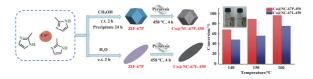
Effect of Different Morphologies Induced by Solvent on ZIF-67 Derived Co@NC for Catalytic Phenol Hydrogenation

WANG Dong-wei, MA Zhan-wei, LI Jing, FENG Hu-lin, HU Bin

J. Mol. Catal. (China) 2024, 38(5): 399-408.

Different morphology Co@NC catalysts were prepared by two step process: solvent control growth and pyrolysis method. The Co@NC-67P-450 and Co@NC-67L-450 catalysts with different morphologies were obtained, and the catalytic activity of the catalysts was evaluated by hydrogenation of phenol. The polyhedral Co@NC-67P-450 catalyst has a relatively high Co $-N_x$ content and exhibits excellent phenol hydrogenation activity (conversion 96.9%, selectivity 99.9%) at 160 °C, 3 MPa, and 8 h, which is higher than that of leaf shaped Co@NC-67L-450 catalyst (conversion 75.4%, selectivity 99.9%).

Additionally, Co_3O_4 was reduced to the Co^0 during the reaction. It was found that the metal Co nanoparticles were responsible for hydrogen adsorption and dissociation and further reaction for the adsorption and activation of phenol. Besides, the larger $Co-N_x$ content performed the higher catalytic activity. The rich electron N can stabilize Co and regulate the electronic property of Co, and which also can form the hydrogen bond with -OH in phenol. The Co-based catalysts can be easily recovered through the magnetic separation and performed the high stability in recycling experiments. At the same time, the catalytic activity of CoN_x on N_2 and H_2 was verified by using ammonia synthesis as the probe reaction. The results show that $Co-N_x$ also plays a significant role in promoting ammonia synthesis.



Synthesis of Propylene Carbonate from CO₂ Catalyzed by Metal-free Carbon Nitride

SUN Xiao-hua, ZHANG Xue-wen, WANG Fei, XU Jie, XUE Bing

J. Mol. Catal. (China) 2024, 38(5): 409-417.

Cycloaddition of CO₂ with propylene oxide is a sustainable route for the production of propylene carbonate. The most efficient catalysts reported now are mainly ionic liquids and metal halides, however suffering from the disadvantages in catalyst-product separation and production purification. In this sense, it is of interest to develop a heterogeneous efficient catalyst for the cycloaddition of CO₂. Owing to its abundant nitrogen-containing groups, graphitic carbon nitride (*g*-C₃N₄) has been reported for the catalytic cycloaddition of CO₂ to propylene carbonate. However, the activity obtained from *g*-C₃N₄ materials that are prepared by direct thermal condensation is very low. Herein, exfoliated graphitic carbon nitride (*eg*-C₃N₄) material was synthesized by thermal polymerization and

thermal exfoliation using dicyanodiamide as a precursor, and series $eg\text{-}C_3N_4\text{-}S$ materials were prepared by treatment of H_2SO_4 . The physicochemical properties of the obtained materials were characterized by N_2 adsorption-desorption, XRD, FT-IR, XPS, and UV-Vis spectroscopy. The characterization results showed that exfoliation effectively increased the specific surface area of $g\text{-}C_3N_4$, while H_2SO_4 treatment introduced the hydroxyl group. In the catalytic reaction of cycloaddition of CO_2 with propylene oxide, $eg\text{-}C_3N_4\text{-}S$ showed higher catalytic activity than $g\text{-}C_3N_4$ without H_2SO_4 treatment or thermal exfoliation. Under the reaction pressure of 2.0 MPa and temperature of 140 °C, the conversion of propylene oxide and the selectivity to propylene carbonate were 85% and 98%, respectively.



Optimizing the Enzymatic Kinetic Resolution of (R/S)- δ -Tetradecalactone by Response Surface Methodology

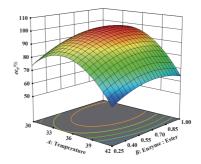
PENG Yan, LI Chun-ni, LONG Xian-wei, LI Jun-cheng, LU Qun

J. Mol. Catal. (China) 2024, 38(5): 418–426.

In this paper, an efficient lipase-catalyzed hydrolysis system of δ -tetradecalactone to optically pure 5-hydroxytetradecanoic acid was established. A series of lipases were screened to obtain lipases ANL and PCL. The effects of organic solvents, pH, enzyme-ester ratio, time and temperature on the yield (Y) and optical purity (ee_p) of the reaction products were studied. The effects of some important factors were

evaluated by response surface methodology and the process was optimized. After optimization, (S)-5-hydroxytetradecanoic acid ($ee_{p1} \ge 99.9\%$, yield 42.0%) and (R)-5-hydroxytetradecanoic acid ($ee_{p2} \ge 99.9\%$, yield 49.0%) were obtained. The developed scheme provides a practical solution for the direct preparation of optically pure 5-hydroxytetradecanoic acid and optically pure δ -tetradecalactone, which has the advantages of simple operation, low energy consumption, easy use of catalyst, high selectivity and separation efficiency. This enzyme-catalyzed synthesis has high efficiency, excellent stereoselectivity, and is in line with environmental benefits. It

provides a promising method for the industrial preparation of chiral hydroxyl acids and optically pure δ -lactones for various applications.



