Advances in UV Raman Spectroscopic Studies on Catalysts and Catalyst Preparation

Can Li
State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, CHINA
Fax: 86-411-4694447; Email: canli@dicp.ac.cn; Website: http://www.canli.dicp.ac.cn

Introduction

There are a number of potential advantages of Raman spectroscopy over other techniques available for catalysis studies. The main limitations of conventional Raman spectroscopy are the relatively low sensitivity and the fluorescence interference. The latter is an even severe problem for the characterization of many real catalysts which often show strong fluorescence arising from the surface species like carbonaceous species derived under working conditions. The fluorescence is nearly absence in the region when the wavelength is shorter than 300 nm. So the fluorescence interference can be avoided by shifting the excitation laser from the visible region where for conventional Raman spectroscopy to the UV region (below 300 nm) where without fluorescence interference. The fluorescence is left behind in the visible region while the Raman spectrum is moved out from the fluorescence region to the UV region. So the fluorescence interference can be avoided for most catalysts in the UV Raman spectroscopy,[1,2] this open the possibility for characterizing the catalysts which are difficult to obtain the visible Raman spectra mainly because of the strong fluorescence interference. Another advantages of UV Raman spectroscopy may be the resonance Raman enhancement in some Raman bands because the UV laser could frequently excite the electronic states of samples.

Results and Discussion

Using UV Raman spectroscopy, we have studied sulfated zirconia,[3] coked FCC catalysts,[4] zeolites and alumina-supported oxides[2,5] that all have strong fluorescence background in their visible Raman spectra, but free of fluorescence interference in the UV Raman spectra. The UV Raman spectroscopy opens the possibility for characterizing those catalysts that are difficult to study by conventionally used visible Raman spectroscopy. This also allows us to study catalysts under working conditions with in-situ Raman spectroscopy.

One of the very interesting issues in transition metal substituted zeolites or molecular sieves is to identify the framework transition metal ions. The charge transfer transition between the framework oxygen atom and framework transition metal atom, namely, $p\pi \rightarrow d\pi$ transition falls in the 200-350 nm region for most zeolites with the framework transition metal atoms (e.g., 220 nm for TS-1, 250 nm for Fe-ZSM-5, and 270 nm for V-MCM-41). Thus, it is possible to identify the framework transition metal atoms based on the UV resonance Raman effect. We have studied the transition metal ions in the framework of molecular sieves using the UV resonance Raman spectroscopy. For examples, titanium ions in TS-1,[6] iron ions in Fe-ZSM-5[7] and vanadium ions in V-MCM-41[8] were successfully identified. Recent study on Fe-ZSM-5 shows that UV Raman spectroscopy can follow the synthesis of Fe-ZSM-5 from the very beginning of the zeolite synthesis through the formation of Fe-ZSM-5.

The visible Raman study of the supported molybdate has been limited to the low loading of molybdate because of the low sensitivity and the strong fluorescence interference of the conventional Raman spectroscopy. Our recent studies showed that UV resonance Raman spectroscopy is a very sensitive technique for the characterization of the coordination structures of supported molybdate even with extremely low loading even down to 0.1 wt% MoO_3. This makes it possible to get the information of the interaction between the surface molybdate species and the support particularly when the concentration of the surface molybdate species is very low. The low concentration of supported vanadium oxide can be also detected by UV resonance Raman spectroscopy.

Zirconia exhibits three different phases: monoclinic (m-ZrO_2), tetragonal (t-ZrO_2) and cubic (c-ZrO_2). t-ZrO_2 is a metastable phase of ZrO_2 at low temperatures and it changes into m-ZrO2 at elevated temperatures. Stabilized tetragonal zirconia is considered as an important structure for ceramics and sulfated zirconia catalyst. But the phase transformation from the metastable tetragonal (t) phase to the monoclinic (m) phase of crystalline ZrO_2 prevents its applications from a broader temperature ranges. Many studies have addressed the factors that affect the phase transformation of tetragonal zirconia, however, past investigations provided the information mainly on the bulk of ZrO_2. We present our recent results[10] about UV Raman spectroscopic studies on the phase transformation of zirconia, sulfated zirconia and yttrium oxide doped zirconia. It is found that the UV Raman spectroscopy is a surface sensitive technique for zirconia because zirconia has UV absorption. The UV Raman spectra together with visible Raman spectra and XRD patterns indicate that the phase transformation starts from the surface region of the particle and then extends into the bulk. Recent advances in UV Raman spectroscopic characterization of catalysts show that this new technique can successfully follow the detailed structural evolution of a catalyst under the synthesis procedure.[11-13]

Acknowledgements

This work was financially supported by the Natural Science Foundation of China(NSFC, Grant 29625305, 20073045), and the State Key Project for Basic Research from the Ministry of Science and Technology (Grant G1999022407). The author thanks his students for their contribution to this work

References

1. C. Li, and P.C. Stair, Stud. Surf. Sci. Catal., **105**(1997)599
2. P.C. Stair and C. Li, J. Vac. Sci. Technol., **A15**(1997)1679
3. C. Li and P. C. Stair, Catal. Lett., **36**(1996)119
4. J. Li, G. Xiong, Z. Feng, Z. Liu, Q. Xin and C. Li, Micro. Meso. Mater., **39**(2000)275
5. C. Li, and P.C. Stair, Stud. Surf. Sci. Catal., **101**(1996)881
6. C. Li, G. Xiong, Q. Xin, J.-K. Liu, P.-L. Ying, Z.-C. Feng, J. Li, W.-B. Yang, Y.-Z. Yang, G.-R. Wang, X.-Y. Liu, M. Lin, X.-Q. Wang and E.-Z. Min, Angewated Chem. Int. Engl.Ed., **38**(1999)2220;
7. Y. Yu, G. Xiong, C. Li and F.-S. Xiao, J. Catal., **194**(2000)487
8. G. Xiong, C. Li, H.-Y. Li, Q. Xin and Z.-C. Feng, Chem. Commun., (2000)677-678.
9. G. Xiong, Z.-C. Feng, J. Li, Q.-H. Yang, P.-L. Ying, Q. Xin and C. Li, J. Phys. Chem., **104**(2000)3581
10. M.-J. Li, Z.-C. Feng, G. Xiong, P.-L Ying, Q. Xin, C. Li, J. Phy. Chem. B, **105**(2001)8107
11. C. Li, G. Xiong, J.-K. Liu, P.-L. Ying, Q. Xin, Z.-C. Feng, J. Phys. Chem. B, 105(2001)2993.
12. C. Li., J. Catal., 2002, in press
13. C. Li, M.-J. Li, J. Raman Spectroscopy, 33(2002)301.