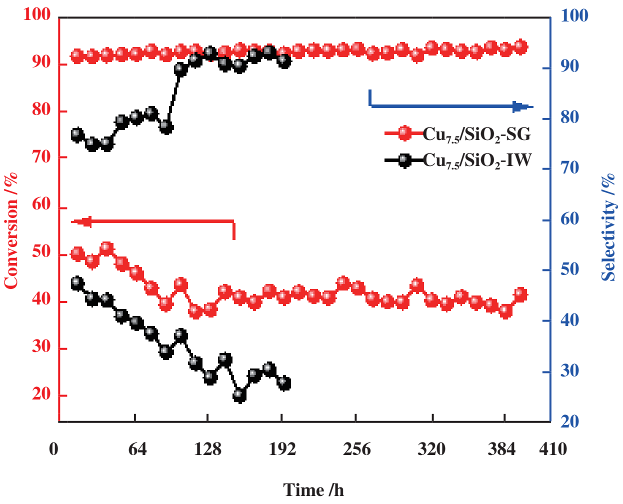
Acceptorless Dehydrogenation of Ethanol to Acetaldehyde using Highly Active Cu Catalyst

YUAN Hang-kong, HUANG Yong-ji, WANG Bin, SUN Yu-bin,
YANG Dong-yuan, CUI Xin-jiang

J. Mol. Catal. (China) **2023**, 37(1): 001–011

Herein, we developed a highly active, stable $Cu_{7.5}/SiO_2$-SG heterogeneous catalyst for the acceptorless dehydrogenation of ethanol to acetaldehyde employing the ammonia evaporation method. Compared with $Cu_{7.5}/SiO_2$-IW catalyst by the wet impregnation method, the introduction of ammonia has been speculated to be favorable (i) to the formation of a homogeneous dispersion of Cu species and high distribution of the Cu nanoparticles in the treatment afterward and (ii) to enhance the formation rate of silica matrixes which acts as cages to confine the Cu nanoparticles, and inhibit the aggregation of the Cu nanoparticles. Applying the typical $Cu_{7.5}/SiO_2$-SG catalyst in the dehydrogenation of ethanol affords excellent outperformed thermal stability (up to 400 h) in a fixed-bed reactor without any balance gas.

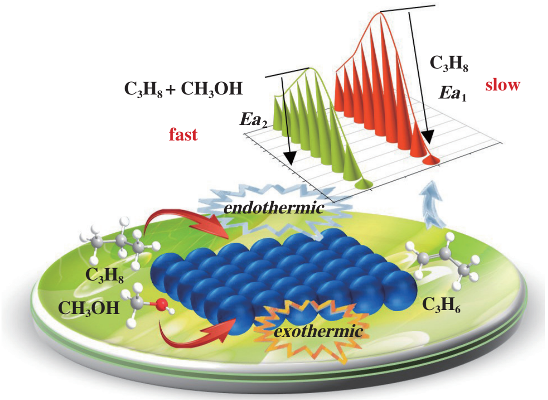


Thermodynamics and Kinetic Reaction Performance Analysis of Propane Methanol to Olefins Process

HUANG Ling-xiang, LI Hai-yan, MA Yue, DU Wei,
SHEN Bao-jian

J. Mol. Catal. (China) **2023**, 37(1): 012–022

The paper studies the thermodynamic and kinetic process of propane and methanol to olefins reaction by calculation and experiment. For the system of propane and methanol as co-reactants, propane dehydrogenation (endothermic reaction) and methanol to olefins (strong exothermic reaction) are thermally coupled reactions, which can effectively utilize heat and maximize economic benefits. Methanol as a co-feed with propane for oxidative dehydrogenation will inevitably produce by-products. Therefore, the analysis of propane methanol thermodynamics has important guiding significance for catalyst design and energy consumption analysis. The effect of adding methanol on propane dehydrogenation was further studied. The apparent activation energy of propane co-reaction on Fe-Zn/Al_2O_3 catalyst was investigated. The experiment of measuring apparent activation energy was designed, and the experimental data of apparent activation energy of propane dehydrogenation were further obtained.



