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学位論文の要約

Doctoral Thesis Summary

博士の専攻分野の名称 博士 (理学) 氏名 江川霞

Degree requested Doctor of Science Name: Chuanxia Jiang

学位論文題名

Oxidation and Hydrogenation Reactions over Supported Platinum Catalysts.

(担持白金触媒による酸化および水素化反応)

Plant fresh keeping and polystyrene industrialization are very important in today's society. Ethylene, as a plant hormone, released from plant hinders plant fresh keeping because it accelerates plant spoiling and decay. Similarly, the formation of the phenylacetylene as a poisoning impurity in styrene feedstocks causes deactivation of the styrene polymerization catalyst and degrades polystyrene properties in industrial production. The removal of ethylene and phenylacetylene is not so easy. Low-temperature catalytic oxidation or hydrogenation is a good way for solving these problems. The aims of this thesis include two parts: one is the development of active catalysts for the elimination of ethylene at low temperature as well as their reaction mechanism; the other is the study of selective hydrogenation of phenylacetylene into styrene by using novel Pt/ZTC catalyst. This thesis is divided into six parts. The main core of this text is composed of the Chapters II, III, IV and V.

Chapter II consists of the screening of transition metal and supports effects for the oxidation of ethylene. All of catalysts were prepared by a simple wet impregnation method and characterized by XRD, N₂ adsorption, TEM and CO chemisorptions. A series of catalysts with various transition metal nanoparticles were supported on MCM-41. Figure 1 shows the light-off curves of ethylene conversion over different metals on MCM-41. Complete oxidation of ethylene was observed on Pt/MCM-41 over a wide range of reaction temperatures (25-200°C). However, ethylene conversion was less than 40% for Pd/MCM-41 and Au/MCM-41 at 25-50°C. An increase in reaction temperature afforded >99.8% conversion over 145°C for Pd/MCM-41 and 96% conversion at 200°C for Au/MCM-41. At any given temperature, Ag/MCM-41 catalyst provided only 40% ethylene conversion. From these results, it can be concluded that Pt is the most effective metal for ethylene oxidation under these conditions. Pt was chosen for further study because of its high performance. The effect of the support was also investigated using Pt catalysts supported on MCM-41, SiO₂, Al₂O₃, ZrO₂, TiO₂ and CeO₂ (Figure 2). The catalytic activities were ranked as follows: Pt/MCM-41 > Pt/SiO₂ > Pt/Al₂O₃ > Pt/TiO₂, Pt/ZrO₂ > Pt/CeO₂. The difference in catalytic activity between Pt/MCM-41 and Pt/SiO₂ might be attributed to the difference in particle size and surface area of Pt. In this regard, it is interesting that extremely low ethylene elimination efficiency was obtained with Pt catalysts supported on Al₂O₃, ZrO₂, TiO₂ and CeO₂, where particle sizes are smaller than active Pt/MCM-41 and Pt/SiO₂ catalysts. Finally, the most effective catalyst was applied in more practical conditions with trace ethylene (50 ppm) at lower temperature (0°C). As

shown in Table 1, the ethylene conversion reached 97% by using 2 wt% Pt/MCM-41, which was higher than the reported data under almost the same reaction conditions.[1, 2] It was shown in Figure 3 that the conversion of ethylene over 1% Pt/MCM-41 at 0°C was >99.8%, which is higher than that of previous reported results and the perfect conversion of ethylene was maintained for more than 1 h. The gradual deactivation observed in Figure 3 may be attributed to adsorption of water on the catalyst surface, but high catalytic activity was recovered by heating the catalyst at 200°C under a He flow for 1 h.

