the atomic gold clusters are discussed in terms of the reaction mechanism and the nature of active sites. Bibliography — 345 references.

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1145

B.P.Tumanyan, ^a N.N.Petrukhina, ^a G.P.Kayukova, ^{b,c} D.K.Nurgaliev, ^c L.E.Foss, ^b G.V.Romanov ^{b,c}

The results of studies of the changes in the elemental and SARA compositions, physicochemical and rheological properties of heavy high-viscosity crude oils upon catalytic and non-catalytic aquathermolysis are generalized. The chemistry of transformations of model hydrocarbons and heteroatomic compounds in aqueous media at high temperature, including subcritical and supercritical conditions, is considered. Comparative analysis of methods for promoting oil conversion via a quathermolysis using hydrogen donors, oil-soluble and water-soluble nanodispersed catalysts, ionic hydrogenation processes and various ways for reservoir heating is presented. Problems and prospects of oil-field implementation of catalytic aquathermolysis for upgrading high-viscosity oils and natural bitumen are discussed. Bibliography—234 references.

The role of zeolite in Fischer – Tropsch synthesis in the presence of cobalt – zeolite catalysts

1176

L.V.Sineva, a E.Yu.Asalieva, a, b V.Z.Mordkovich a

The review is devoted to the Fischer-Tropsch synthesis for single-stage syncrude production from CO and H₂ catalyzed by cobalt- and zeolite-containing catalytic systems. Various types of bifunctional catalysts (hybrid, composite) combining a Fischer-Tropsch synthesis catalyst and a zeolite are surveyed. Special attention is given to the mechanisms of transformations of hydrocarbons, Fischer-Tropsch synthesis products, on the zeolite acid sites under the synthesis conditions. Bibliography — 142 references.

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