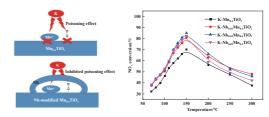
Promotion Effect of Nb-modification of MnTiO_x Catalysts in Low-temperature NH₃-SCR Reactivity and K-resistant

YU Rui, ZHU Fan, SHI Guang, CUI Jun-ming, ZHANG Wei-ping

J. Mol. Catal. (China) 2024, 38(5): 427-436.

 $MnTiO_x$ catalyst exhibits excellent low-temperature activity and has good prospects for selective catalytic reduction by NH₃ (NH₃-SCR) of sintering flue gas in steel industry. However, in actual application, $MnTiO_x$ catalyst is very sensitive to alkali metal (e.g. K) poisoning. Therefore, in this paper, $MnTiO_x$ was modified by Nb to improve the resistance of alkali metal K poisoning. NH₃-SCR performances of $Mn_{0.4}TiO_x$ and Nb modified $Mn_{0.4}TiO_x$ catalysts in the presence of alkali metal K poisoning were studied. The Nb-modified $MnTiO_x$ catalysts showed significantly higher low-temperature

NH₃-SCR performance and alkali metal K-resistance than the original catalyst. The results suggested that when the Nb content is low, K forms a more obvious K-Mn oxide species on the catalyst, reducing the number and strength of acidic sites, and lowering the proportion of Mn⁴⁺ and active oxygen species, which might be responsible for the decreased reaction activity after K poisoning. Introducing Nb increases the number and proportion of acidic sites, Mn⁴⁺, and active oxygen species on the catalyst, and the decrease in these species after K poisoning is significantly reduced, which leads to the improvement of the reaction activity and resistance to alkali metal poisoning of the MnTiO_x catalysts after introducing Nb.



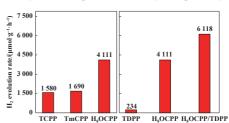
Synthesis of Carboxyphenyl Porphyrins and Photocatalytic Properties of Their Composites

WANG Yu-ting, CHEN Hui, LI Yan-ting, LIN Wan-ming

J. Mol. Catal. (China) 2024, 38(5): 437-447.

Porphyrins are heterocyclic compounds containing large conjugated systems, which have strong structural modifiability and visible light absorption ability, and are widely used in the design and development of new photocatalysts and photosensitizers. Further study on the factors affecting photochemical and physical properties of porphyrins is helpful to improve its application efficiency and expand its application range. In this paper, the photocatalytic decomposition of

aquatic hydrogen by meso carboxyl benzene-substituted porphyrin was studied from both intrinsic and external factors. Based on the intrinsic factors, three carboxyl porphyrins reveal the effect of the number of strong polar substituents on the photocatalytic performance of porphyrins. From the external factors, the addition of amino modified molecules can improve the aggregation degree of carboxyl porphyrins, so as to enhance the photocatalytic decomposition activity of aquatic hydrogen.



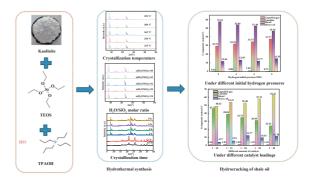
Hydrocracking Performance of Kaolinite-Based ZSM-5 Zeolite for Jimsar Shale Oil

LIU Jia-hui, CHEN Chang-hong, ZELALA Ainiwar, LIU Kai-fei, YANG Wu-kui, AISHA Nulahong

J. Mol. Catal. (China) 2024, 38(5): 448-456.

ZSM-5 zeolite, with its unique crystal structure, exhibits excellent catalytic performance in the chemical industry. Kaolinite, as a non-metallic mineral resource, is widely used as a filler in papermaking, coatings, paints, and plastics. Synthesizing zeolites using natural kaolinite as raw material holds a significant research value. In this study, nano-sized ZSM-5 zeolite with a microporous structure was synthesized using kaolinite as the raw material via a seed-assisted hydrothermal method. The optimal synthesis conditions were

determined as follows: the crystallization temperature of 195 °C, the crystallization time of 2 h, and the H₂O/SiO₂ mole ratio of 48. The synthesized ZSM-5 zeolite was applied to the hydrocracking of 220~350 °C fractions of Jimsar shale oil in Xinjiang, which achieved a gasoline yield of 45.23% under the conditions of 4 MPa hydrogen initial pressure and the catalyst dosage of 1 g catalyst per 10 g shale oil.