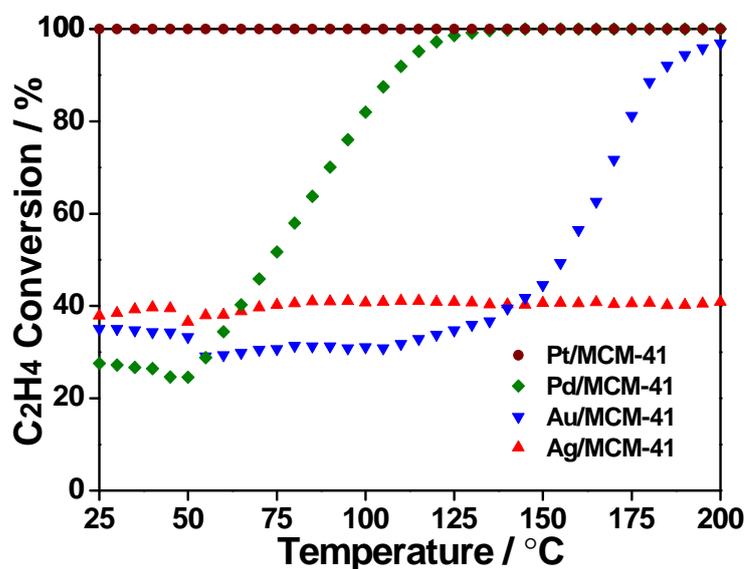


Figure 1. Light-off curves of catalytic ethylene conversion over different metals supported on MCM-41. Metal loading: 5 wt%; space velocity (SV): 1500 mL h⁻¹ g⁻¹; catalyst: 0.2 g; C₂H₄: 0.32 vol%; O₂: 20 vol%; N₂: 5 vol%; He balance.

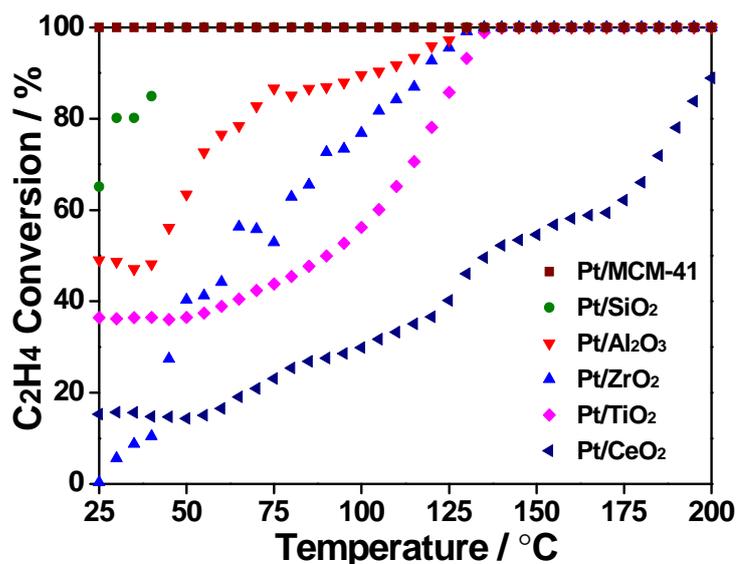


Figure 2. Light-off curves of catalytic ethylene conversion over Pt nanoparticles on different supports. Pt loading: 5 wt%; space velocity (SV): 1500 mL h⁻¹ g⁻¹; catalyst: 0.2 g; C₂H₄: 0.32 vol%; O₂: 20 vol%; N₂: 5 vol%; He balance.

Table 1. Comparison of catalytic performance.

Catalyst	Metal loading (wt%)	Conversion (%)	T (°C)	Ethylene (ppm)	SV (mL h ⁻¹ g ⁻¹)	Ref.
Au/Co ₃ O ₄	2.5	76	0	50	14400	[1]
Au/Co ₃ O ₄	1.95	93.7	0	50	9000	[2]
Pt/MCM-41	1.95	96.8	0	50	9000	This study

