Hydrotreating catalysts supported on polymer coated silica

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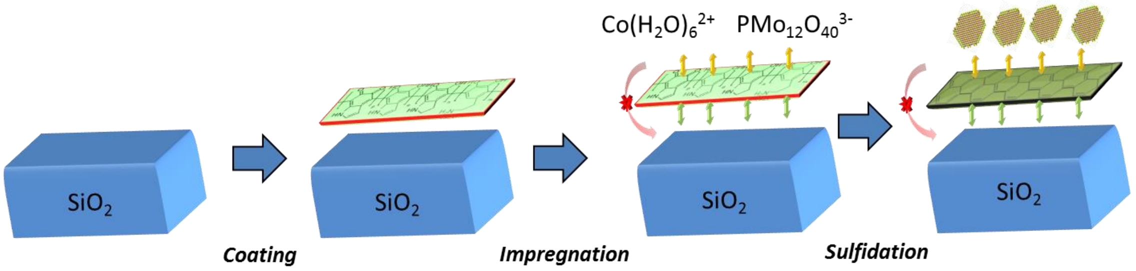
Abstract: During this presentation, the successful implementation of polymer-coating strategies to develop highly active CoMoS hydrotreating catalysts supported on silica will be reported. In this regard, the example of polydopamine as coating will be highlighted. The catalysts prepared on (poly)dopamine coated silica showed enhanced activity for the hydrogenation of toluene reaction. Polydopamine coating lowers the MoS_2 nanocrystallites' stacking on silica, thereby improving the accessibility of active edge sites. The origin of this increase in catalytic activity may be found in the higher capacity of polydopamine functional groups to disperse the active phase.

Keywords: Hydrotreatment, Catalyst preparation, Sulfides.

1. Introduction

Environmental regulations are continuously strengthened to limit the emission of pollutants from fossil fuels combustion.[1] These constraints drive the need to develop highly active and efficient hydrotreating catalysts. Industrial hydrotreating catalysts contain Mo (and/or W) as the active metal usually promoted by Co (and/or Ni) and supported on Al_2O_3, SiO_2 or TiO_2.[2] Support effects constitute an important field of investigation in hydrotreating catalysis. Indeed, metal-support interactions are known to influence various characteristics of the active phase such as its morphology, slabs orientation, or electronic properties.[2] However, silica-supported catalysts generally show lower activity than alumina counterparts due to the relatively inert surface making it difficult to form the highly dispersed and promoted sulfide phase, especially at high loadings. In order to circumvent such limitations, coating the surface of silica with a polymer that contains different functional groups able to interact with metallic precursors is one of the suitable option to improve surface reactivity and dispersion.[3,4] This presentation thus aims at demonstrate the successful implementation of polymer-coating strategies to develop highly active CoMoS hydrotreating catalysts supported on silica. In this regard, the example of polydopamine as coating will be highlighted.

Figure 1. Methodology for polymer-coating of silica in order to tune the metal-support interactions.



2. Experimental

The desired amount of dopamine-hydrochloride was dissolved in water and impregnated by incipient wetness impregnation onto SiO_2(1.6 mm diameter cylindrical extrudates, $V_p = 1.10$ cm^{3}g^{-1}, $S_{BET} = 233$ m^{2}g^{-1}, $d_p = 12.9$ nm). Impregnation was followed by a maturation step in a water saturated atmosphere, for overnight at room temperature. Then, a drying step was performed for 20 h at 90°C which yielded Pdop coated silica (Pdop/SiO_2). Series of CoMo/Pdop/SiO_2 and CoMo/SiO_2 catalysts with 10 or 20 wt% loading of MoO_3 were prepared by incipient wetness impregnation method and labelled as 10(20)%CoMo/Pdop/SiO_2 and 10(20)%CoMo/SiO_2. Phosphomolybdic acid ($H_3PMo_{12}O_{40}.30H_2O$) and

$Co(NO_3)_2.6H_2O$ were used as precursors dissolved in ethanol. Following a maturation step, the catalysts were dried in a rotary evaporator under reduced pressure.

For catalytic tests, the sulfidation of the catalysts was performed using a feed composed of DMDS (4 wt%) in n-heptane (96 wt%). The catalysts were then evaluated in toluene hydrogenation.

3. Results and discussion

The polymer-coated supports were first characterized by UV and FTIR spectroscopies. Solid-state UV analysis of the Pdop/SiO_2 support showed an absorbance band at about 280 nm corresponding to catechol groups of dopamine. In addition, an increase in absorbance in the region of 400-800 nm which is characteristic for the polymerization of dopamine, arising from different functional groups in Pdop was also observed. In addition with thermogravimetric measurements, we thus could confirm that dopamine was partially polymerized on the silica surface. FTIR measurements indicated a low interaction between catechol functional groups of polydopamine and silanol groups of SiO_2. When Mo precursors were added to Pdop coated SiO_2, the catechol groups present in Pdop could thus form a complex with the Mo ions.[5]

The sulfidation of Mo and Co supported on SiO_2 and Pdop/SiO_2 (20 wt% of targeted MoO_3 loading) was analyzed *in-situ* by XRD, to follow the formation of MoS_2 and Co_9S_8 crystalline phases with the increase in temperature. The formation of a crystalline MoS_2 phase begins gradually on both supports above 200°C. The increase in the intensity of the XRD reflections with temperature follows a similar trend for both supports, showing that the Pdop coating did not modify significantly the formation and growth of sulfide crystals, despite the complexation of Mo ions with catechol groups in Pdop.

The different sulfide CoMoS catalysts supported on Pdop/SiO_2 were further characterized by TEM and XPS. At both low and high Mo loadings, the stacking of the MoS_2 slabs on Pdop/SiO_2 -as observed by TEM- was significantly lower than on the corresponding bare SiO_2. Thanks to the presence of Pdop functional groups, MoS_2 slabs were also more regularly distributed on the surface of silica support converting a poor dispersing oxide surface into a highly dispersing one. These features indicated an improved dispersion of the active phase and presumably a better accessibility of the active edge sites. Results from XPS did not show any observable difference in the degree of sulfidation of Mo ions for all the catalysts (both at low and high Mo loadings). At low Mo loading, the degree of promotion was enhanced on Pdop/SiO_2 leading to an increase in CoMoS (+ 57%) sites compared to pure SiO_2. However, these features were not observed on Pdop/SiO_2 with high Mo loading. Therefore, it is not expected to be the primary reason for the increase in catalytic activity.

At both low and high Mo loadings, the conversion of toluene using the Pdop/SiO_2 support increases by 30-40% when compared with the catalysts supported on pure SiO_2. Consequently, the corresponding first order rate constants normalized per mole of Mo loaded in the reactor (k') increased by a factor of about 1.5 to nearly 2 showing a large increase of the intrinsic activity. At high Mo loading, k' decreases on both Pdop/SiO_2 and pure SiO_2, indicating that the active catalytic sites does not increase proportionally with the Mo content.

4. Conclusions

In conclusion, we have reported a facile method to coat SiO_2 with Pdop. The nature of the interaction between the support and the Pdop functional groups plays a key role in the dispersion of the MoS_2 crystallites. On Pdop/SiO_2, as there is no strong interaction between the support and Pdop, functional groups on Pdop helps in dispersing metal precursors. The improved catalytic activity could be attributed to the decreased aggregation of MoS_2 nanocrystallites leading to increase in edge site accessibility.

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