

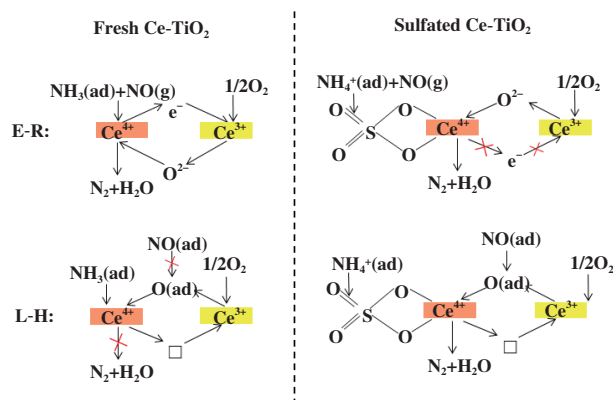
Effect of Pre-sulfation Treatment on NH_3 -SCR Performance over Ce-TiO_2 Catalyst and Its Reaction Mechanism

YANG Bao-xuan, ZHOU Jiao, YAO Shu-heng

J. Mol. Catal. (China) **2022**, 36(4): 301–312

A series of sulfated Ce-TiO_2 catalysts for selective catalytic reduction (SCR) were obtained by sulfation treatment in $\text{SO}_2 + \text{O}_2$ atmosphere. The reaction between NH_3 and NO over the fresh Ce-TiO_2 catalyst follows the E-R reaction pathway while the L-H reaction pathway is unable to perform. As for the sulfated Ce-TiO_2 catalyst, the E-R pathway is inhibited with the enhanced L-H pathway. The significant decline of SCR activity over sulfated catalyst is due to the severely inhibited E-R reaction pathway. With the increase of reaction temperature, the gradual recovering of the SCR activity is attributed to the recovered E-R reaction pathway, combining with the enhanced L-H pathway, which contributes to the even higher SCR activity than fresh Ce-TiO_2

catalyst. Our study shows that the Ce-TiO_2 catalyst is potential for the engineering application at $240\sim 300\text{ }^\circ\text{C}$ and the strategy for designing cerium-based catalysts with superior SO_2 resistance at low temperature ($<200\text{ }^\circ\text{C}$) is considered as the following two aspects: (1) preventing the sulfation of ceria by increasing ceria and catalyst support strength, and (2) doping the metal less susceptible to sulfur dioxide attack, which can be screened by DFT study.



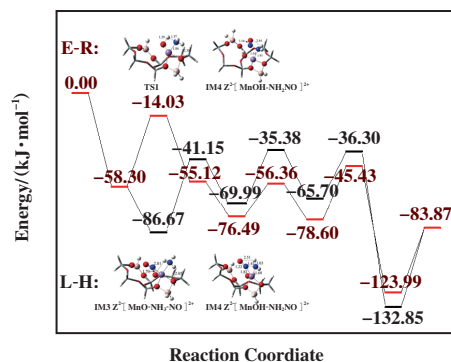
Study on NH_3 -SCR Reaction Mechanism over MnZSM-5 Catalyst

LI Bao-zhong, WANG Kuan-ling, LI Ying-xia

J. Mol. Catal. (China) **2022**, 36(4): 313–320

The possible reaction paths of NH_3 -SCR over Mn/ZSM-5 catalysts were investigated. Since the energy barriers of the reaction paths following E-R mechanism and L-H mechanism are 185.05 kJ/mol and 190.27 kJ/mol , respectively, with little difference, it's considered that the two reaction paths can occur simultaneously at a certain temperature. That is, NO

can participate in the reaction with gaseous NO and adsorbed $[\text{NO}]$ to form an important intermediate $[\text{NH}_2\text{NO}]$.



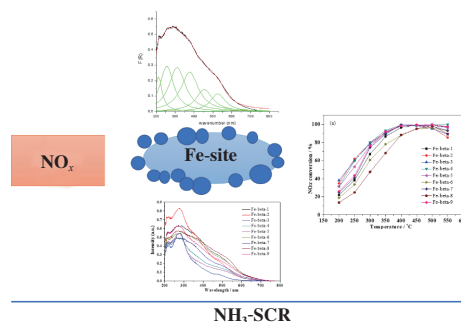
Effect of Iron Sites and Synthesis Procedure of Fe-beta Catalysts on NH_3 -SCR Performance

YU Fei, MA Jiang-li, REN De-zhi, LAI Hui-long, YIN Xue-mei, ZHAO Yun-kun, CHANG Shi-ying