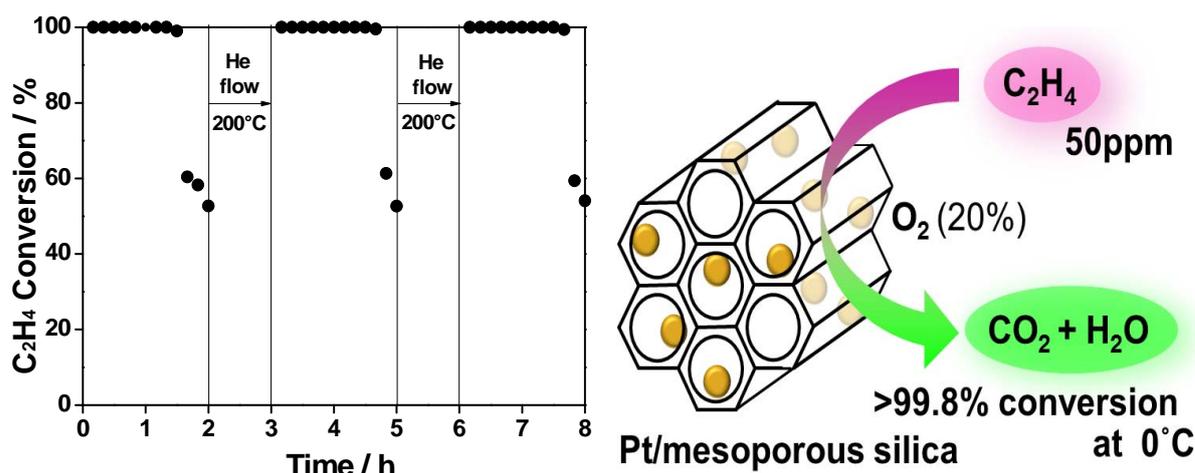
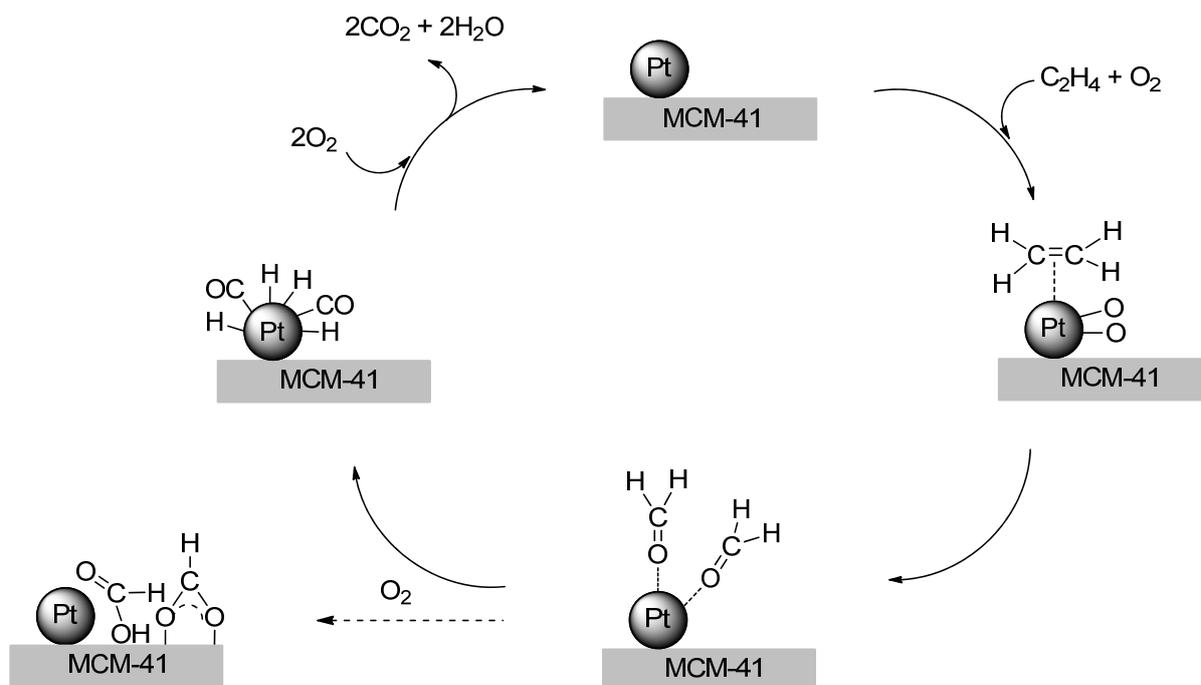