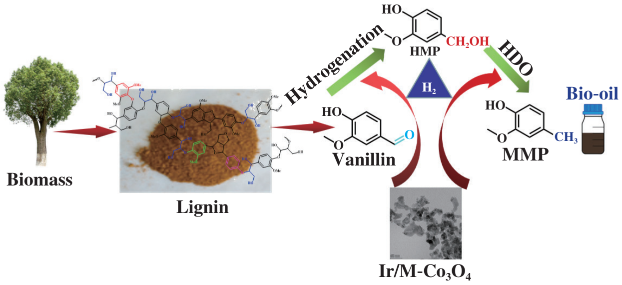
Highly Dispersed Iridium Nanoparticles Supported on Co_3O_4 as an Efficient Catalyst for Hydrodeoxygenation of Vanillin

DING Chuang-chi, MENG Sen, LIU Bin, DU Quan-chao,
REN Chuan-qing, JI Jian-wei

J. Mol. Catal. (China) **2023**, 37(1): 023–032

In this paper, highly active Ir/M-Co_3O_4 catalysts were prepared by impregnation method using metal-organic framework M-Co_3O_4 as the carrier, and the loaded Ir content was 1%. The catalyst showed excellent catalytic performance in the reaction of vanillin hydrodeoxygenation for the preparation of 4-methylguaiacol. The synthesized MOF-Co_3O_4 had a unique layered structure and a large specific surface area, which was conducive to the highly dispersed distribution of Ir nanoparticles and the occurrence of HDO reaction. Moreover, the catalyst exhibited relatively good stability. After four cycles, the Ir0 was oxidized to Ir^{4+}, which

resulted in a decrease in its activity. But its activity could be restored after calcining and reducing. This paper confirmed that Ir/M-Co_3O_4 was a potential catalyst for hydrodeoxygenation, and the strategy of this work provided a new low-cost catalytic system for efficient production of valuable chemicals and future biofuels from lignin derivatives.

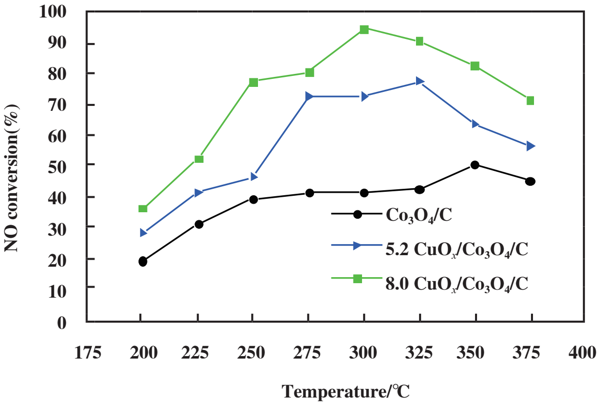


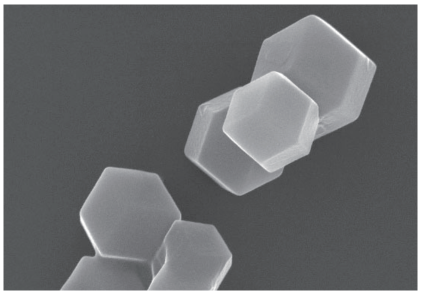
Selective Catalytic Reduction of NO by CO over Cu-doped Co_3O_4/C Catalysts Derived from ZIF-67

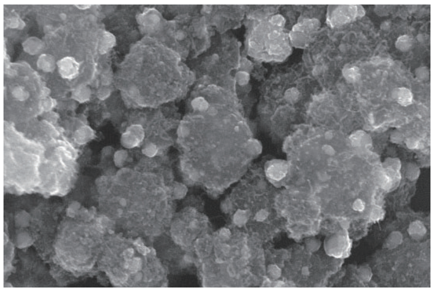
WANG Zhu-feng, HUANG Jia-wei, LUO Bing-bing, SU Ya-xin

