

的宽缓向斜页岩气保存条件较好;(3)Ro以及新获得的低温热年代学测试数据研究结果表明四川盆地热历史可大致以260 Ma为界分为P2末期之前的热流升高阶段和之后的热流降低阶段及随后的低热流发展阶段,晚二叠世峨眉山地幔柱和中晚三叠世以来前陆盆地演化是四川盆地热演化主要影响因素。

关键词:下扬子地区 四川盆地 构造演化 构造变形样式 页岩气保存

Progress Report of Tectono-thermal Evolution and Alternation and Preservation of Shale Gas

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Abstract: For the first two years, our research focused on the Tectono-thermal evolution and shale gas formation geological background of typical basins in southern China. And we have started to investigate the influences of structural alternation on the shale reservoir and shale gas occurrence. 10 faculties and 12 graduate students worked in this project. More than 2000 papers of geological background have been collected. 653 samples from 128 observation sites were collected during the past 7 field works. And we have mapped 10 geological cross sections and accomplished more than 700 experimental tests. The major progresses so far include: 1)Based on the analysis of field observation,drilling data and geophysical data,we interpreted the structural deformation characteristics and basin evolution of Lower Yangtze region and its influence on the distribution and preservation potential of the key shale layers. We suggest that the detachment-fold belt of Jiangyin-Wuxi is relative structural stable belt in the Lower Yangtze region; 2)Based on the field observation, sample collection and SEM analysis, and DEM modeling of compressional structural deformation, we investigated the influence of structural alternation on the reservoir properties of the Lower Yangtze shale, and concluded that strong compression and shear deformation do great damage to the pore structure of the shale, but the damage resulted from faulting is limited to the zone close to the fault, the broad synclines within the fold-and-thrust belts still have good shale gas preservation potential, 3)Based on Ro and low temperature thermochronology data, we divided the thermal history of Sichuan basin into two stages, the heat flux increasing and decreasing stages before and after later permian respectively. Emeishan mantle plume in the later permian and the tectono-thermal evolution of foreland basin since mid-later triassic are the controlling factors for the thermal evolution of the Sichuan basin.

Key Words: Lower Yangtze region,Sichuan basin,Tectonic revolution,Structural deformation styles,Shale gas preservation

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糖类衍生物催化制液体烷烃燃料的基础研究

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摘要: 该研究针对第三个关键科学问题“解聚产物催化转化制备先进液体燃料的机理及产物选择性控制规律”开展基础性研究工作。在糖类衍生物水相催化制液体烷烃燃料的反应机理、产物控制规律研究和相关高效催化体系设计等方面进行了探索。针对糖类衍生物水相催化合成HMF,发展了高效的类微乳反应体系和NaHSO₄-ZnSO₄催化体系,可有效避免副产物生成和HMF的进一步降解,获得高达57%的HMF收率。发展MOFs内嵌杂多酸和Ru粒子的高效催化剂,通过金属与酸的功能匹配,实现了纤维素等一步转化为山梨醇,山梨醇收率达到58%。制备了Ni基金属-酸双功能催化剂应用于山梨醇/木糖醇转化为C5/C6烷烃,通过金属组分、载体等的调控作用和反应机理研究,实现C5/C6烷烃产物的定向催化合成,收率超过90%。针对糠醛与丙酮的缩合反应,设计合成了高效MgO/NaY固体碱催化剂,碱性质及MgO与NaY的协同催化作用可有效活化糠醛与丙酮分子,加快反应速率,获得高达98%的C8-C15缩合产物,设计合成了Pt/SiO₂-ZrO₂催化剂,通过调控催化剂的组成结构和产物加氢脱氧路径分析,获得收率达到70%的C8-C15烷烃产物,催化剂连续运行120 h不失活,具有较好的稳定性。针对酚类衍生物催化制液体烷烃燃料,设计合成了离子液共聚物负载的Ru催化剂,通过离子液共聚物稳定Ru纳米粒子的金属-酸双功能的协同催化作用(金属中心的C-C键加氢饱和,酸中心的C-O断裂),实现了苯酚及其衍生物加氢脱氧高效转化为液体烷烃。针对苯酚选择性加氢制环己酮,设计合成了高效的聚苯胺修饰碳纳米管负载Pd催化剂,通过聚苯胺修饰碳纳米管的电子调控对苯酚及其衍生物的选择性吸附和Pd活性组分的协同加氢作用,实现了苯酚及其衍生物定向转化为环己酮衍生物,环己酮收率高达99%。在上述研究基础上,我们率先在国内建立了年产150吨规模的生物汽油验证研究系统。

关键词:糖 水相催化 液体烷烃 基础研究

Basic Research on Liquid Alkanes From Sugar Derivatives by Aqueous Phase Catalysis