Figure 3. Complete oxidation of trace ethylene at 0°C by Pt nanoparticles supported on mesoporous silica. Pt loading: 1 wt%; SV: 1500 mL h⁻¹ g⁻¹; catalyst: 0.40 g; C₂H₄: 50 ppm; O₂: 20 vol%; N₂: 5 vol%; He balance.

Chapter III describes the mechanistic study of the supports effects on the catalytic oxidation of ethylene by in-situ DRIFTS. Various metal oxide supports were used for a detailed study (MCM-41, SiO₂, γ -Al₂O₃, ZrO₂, TiO₂ and CeO₂). The activity order for oxidation reaction was found to be Pt/MCM-41 \approx Pt/SiO₂ > Pt/ γ -Al₂O₃ \approx Pt/ZrO₂ \approx Pt/TiO₂ > Pt/CeO₂. The physicochemical properties of Pt catalysts were determined by XRD, N₂ adsorption, TEM and CO chemisorptions. It was found that interaction between Pt and supports was the key factor for catalytic activity. Reaction pathways were proposed by performing in situ DRIFTS experiment. Similar reaction pathways were found on both Pt/MCM-41 and Pt/SiO₂ where C₂H₄ and O₂ quickly react over Pt surface form HCHO. This was followed by decomposition of HCHO into CO and H species, which react with O species to give CO₂ and H₂O, respectively. In this process a small amount of formic acid and formate species were generated from HCHO on Pt as a by-product and spilled over onto MCM-41. Proposed mechanism for ethylene oxidation on Pt/MCM-41 was shown in Scheme 1. C₂H₄ and O₂ adsorbed on Pt/ γ -Al₂O₃, Pt/ZrO₂ or Pt/TiO₂, quickly reacted to form acetaldehyde, which further oxidized into surface acetate and CO species. These CO species oxidized partially into CO₂ over Pt/ γ -Al₂O₃. However, it oxidized into formate species on Pt/ZrO₂ and Pt/TiO₂. In case of Pt/CeO₂ the CO species were formed when C₂H₄ and O₂ adsorbed on Pt/CeO₂, which was further oxidized into carbonate species adsorbed on CeO₂.



Scheme 1. Proposed mechanism for ethylene oxidation on Pt/MCM-41.

Chapter IV investigates the pore structure and surface silanol group of silica and metal doping in SBA-15 effect on the catalytic activity of ethylene oxidation. It is interesting to note that in spite of large differences in pore structure and surface silanol groups among all samples, similar ethylene oxidation performance was obtained. However, the doping of heteroatoms in SBA-15 substantially decreases catalytic activity towards ethylene oxidation. DRIFTS investigation showed that the doping of heteroatoms caused strong adsorption of CO and acetate species on the catalyst surface. The adsorbed species needed relatively higher temperature for its complete removal.

Chapter V is dedicated to the application of novel ZTC supported Pt catalyst on selective hydrogenation of phenylacetylene to styrene. The influence of precursors and supports on the catalytic activity was studied. The Pt catalyst on ZTC prepared from a cationic Pt precursor gave highly dispersed Pt nanoparticles and exhibited the highest conversion in the hydrogenation of phenylacetylene. The striking difference in conversion among the tested catalysts can be attributed to the difference in Pt particle size. The catalysts with smaller Pt nanoparticles gave the higher conversions due to the higher Pt surface area available for the reaction.

Finally, Chapter VI provides and summarizes some general conclusions.

References

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