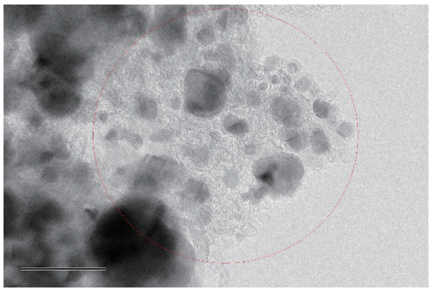
J. Mol. Catal. (China) **2023**, 37(1): 033–042

ZIF-67-derived Co_3O_4/C was modified by introducing Cu, and a series of CuO_x/Co_3O_4/C catalysts were obtained by pyrolysis and oxidation after loading copper on the carrier by the impregnation method. The physical and chemical characteristics of catalysts were characterized by ICP, SEM, XRD, TGA, XPS, BET, and H_2-TPR techniques. The results show that copper has a promoting effect on cobalt.




SEM images of ZIF-67


SEM images of 8.0 CuO_x/Co_3O_4/C

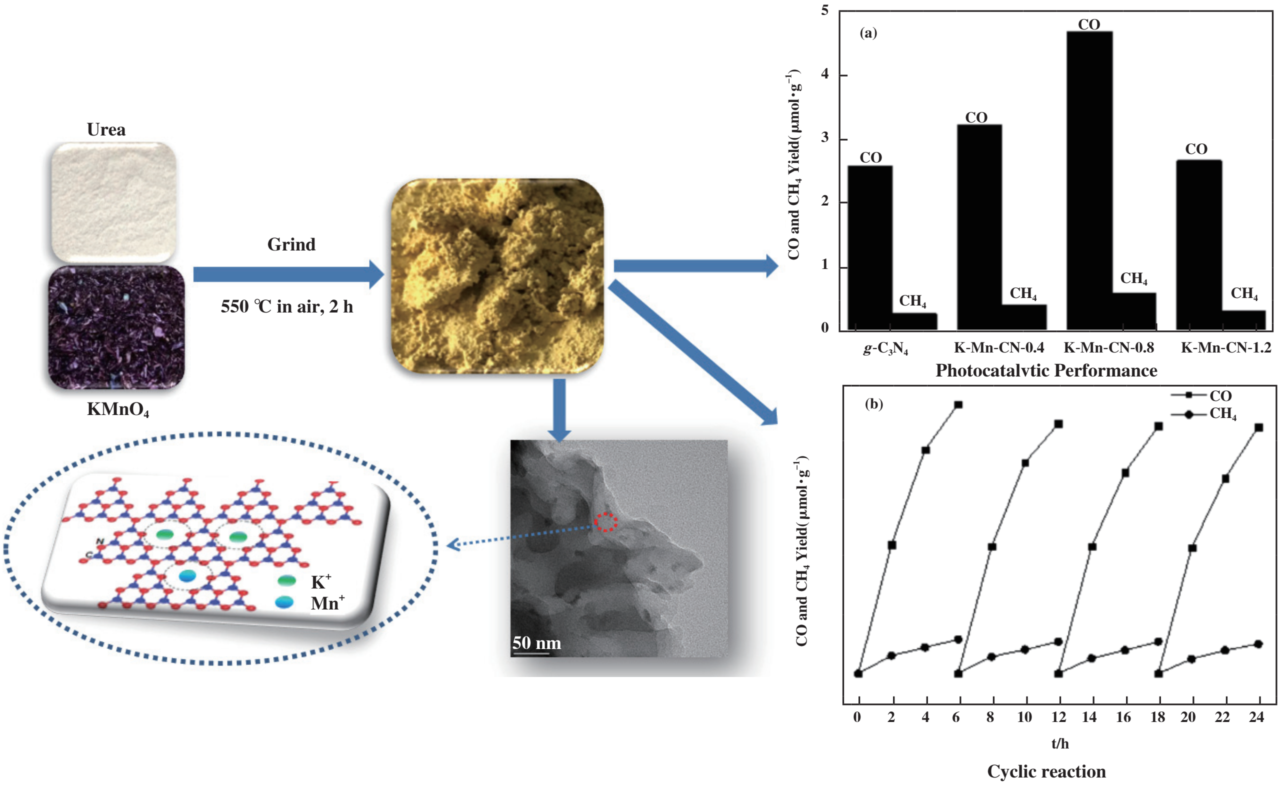

TEM images of 8.0 CuO_x/Co_3O_4/C

Preparation of K and Mn-modifed g-C_3N_4 Photocatalyst by a Facile One-pot Calcination Method for Enhanced Photocatalytic CO_2 Reduction

