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Sulfated zirconia as support for gold based catalysts for LT-WGSR

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Introduction

The development of a new generation of catalysts with high activity towards the conversion of CO at low temperatures, easy to activate and with good stability to air and liquid water, is highly desirable, since commercially available LT-WGS samples do not meet these requirements [1]. Gold nanoparticles supported over metal oxides as catalytic systems for the LT-WGSR have been the subject of numerous studies and recently also Au/ZrO₂ samples have been successfully investigated [2].

The goal of the present work is to examine the effects of the addition of various amounts of sulfates to a zirconia support and their possible role during the Au deposition-precipitation step. In fact, while it is known that sulfates addition alters chemical and surface features of the zirconia support, it would be very interesting to prove an active role of SO₄⁻ in the delicate phase of gold deposition on the support, and subsequently on Au dispersion and catalytic activity. Other aspects, such as the stability of the new samples, the effects of gold content and of calcination treatment will be discussed too.

Experimental

Zr(OH)₄ was sulfated by incipient wetness impregnation with 1, 2, 4, 8 wt % amount of sulfates respectively, and then various gold amounts (1 or 3 wt%) were added by deposition-precipitation (dp) on the calcined supports [2]. Some catalysts were synthesized after sulfates remotion from the zirconia. Fresh and used samples were characterized by N₂ adsorption analysis, sulfates and gold content analysis, thermogravimetric analysis, TPR and TPO, XRD, HRTEM, FTIR spectroscopy and pulse-flow CO chemisorption [3].

WGSR has been studied, after a proper pretreatment, in the 423-453 K range, with a feed mixture containing 1.9 % vol. CO, 39.7 % vol. H₂, 9.5 % vol. CO₂, 11.4 % vol. N₂, 37.5 % vol. H₂O (space velocity 9400 h⁻¹).

Results and discussion

N₂ adsorption analyses revealed the positive role of sulfates, that alter the structural properties of the support enhancing its specific surface area and thus favouring a better dispersion of gold particles on the support and accordingly a better catalytic activity. However, the final catalysts do not contain sulfates anymore, due to the methodology of gold deposition-precipitation that is carried out at a basic pH [2]. So, SO₄⁻ do not behave as promoters of the gold active phase in the final samples. The synthesis of new gold catalysts after sulfates remotion from the support has evidenced that sulfates have an active role during



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the step of Au dp as well. In fact samples over sulfated zirconia present much higher dispersion and catalytic activity than samples with the identical surface area and gold amount over sulfates-free support. So sulfates addition to zirconia means a twofold advantage: i) higher gold dispersion due to higher surface area; ii) higher gold dispersion due to the positive role of SO_4^- groups than slowly act addressing the deposition of Au nanoparticles to suitable sites.

CO chemisorption measurements, XRD, FTIR data of adsorbed CO and HRTEM analyses have shown a very high dispersion of gold on all the fresh samples. On the contrary, after some months from the catalyst 's synthesis, gold dispersion dramatically decreases if the sample is not properly treated. We have checked various pretreatments, and verified that a thermal process in air at 453K allows to maintain after six months the same gold dispersion and catalytic activity of the fresh sample.

The stability of the new catalytic systems during the LT-WGSR has been investigated too, and these samples perform really very good. For example after 72 hours of time on stream at 453K, the 3wt% Au/ZrO₂ catalyst presents a stable conversion of about 90% and gold nanoparticles with a mean particle size of 1.5 nm, which is comparable to that of the as prepared catalyst.

Conclusions

The high activity showed by the gold on zirconia catalysts in the water-gas shift reaction was enhanced by the twofold action of sulfates on the support. In fact they lead to a better dispersion of metal on the support both increasing the surface area and acting during the deposition precipitation of gold nanoparticles.

References

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