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A series of Fe-Beta molecular sieves were prepared by ion exchange method under different synthesis conditions. UV-vis study reveals that three types of iron species, isolated Fe^{3+} , oligomeric Fe_xO_y clusters, and large-scale Fe_2O_3 clusters, coexist on the Fe-beta. Based on the investigation of effects on the NH_3 -SCR activity, the isolated Fe^{3+} and oligomeric Fe^{3+} species were the main active site. The large-scale Fe_2O_3 clusters mainly

contributed to ammonia oxidation and cause the performance deterioration. The synthesis conditions such as pH, temperature, precursor type, Si/Al, and the calcination condition would affect the active sites composition and distribution. Regulating the synthesis conditions can effectively control the distribution of active species based on different catalyst activity requirement.



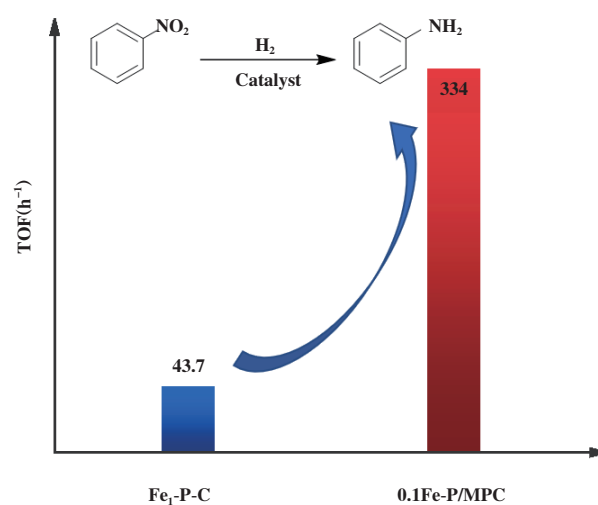
Mesoporous Carbon Supported Highly Dispersed Fe-P Catalyst for Nitrobenzene Hydrogenation

NIE Chao, LIU Qi, GAO Guang, ZHAO Ze-lun, LI Fu-wei

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In this work, a series of mesoporous carbon (MPC)-anchored Fe-P catalysts were prepared by the impregnation-pyrolysis method and the Fe-P catalysts with different structures could be obtained through regulating different ratios of Fe^{3+} /phytic acid precursors. Combining with the X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), N_2 physical adsorption analyses, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) characterization, it was found that the highly dispersed Fe-P catalyst (0.1Fe-P/MPC) has the best catalytic activity ($\text{TOF} = 334 \text{ h}^{-1}$) for nitrobenzene hydrogenation to aniline, which is about 7 times higher than that of the single-atom Fe1-P-C catalyst ($\text{TOF} = 43.7 \text{ h}^{-1}$) under the same reaction conditions. Furthermore, the catalyst cycle stability experiments confirmed that the 0.1Fe-P/MPC catalyst has good stability, and there is no obvious decrease in activity after 5 cycles of use. In contrast, the nitrobenzene hydrogenation activity of the 0.2Fe-P/

MPC catalyst decreased significantly (conversion = 23%), which may be caused by metal agglomeration (STEM characterization shows obvious metal agglomerate particles). For the 0.5Fe-P/MPC catalyst (XRD characterization shows Fe_2P metal phosphide), there is almost no hydrogenation activity, suggesting that the Fe_2P is not the active site. This work provides a promising example for the development of low-cost and high-performance nitrobenzene hydrogenation catalysts.



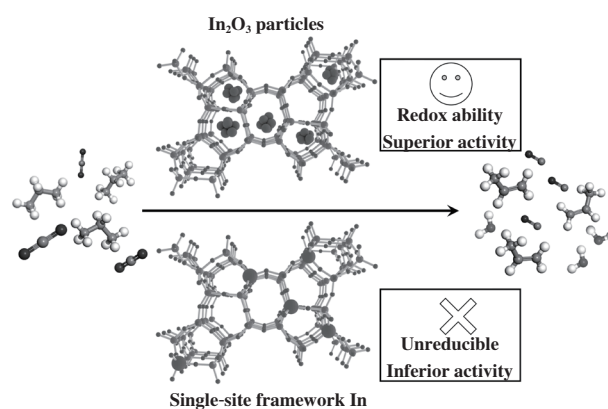
Structural-Activity Relationship of Indium-Based Catalysts for CO_2 Oxidative Propane Dehydrogenation