TANG Li-ping, ZHANG Hui-ming, GUO Wen-jie,
HU Ying-ying, JIA Jing-jing

J. Mol. Catal. (China) **2023**, 37(1): 043–052

K and Mn-modifed g-C_3N_4 composites were prepared by one-pot calcining method with urea and $KMnO_4$ as precursor, and applied to photocatalytic CO_2 reduction. The systematic characterization results revealed that the K, O and Mn elements were co-doped into the CN framework successfully to form n-π* conjugate forms and a part of Mn element existed in the form of MnO_2. Due to the doping of K and Mn, the visible light response was improved and the charge separation efficiency was increased. The experimental results showed that the yields of CO and CH_4 of K and Mn-modifed g-C_3N_4 were 4.66 and 0.59 μmol · g^{-1} respectively, which is 1.82 and 2.18 times higher than that of pure g-C_3N_4. After four cycles of catalyst K-Mn-CN-0.8, the yields of CO and CH_4 decreased slightly. The reason may be due to the adsorption of reaction products or intermediate products on the active site of the photocatalyst, which inhibit the subsequent reaction.

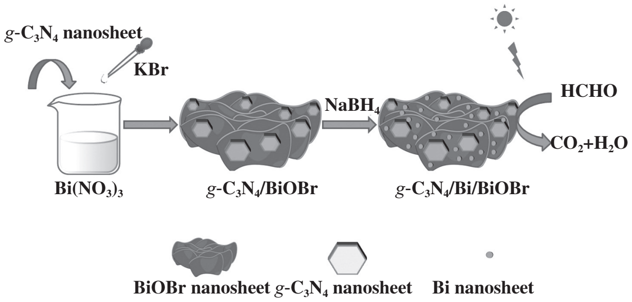


Preparation of *Z*-Scheme g-C_3N_4/Bi/BiOBr Heterojunction Photocatalyst and Its Visible Light Degradation of Formaldehyde Gas

PENG Jiang-wei, JIANG Zhuo-ting, JIANG Kui-bing,
JIANG Sen, ZHU Hui-rong, YAN Gang, GUO Xiang-wei

J. Mol. Catal. (China) **2023**, 37(1): 053–062

A ternary heterojunction photocatalyst g-C_3N_4/Bi/BiOBr was synthesized by BiOBr nanosheets and g-C_3N_4, followed by in-situ reduction. The prepared g-C_3N_4/Bi/BiOBr has enhanced photocatalytic activity toward formaldehyde under visible light irradiation than that of g-C_3N_4, BiOBr monomer and g-C_3N_4/BiOBr binary complex. 20%-g-C_3N_4/Bi/BiOBr can be formed within 60 minutes ($\lambda > 400$ nm) to degrade 80% of gaseous formaldehyde (initial concentration 0.16 mg · L-^{1}). The improvement of the photocatalytic efficiency of g-C_3N_4/Bi/BiOBr is attributed to the improved light absorption ability and the synergistic effect of each component. As a charge transfer medium, metal Bi effectively adds the carrier separation ability of other components.



