Influence of CeO_2 addition sequence on the physicochemical properties of Fe_2O_3 /γ-Al_2O_3 catalysts

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Abstract:

A series of ceria modified Fe_2O_3/γ-Al_2O_3 samples were prepared via co-impregnation and step-wise impregnation method, respectively. The different impregnation sequence could influence the existence states and the interaction of the active species, which in turn affect the physicochemical properties of the catalysts. The co-impregnation method have the smallest CeO_2 particle size. And there were two different Fe^{3+} species: isolated Fe^{3+} located in sites of tetrahedral coordinated and clusters in a distorted octahedral environment in all samples. The number of cluster Fe^{3+} follows: Fe/Al > FeCe/Al-CI > FeCe/Al-SI, which means that the addition of CeO_2 could promote the dispersion of Fe^{3+} species.

Keywords: FeCe/Al catalysis, impregnation sequence, physicochemical properties.

1. Introduction

Fe_2O_3/γ-Al_2O_3 is a widely used catalyst in many industrial reactions. CeO_2 usually act as a promoter because it's Ce^{3+}/Ce^{4+} redox pairing and oxygen storage capacity. The synergy can be achieved between Ce and Fe via Ce^{3+}/Ce^{4+} and Fe^{2+}/Fe^{3+}. In this work, we studied the influence of CeO_2 impregnation sequence on the Fe^{3+} species existence states and physicochemical properties.

2. Experimental

The prepare method were reported in our previous work [1]. In this system, Co-impregnation and Step-wise impregnation methods prepared Fe_2O_3-CeO_2/γ-Al_2O_3 were short for FeCe/Al-CI and FeCe/Al-SI. FeCe/Al-CI-H and FeCe/Al-CI-H represent for the samples pretreated by HNO_3 solution, respectively.

3. Results and discussion

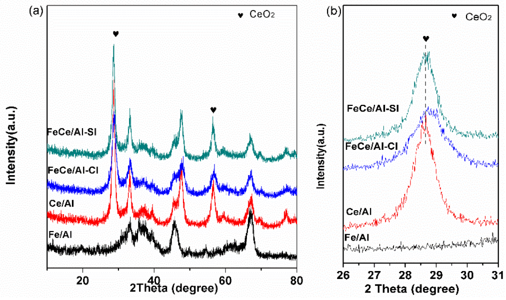


Figure 1. XRD results of the catalysts.

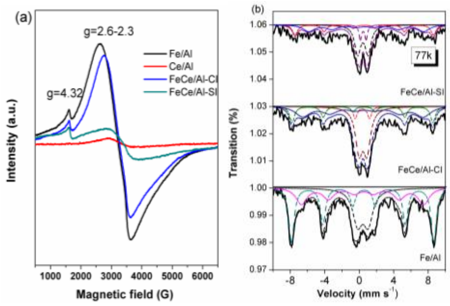


Figure 2. The results of (a) EPR and (b) Mössbauer spectroscopy.

From Figure 1(a) we can concluded that Fe_2O_3 species were highly dispersed or existed as small clusters below XRD detection limitation. While CeO_2 were presented as crystal particles in the CeO_2 containing samples. The broaden and high angle shifted CeO_2 characteristic diffraction peaks in Figure 1(b) of

FeCe/Al-CI compared to FeCe/Al-SI and Fe/Al suggested smaller CeO_2 particle size and Fe^{3+} doped CeO_2 were generated though co-impregnation method.

EPR results (Figure 2a) told us that there were two kinds of Fe species presented in the samples. Signals at g=4.32 were assigned to isolated Fe^{3+} located in sites of tetrahedral coordinated or distorted tetrahedral coordinated subjected to strong crystal field effect. In addition, signals at g=2.6-2.3 were due to the Fe_2O_3 clusters existed in a distorted octahedral environment [2]. The signal intensity is proportional to the number of EPR active species, so the amount of Fe_2O_3 clusters follows: Fe/Al > FeCe/Al-CI > FeCe/Al-SI.