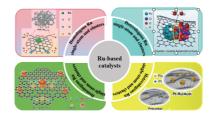
Ru-based Single-atom and Cluster Catalysts for Alkaline Hydrogen Evolution Reaction

DAI Zi-ruo, WANG Hai-bin, CONG Yuan-yuan

J. Mol. Catal. (China) 2024, 38(5): 457-466.

Platinum (Pt)-based catalysts exhibit excellent performance in the alkaline hydrogen evolution reaction (HER), but their high price and limited reserves restrict their large-scale application. Ruthenium (Ru) has a lower price than Pt and possesses similar hydrogen bonding energy to Pt, making Rubased catalysts highly promising for HER. Single atom catalysts (SAC) offer advantages such as high atom utilization and low metal load, while cluster catalysts provide different active sites. The synergistic competition effect between SAC and cluster catalyst can significantly enhance the performance of alkaline HER. Ru-based single atom and cluster catalysts not

only have low noble metal load but also demonstrate better HER performance compared to most other types of Ru-based and non-Ru-based catalysts. The highlights of this review are as follows: 1) In addition to conventional synthesis methods, new approaches like limited chemical strategies and plasma technology are included to achieve fast and simple synthesis; 2) Unique morphology and structure enable the synergistic effect of single atoms and clusters, thereby improving HER performance; 3) Some of these catalysts have met industrial application conditions, exhibiting outstanding HER performance at high current density while maintaining satisfactory stability. This paves the way for the development of industrial catalysts.



Recent Progress on the Heterogenization of Molecular Cobalt Polypyridine Complexes for Photocatalytic CO₂ Reduction

YI Fu-hao, LIAO Guo-shen, CAI Li-rong, CHEN Gui, CHEN Ling-jing

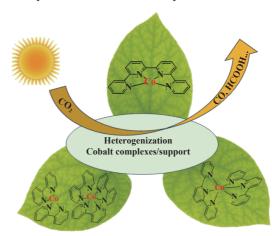
J. Mol. Catal. (China) 2024, 38(5): 467-482.

The use of solar energy to reduce carbon dioxide (CO₂) to

high value-added fuels is an effective strategy to address energy and environmental issues under the current background of carbon peaking and carbon neutrality goals. Molecular metal complexes, especially the nonprecious metal-based catalysts, and semiconductors are widely applied in photoreduction of CO₂ into various compounds including CO, formate, CH₄, and other hydrocarbons, and each has its own advantages. In more recent years, a new catalytic system with molecule/ semiconductor hybrid materials has been designed by their integration aiming to foster strengths and circumvent

weaknesses. Our group has been developing a series of metal complex catalysts for artificial photosynthesis in both homogeneous and heterogeneous systems, and cobalt quaterpyridine complexes showed excellent performance. This article reviews the research progress in the heterogenization of cobalt molecular catalysts bearing organic polypyridine compounds (mainly bipyridine, terpyridine, and quaterpyridine) as ligands for the photocatalytic reduction of carbon dioxide through covalent bonding, non-covalent bonding as well as the construction of ordered polymers. The effects of catalyst structures and the morphology of support immobilization strategies on catalytic efficiency, selectivity, and stability were discussed, with the aim of guiding the future design of hybrid earth-abundant metal molecular complexes. The challenges in

the development of heterogenized molecular catalysts for photocatalytic CO₂ reduction are finally discussed.



Research Progress on Transition Metal Catalysts of *tert*-Butyl Sulfinamide

ZHANG Zi-hao, JIN Bo-yu, LIU Shan-shan

J. Mol. Catal. (China) 2024, 38(5): 483-501.

Asymmetric synthesis technology has developed rapidly in the field of organic synthesis, leading to significant advances in transition metal chiral complex catalysts. Since 1997, the Ellman research group has synthesized and separated optically pure chiral *tert*-butyl sulfinamide for the first time, which has been applied in the synthesis of transition metal catalysts. Due to the advantages of simple structure, facile synthesis, and excellent catalytic performance, transition metal catalysts based on *tert*-butyl sulfinamide have become a research hotspot in the

field of asymmetric catalysis. Many research groups at home and abroad have been competing to design and synthesize new *tert*-butyl sulfinamide transition metal catalysts, and study their potential application. The *tert*-butyl sulfinamide transition metal catalysts reported in this review in the past ten years are classified in terms of ligand coordination atoms and functional groups, and can be divided into four categories: *tert*-butyl sulfinamide-sulfur ligand, *tert*-butyl sulfinamide- phosphorus ligand, *tert*-butyl sulfinamide ligand (coordination atoms are S, N or S, O). The synthesis methods and applications of these catalysts are briefly described. This review summarizes the development trend of transition metal catalysts based on *tert*-butyl sulfinamide, points out the direction for further research and provides important references for related research in this field.