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Titre de la thèse : « Oxydation catalytique des composés organiques volatils à l'aide de catalyseurs de type oxyde »

Résumé de la thèse : In this research works, composite oxides, noble metal supported oxides and noble supported MCFs were prepared, and their catalytic performances were investigated for the catalytic oxidation of vinyl chloride (VC). The catalytic activity, catalyst stability, by-products and so on were investigated. The Co-Ce composite oxide catalysts were prepared by citrate sol-gel methods, and tested for the activity of VC oxidation. The high calcination temperature will decrease the catalytic activity, while citric acid has no effect on activity. The catalyst with high performance is the molar ratio of Co/Ce=7:3. The XRD and Raman analyses revealed Ce introduction into Co oxides modifies the textural properties in dispersing cobalt oxide crystallites, making their size smaller and increasing the surface area of the catalyst. The H_2-TPR and O_2-TPD analyses showed these Co-Ce composite oxide catalysts presented higher reducibility properties and surface/lattice oxygen mobility. The XPS analyse certified that the Ce introduction favored the presence of Co^{2+} and Ce^{3+} species, which changed the coordination environment of the oxygen lattice and generated more oxygen vacancies. At last, this catalyst exhibited a good performance and stability during 110 h of time on stream at 300 °C.Ru-modified cobalt oxides were prepared by 1) impregnating ruthenium chloride hydrate on cobalt oxides, Ru-supported catalysts (Ru/Co_3O_4) and 2) Ru-doped catalysts ($Ru\text{-}Co_3O_4$), where the Ru ions were added to precursor solution, by one-step sol-gel method with cobalt nitrate. The effects of Ru have been studied for the VC oxidation. The EDX-mapping in TEM showed that the dispersion of Ru oxides on the cobalt oxides surface was different between the doped and supported. The H_2-TPR showed Ru supported improve the reduction ability than doped ones. The XPS analyse certified that the Ru^{4+} will be in synergy with Co^{2+} concentration and this would also change the chemical coordination of oxygen on the surface. High relative proportion of Co^{2+} and Ru^{4+} will also devote to oxygen defects or vacancies. This would increased the catalytic activity and decrease the amount of chlorinated by-products. A novel heterostructured material, cobalt phosphate-SiO_2 mesostructured cellular foams (CoPO-MCFs), was successfully synthesized by the in-situ growth method. A ruthenium precursor can be readily introduced and highly dispersed on CoPO nanophases of CoPO-MCFs through an impregnation method. The resulting Ru/CoPO-MCFs catalyst was used for catalytic oxidation of VC or CO. The XRD and N_2 sorption analyses revealed that the heterostructured CoPO-MCFs mesoporous materials were successfully prepared by a general in-situ growth synthesis. NH_3-TPD analyse showed this unique heterostructural structures of CoPO-MCFs improved the acidity of MCFs. The H_2-TPR analyse showed that the enhanced reduction capability for 1%Ru/CoPO-MCFs catalyst could be induced by strong interaction between Ru oxides and CoPO nanophases. The XPS confirmed that a higher amount of surface oxygen species. The activation energy calculated from Arrhenius plots showed a lower value for VC oxidation. The influence of Co_3O_4 morphology, including cube and sphere, on catalytic activity of methylbenzene and vinyl chloride was studied. The Co_3O_4 cube had shown better activity and stability than that of the Co_3O_4 sphere. The cube structure, with Co^{2+} exposed on the surface, acted as the active site of the oxidation.

Keywords: Co_3O_4; CeO_2; Ruthenium; heterostructural MCFs; vinyl chloride