SONG Shao-jia, ZHANG Xuan, CHEN Yi-shuang, LONG Bai-ting, SONG Wei-yu

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CO_2 assisted propane dehydrogenation ($\text{CO}_2\text{-PDH}$) is promising to improve the per pass conversion of propane and the resource utilization of CO_2 . It is of industrial and scientific interest to explore efficient and non-toxic $\text{CO}_2\text{-PDH}$ catalysts. This work investigated the structure-activity relationship of indium-based catalysts in $\text{CO}_2\text{-PDH}$ reactions. A series of indium-based catalysts with different synthesis methods and supports were prepared. The indium site structure was investigated by X-ray diffraction, Raman, H_2 temperature programmed reduction and scanning electron microscopy measurements. By correlating with the activity data, one could conclude that the impregnated In/S1 catalysts contain In_2O_3 nanoparticles with InO_6 structural moiety, which could undergo the $\text{In}^{\delta+}/\text{In}^0$ redox cycle during the $\text{CO}_2\text{-PDH}$ process. The activity results under different reaction atmosphere also verify such conclusion. In comparison, the

hydrothermal synthesized In-S1 sample does not contain this InO_6 structure, as it does not show any reduction signals in H_2 -TPR measurements. Such redox cycle derived by InO_6 moiety plays an important role in $\text{CO}_2\text{-PDH}$ process. Besides, the CO_2 -TPD measurements also reveal that the smaller ten membered silicalite-1 zeolite is more favorable for CO_2 adsorption/activation than the twelve membered BEA topological Si-Beta zeolite. As a result, the 5In/S1 catalyst shows superior activity than 5In/Si-Beta counterpart although the latter case also contains InO_6 moiety.



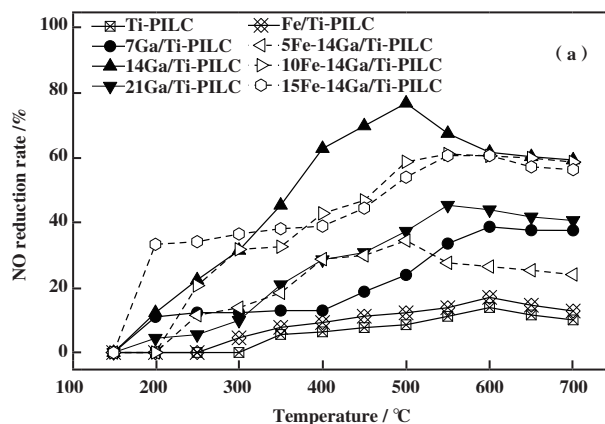
Study on CH₄-SCR Performance by Ga-Fe Catalysts Supported on Ti-pillared Interlayered Clays (Ti-PILC)

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The supported Ti-PILC prepared with TiCl₄ as Ti source not only has large specific surface area, but also can make the catalyst have good structural stability. Loading active metal Ga on Ti-PILC can significantly improve the denitration efficiency of the catalyst in the CH₄-SCR reaction system, and achieve the highest NO removal efficiency of the current PILC series catalyst-reaching 77% at 500 °C. Although the denitration activity of active metal Fe loaded on Ti-PILC is not as high as that of Ga/Ti-PILC, the introduction of Fe into 14Ga/Ti-PILC can improve the water resistance and sulfur resistance of the catalyst and achieve the best 61% NO removal rate. Through relevant characterization analysis, it is found that this may be because the introduction

of an appropriate amount of Fe which increases the pore size of the catalyst, while the large pore size reduces the retention time of water vapor and SO₂ on its surface when passing through the catalyst, furthermore, the competitive adsorption capacity of water vapor and SO₂ is weakened, so as to reduce the impact of water vapor and SO₂ on the Ga active center on the catalyst surface, and improve the resistance of the catalyst to the impact of water vapor and SO₂.



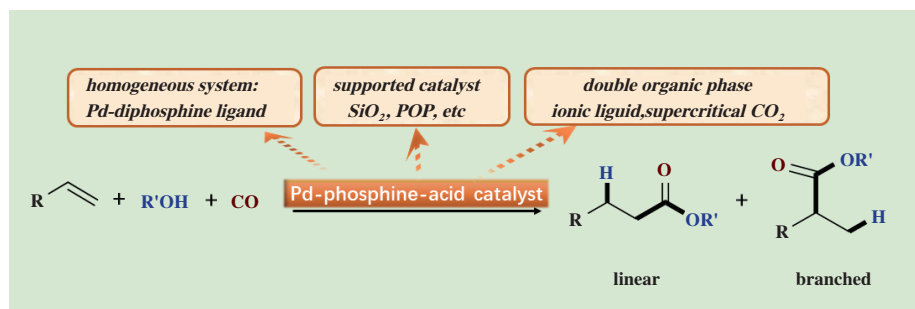
Research Progress of Alkene Hydroesterification Catalyzed by Palladium–phosphine–acid System