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Abstract: Aiming to the third key scientific issue "transformation route and mechanism for advanced liquid fuel production from decomposed products by aqueous phase catalysis" of the project, we used sugar derivatives as the feedstock to synthesize liquid C5/C6 and C8-C15 alkanes with the emphasis on the reaction mechanism and goal products controlling methods, and relative catalysts designation. For biomass derived HMF platform, we developed the highly efficient analogue micro-emulsion reaction system and NaHSO₄-ZnSO₄ combined catalyst, which obtained the HMF yield of 57%. For one-step conversion of cellulose to sorbitol, we fabricated highly active MOFs encapsulated heteropolyacid and Ru nanoparticle as the catalyst and the 58% of sorbitol yield could be observed by mediating the acid-metal balance in the catalyst. We synthesized the efficient Ni based bi-functional catalysts for sorbitol/xylitol conversion to C5/C6 alkanes. By choosing metal, support and their assembly together with the investigation on the hydrodeoxygenation (HDO) mechanism, more than 90% of C5/C6 alkanes yield could be obtained. For jet fuel with the carbon chain length of C8-C15 alkanes, we designed MgO/NaY for C-C bond coupling in furfural and acetone. The synergistic effect of MgO and NaY activated the α-H in acetone and carbonyl group in furfural, which accelerates the condensation rate and obtains the C8-C15 condensation products yield of more than 98%. To achieve production of C8-C15 alkanes, we used Pt/SiO₂-ZrO₂ for HDO of C8-C15 condensation products. Due to the weak acidity of the catalyst and high C-O bond cracking property of Pt, the catalyst possessed 70% of goal products yield and showed the excellent catalytic stability of more than 120 h. For phenol derivatives conversion to liquid alkane fuel, we fabricated Ru supported on ionic liquid contained copolymer as the catalyst. By using the cooperative effect between the Ru catalyzed C=C bond saturation and acid catalyzed C-O bond cracking. For selective hydrogenation of phenol to cyclopentanone, we synthesized Pd supported carbon nanotube modified with polyaniline. Due to the selective adsorption phenol on polyaniline and hydrogenation on Pd, more than 99% of cyclopentanone could be obtained. Based on the mentioned investigation, we built up a pilot scaled facility of 150t/a for bio-gasoline production for the first time in China, which demonstrated a platform for practical production of bio-fuel on a large scale.

Key Words: Sugar; Aqueous phase catalysis; Liquid alkane; Basic research

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热气化生物质制氢催化剂及热力学分析研究

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摘要: 在反应过程中加入催化剂可在更温和的水热条件下实现生物质高效气化制氢。在众多催化剂中, Ni系催化剂因其廉价并在反应中表现出较高的活性等优点而被认为是很有发展前景的制氢催化剂。该课题组针对Ni/Al₂O₃酸性位易于积碳引起催化剂失活的弱点, 通过金属助剂的辅助作用对Al₂O₃为载体的负载Ni催化剂进行改性。选用Cu、Co、Sn、Ce和碱性Mg, 通过共浸渍、分步浸渍和共沉淀等方法制备双金属Ni-M或者复合氧化物载体催化剂。结果表明, 金属助剂Ce的引入有效提高了Ni系催化剂的催化产氢活性, 催化剂的抗积碳性能亦得到有效改进, 表明金属Ce是非常合适的金属助剂。MgAl₂O₄使催化剂水热稳定性得到改善, 碱性Mg助剂可以有效抑制Ni-Al催化剂的表面结晶碳的形成。较低的热处理温度, 或者分步浸渍制备Ni-Mg-Al催化剂能获取更多有效的活性位。碱性Mg助剂可以改善Ni-Al催化剂的催化活性及水热稳定性。对于溶胶-凝胶法制备的Rutile TiO₂负载Ni催化剂, 降低催化剂热处理温度可以获取分散性更高的Ni晶粒, 从而提供较多的活性位, 以促进生物质在水热条件下C-C键的断裂, 水汽转化反应和甲烷化反应, 从而提高生物质转化率。通过利用Aspen Plus软件根据Gibbs自由能最小化原理采用PR状态方程, 以MHV2混合规则建立热力学模型来模拟水热条件下气化生物质及其模型化合物产氢的过程, 对水热气化生物质及模型化合物进行了理论分析, 计算出在一定温度和压力条件下达到平衡时系统的产气量, 提供了催化气化生物质的方向和限度的数据。

关键词: 制氢 水热气化 生物质 催化剂 热力学模型

Hydrogen Production by Hydrothermal Gasification of Biomass: Catalysts and Thermodynamic Analysis

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Abstract: Highly efficient hydrogen production from biomass can be realized by using catalysts in the reaction process under more mild hydrothermal conditions. Among various catalysts, Ni based catalysts are considered as the most promising catalyst for hydrogen production due to its low cost and good catalytic activity. In order to solve the problem of catalyst deactivation caused by carbon deposition at the acid site of Ni/Al₂O₃, the additives were studied to modify the Ni based catalysts loaded on Al₂O₃ in our research group. Cu, Co, Ce and Mg were chosen as additive and bimetal Ni-M or complex oxide catalysts were prepared by co-impregnation, impregnation by step, and co-precipitation, etc. The results show that the introduction of metal Ce can effectively improve the catalytic activity of hydrogen