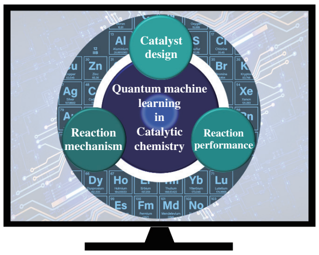
Application of Quantum Machine Learning in the Research of Catalytic Chemistry

QIAN Bo

J. Mol. Catal. (China) **2023**, 37(1): 063–072

With the rapid development of computational science and artificial intelligence, the effective combination of machine learning with quantum chemistry breaks through the limitations of traditional quantum chemistry, leading to the generation of quantum machine learning. Quantum machine learning could accurately predict the required quantum chemical properties through employing excellent training data and machine learning algorithm without solving the Schrodinger equation of each atomic system, of which the calculation speed is many orders of magnitude faster than traditional quantum chemistry methods. In the research of catalytic chemistry, quantum machine learning assists scientists to make accurate, fast, and real–time predictions

for catalyst design, catalytic reaction performance and catalytic reaction mechanism. We believe that quantum machine learning will become a common and powerful tool to accelerate the progress of catalytic chemistry, providing an unprecedented revolution for catalytic science.

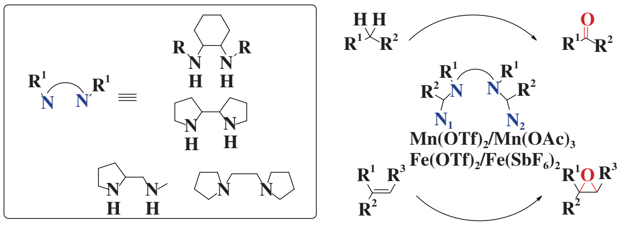


Advances in Biomimetic Asymmetric Oxidation Catalyzed by N_4 Metal Complexes

TIAN Jing, SUN Wei

J. Mol. Catal. (China) **2023**, 37(1): 073–093

Non-heme N_4 iron and manganese complexes are prevailing in the field of biomimetic catalytic asymmetric oxidation. Under mild reaction conditions, asymmetric epoxidation and oxidation of C — H bonds can be efficiently performed with these chiral N_4 iron or manganese complexes using hydrogen peroxide by mimicking the active site of non-heme enzymes. Such catalysts usually consist of a diamine backbone and two nitrogen-containing groups, which are coordinated with manganese and iron to form twisted octahedral configurations. In the design of N_4 ligands, N,N'-dimethyl-1,2-cyclohexanediamine, bipyrrole, and derivatives of *L*-proline have proven to be are the suitable candidates, and substituted pyridine and benzimidazole have been used together to build the N_4 ligands. The chiral center of diamine is delivered to oxidized products in the catalytic system, resulting in highly optically pure compounds with oxygen-containing functional groups. Notably, the fine-tuning of structures of ligands has a significant effect on the oxidation reaction. Electron-donating substituents on the pyridine group obviously improve efficiency and enantioselectivity of the asymmetric epoxidation, reducing the loading of catalyst. Large sterically hindered substituents are the supporting factor to achieve selective oxidation of remote C — H bonds and γ — C — H bonds lactonization of α-amino acids. Large sterically hindered carboxylic acids are also beneficial to improve the enantioselectivity of asymmetric oxidations. Unsaturated enones, enamides, substituted styrenes and spiroketones are smoothly oxidized (>99% ee). In this paper, the advances of asymmetric epoxidation and oxidation of C — H bonds catalyzed by non-heme complexes is reviewed in the past two decades, and the development of this field is prospected.



Modification of Metal Organic Framework Materials and Their Application in Photo-catalytic Hydrogen Evolution

LI Bo-yuan, HE Feng-gui, ZHANG Ming-hui,
ABDUKADER Abdukayum

J. Mol. Catal. (China) **2023**, 37(1): 094–107

Photocatalytic hydrogen evolution is considered as a potential strategy to overcome the energy crisis. Metal organic frameworks (MOFs) have attracted great interest in photocatalytic hydrogen evolution due to their porosity, high specific surface area and tunable band gap. Various modification methods of MOFs including modification of organic ligands or metal centers, loading of metal nanoparticles, dye sensitization, and combination with other functional materials are presented. The issues and potential solutions for MOF-based photocatalysts for hydrogen evolution are discussed, and the promising prospects of MOFs-based photocatalysts for hydrogen evolution are also highlighted.