LU Yan–mei, LAN Yong–cheng, YUN Dong, XIA Chun–gu, LIU Jian–hua

J. Mol. Catal. (China) **2022**, 36(4): 360–373

Alkene hydroesterification is an important branch of carbonyl synthesis, which has attracted much attention for a long time. Palladium–phosphine–acid catalytic system has been

widely and deeply studied in alkene hydroesterification because of its mild reaction conditions, good substrate universality and excellent catalytic performance. Therefore, the research and application of homogeneous and heterogeneous palladium–phosphine–acid catalytic system in alkene hydroesterification are briefly reviewed, and the catalytic mechanism, catalyst composition and performance are discussed. Finally, it is pointed out that the heterogeneous palladium–phosphine–acid catalytic system with high stability and good recover ability will be the research focus in this field.



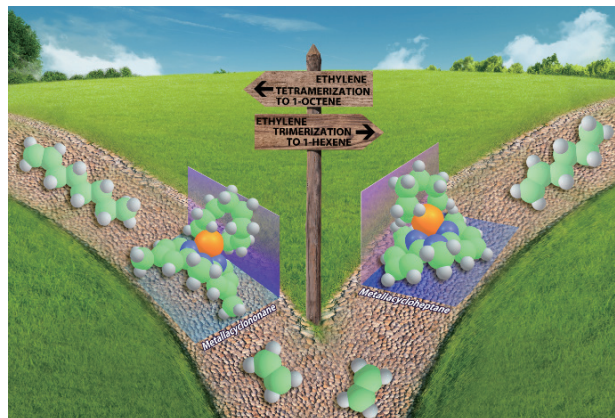
Selective Ethylene Tri-/tetramerization Catalyzed by Chromium-Based Catalysts and Oligomerization Mechanism

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1-Hexene and 1-octene are two kinds of important linear α -olefins (LAOs), which are mainly used as co-monomers to enhance the performance of industrial polyethylenes. Both academia and industry have long been devoting to develop effective catalysts for the selective oligomerization of ethylene into 1-hexene and 1-octene. Chromium catalysts are believed to be advantageous compared to other catalysts. In this review, the chromium-based catalysts with excellent catalytic performance for ethylene tri-/tetramerization are summarized, including the Phillips catalyst system for ethylene trimerization, the well-

studied Cr/PNP catalysts for ethylene tri-/tetramerization, and other catalysts bearing N-, P-, Si-based ligands. The catalyst innovation can be accelerated through mechanistic understanding, including the linear Cossee-Arlman mechanism, the mononuclear metallocycle mechanism, the binuclear metallocycle mechanism, the double-coordination mechanism, and other mechanisms.



Research Progress of Solid Catalysts for Catalytic Conversion of Glycerol to Lactic Acid

TANG Cheng, LI Shuang-ming, YU San-san

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With the implementation of China's dual carbon action plan under the new global climate agreement, the development and utilisation of renewable biomass resources has become extremely important. As the main by-product of biodiesel production, glycerol is catalytically converted into various high value-added derivatives, which has attracted extensive attention. Among them, the selective oxidation of glycerol to lactic acid has great application prospects. In recent years, lactic acid production has evolved from traditional fermentation to the greener and more economical catalytic conversion of solid catalysts. In the

catalytic process, the selectivity of lactic acid depends largely on the catalytic reaction conditions and the properties of the catalyst. There are two approaches to current solid catalytic processes: (1) dehydrogenation to lactic acid in alkaline media (using dehydrogenation catalysts: based on Cu and Pt, etc.) or oxidation to lactic acid (using oxidation catalysts: based on Au or Ag, etc.); (2) oxidation to lactic acid in non-alkaline media (using oxidation catalysts with acidic properties: Au and Pt loaded on solid acids, heteropolyacids, etc.). In this paper, from the perspective of reaction environment (alkaline medium or non-alkaline medium), the relevant literature on the conversion of glycerol to lactic acid catalyzed by solid catalysts in recent years is reviewed, the reaction mechanism of the conversion of glycerol to lactic acid is analyzed, and the factors affecting the catalyst activity are discussed, and put forward suggestions and prospects for existing problems and development prospects.