In low temperature (77K) Mössbauer spectroscopy, the samples can be fitted as the superposition of magnetic splitting sextuplet (S) and quadruple splitting doublet (D). Among them, sextuplet were resulted from the fast relaxation of magnetic moment of small particles, and the doublet were promptly ascribed to the highly dispersed Fe^{3+} [3]. From the intensity of sextuplet of the samples, it was easy to see the number of Fe_2O_3 particles follows the order: Fe/Al > FeCe/Al-CI > FeCe/Al-SI, in accordance with the EPR results.

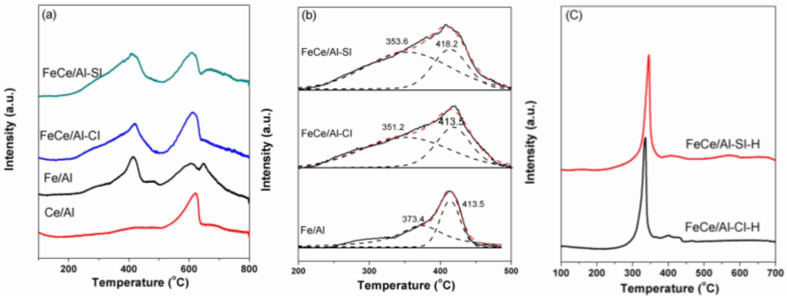
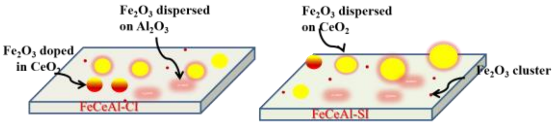


Figure 3. The H_2-TPR results of the synthesized samples.

In order to understand the redox properties of different Fe^{3+} species and the interaction of Fe-O-Ce of the samples, we performed the H_2-TPR characteristic. The reduction of iron species happened step-wise: $Fe_2O_3 \rightarrow FeO \rightarrow Fe^0$. The profiles in 200-500 ℃ can be fitted with two peaks α and β (3b), these two peaks were corresponded to the reduction of isolated Fe^{3+} species and Fe_2O_3 clusters, respectively. H_2-TPR of HNO_3-leaching samples also confirmed the attribution because the cluster Fe_2O_3 were more easily to be removed compared to the highly dispersed Fe^{3+} species. Moreover, the enlarged total reduction areas of FeCe/Al-SI indicated more CeO_2 species were reduced with the help of Fe-O-Ce.

According to the discussed results above, a tentative picture of iron and ceria species in FeCe/Al catalysts can be proposed. Irrespective of the preparation sequence, CeO_2 were present as little particle and Fe_2O_3 displayed a heterogeneous spatial distribution (scheme 1): dispersed on γ-Al_2O_3 as isolated Fe^{3+} ions or clusters, interacted with CeO_2.



Scheme 1. The possible existence states of iron and ceria species in FeCe/Al catalysts.

4. Conclusions

The addition of CeO_2 could promote the dispersion of Fe_2O_3 in Fe_2O_3/γ-Al_2O_3 catalysts. It was found that appropriate impregnation sequence could induce vast difference of the spatial distribution of Fe^{3+} species and CeO_2 particle size, in turn led to different physicochemical properties. With step-wise method, the tetrahedral coordinated isolated Fe^{3+} were enlarged compared to FeCe/Al-CI. Moreover, the strong interaction of Fe-O-Ce in FeCe/Al-SI resulted to its promoted low temperature reduction ability.

References

1. J. F. Sun, C.Y. Ge, X.J. Yao, W.X. Zou, X. Hong, C.J. Tang, L. Dong, Appl. Surf. Sci. 426 (2017) 279.
2. L.H. Dong, B. Zhang, C.J. Tang, L. Dong, Y. Chen, Catal. Sci. Technol. 4 (2014) 482.
3. P.J. Liu, S.B. He, H.Z. Wei, J.H. Wang, C.L. Sun, Ind. Eng. Chem. Res. 54 (2015) 130.