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RESEARCH NOTE

Characterization of Iron Atoms in the Framework of MFI-Type Zeolites by UV Resonance Raman Spectroscopy

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Silicalite-I, ZSM-5, and Fe-ZSM-5 zeolites prepared from two different silicon sources are characterized by UV resonance Raman (UVRR) spectroscopy, X-ray diffraction (XRD), electron spin resonance (ESR), and UV/visible diffuse reflectance spectroscopy (UV/Vis DRS). A new technique for investigating zeolitic structure, UV resonance Raman spectroscopy selectively enhances the Raman bands associated with framework iron atoms incorporated into MFI-type zeolites, and it is very sensitive in identifying the iron atoms in the framework of zeolites, while other techniques such as XRD, ESR, and UV/Vis DRS have failed in uncovering trace amounts of iron atoms in the framework of zeolites.

Key Words: **UV resonance Raman; iron; isomorphous substitution; silicalite-I; MFI-type zeolites; Fe-ZSM-5; electron spin resonance (ESR); UV/visible diffuse reflectance (UV/Vis DRS).**

INTRODUCTION

ZSM-5 and silicalite-I are two members of a new representative class of MFI-type zeolites, which are of considerable significance in the applications to catalysis and separation (1–5). Obermeyer *et al.* (6, 7) studied the nature of metal ions, in which they replaced the Si^{4+} by Al^{3+} and many other transition metals in ZSM-5 structure without changing the framework, and produced highly selective catalytic properties. In the framework of zeolites, even a trace amount of trivalent elements will change in acidity significantly, resulting a change of catalytic activity. Therefore, the characterization of a trace of heteroatoms in ZSM-5 is of great importance. However, it is often difficult to obtain the information on framework heteratoms in zeolites by the usual spectroscopic techniques when the concentration of the transition metal atom is low (8).

As a new technique, UV resonance Raman spectroscopy is used to study the catalysts and other solids (9). The resonance Raman effect selectively increases the intensity of Raman bands associated with framework transition metals while leaving the other Raman bands unchanged. In addition, UV Raman spectroscopy significantly improves the quality and resolution of Raman spectra of zeolites because it avoids fluorescence interference from solid samples. A successful example is an identification of titanium atoms in TS-1 zeolite (10).

Here we investigate a trace amount of iron atoms in the framework of MFI-type zeolite by UV resonance Raman spectroscopy. The effect of isomorphous MFI framework with Ti (11), V (12), and Ge (13) have been studied using conventional visible Raman technique, but in these cases only a large amount of heteroatoms incorporated into the zeolite framework can be definitely identified. The "resonance effect" of UVRR spectroscopy offers a powerful tool in characterizing a trace amount of transition metals in a zeolite framework.

EXPERIMENTAL

Materials

Zeolite samples discussed in this study were synthesized according to the literature (14–16), which were confirmed by powder X-ray diffraction (XRD). To remove any possible nonframework iron species, Fe-ZSM-5 was pretreated with an aqueous solution of hydrochloric acid (0.1 mol/dm^3) at 298 K for 1–2 days, after that it remains framework structure identified by XRD data. All samples were calcined in air at 823 K for 5 h to remove organic templates. Two silicon sources were used to synthesize these zeolites. One was fumed silica, and the other was sodium silicate. The analysis of chemical composition of various zeolites is presented in Table 1.

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TABLE 1

Chemical Composition of Various Zeolites

Sample	Silicon source	Si/Al	SiO_2^*	$Al_2O_3^*$	$Fe_2O_3^*$	Na_2O^*
silicalite-I	fumed silica	∞	99.98	—	—	—
silicalite-I*	sodium silicate	∞	97.85	0.79	0.46	0.43
ZSM-5*	sodium silicate	100	97.56	0.87	0.29	0.51
ZSM-5*	sodium silicate	23	94.29	3.39	0.095	2.09
ZSM-5	fumed silica	98	98.47	0.83	—	—
ZSM-5	fumed silica	25	94.36	3.27	—	2.02
Fe-ZSM-5	fumed silica	95	97.98	—	1.44	0.49
sodium silicate			27.71	0.43	0.26	10.31

Note. (∗) denotes wt%.

Instrumentation

UV Raman spectra were recorded on an UV Raman spectrometer built in State Key Lab of Catalysis, Dalian Institute of Chemical Physics, and the details were reported earlier in (9, 10). Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with a Cu$K\alpha$ radiation, UV/visible diffuse reflectance spectra (UV/Vis DRS) were recorded on a Shimdazu UV-3100 UV-VIS-NIR recording spectrophotomater, chemical composition of samples were analyzed by a Perkin–Elmer Optima DV 3300 ICP-AES instrument, and ESR spectrum was recorded at room temperature on a Bruker ER200D ESR spectrometer equipped with a dual cavity and a 100-kHz modulation unit.

RESULTS AND DISCUSSIONS

In Fig. 1, silicalite-I exhibits two bands at 380 and 802 cm^{-1} (Fig. 1a), the band at 380 cm^{-1} is assigned to a five-membered building unit of MFI-structure zeolites (17, 18), and the 802 cm^{-1} band is assigned to the framework symmetric stretching vibration in ZSM-5 (12, 17). It is very interesting to note that Fe-ZSM-5 exhibits new bands at 516, 580, 1026, 1126, and 1185 cm^{-1}, in addition to the bands at 380 and 802 cm^{-1} (Fig. 1b). The chemical analysis of silicalite-I (Fig. 1a) and Fe-ZSM-5 (Fig. 1b) shows that the difference in chemical composition is only irons in these zeolites. Therefore, the new bands should be related to the contribution of the iron atoms in zeolite. Figure 1c shows UV Raman spectrum of mechanical mixture of Fe_2O_3 with silicalite-I, giving similar bands to those of silicalite-I (Fig. 1a). These results indicate that UV Raman spectroscopy is insensitive to Fe_2O_3 material, and Fe_2O_3 does not exhibit UV Raman bands because the UV Raman bands of Fe_2O_3 are too weak to detect.

In Fig. 2a, silicalite-I* exhibits bands at 380, 515, 802, 1022, 1125, and 1175 cm^{-1}. Compared with those of silicalite-I prepared from fumed silica, four new bands appear at 515, 1022, 1125, and 1175 cm^{-1}. Comparsion of two samples in chemcial composition shows that the only difference is a trace of iron and aluminum impurities. Silicalite-I* prepared from sodium silicate contained an impurity of iron oxide with 0.46 wt% and aluminum oxide with 0.79 wt%. To distinguish the effect of iron and aluminum oxide on UV Raman spectrum, we investigated the UV Raman spectra of ZSM-5 samples with Si/Al ratio at 98 and 25 synthesized by fumed silica. Both samples show bands at 380 and 802 cm^{-1}, which are the same as those of silicalite-I. These results indicate that the aluminum oxide in the zeolites has no special contribution to UV Raman spectra, and the four new UV Raman bands could be merely assigned to the trace amount of iron atoms. Figures 2b and 2c show the UV resonance Raman spectra of ZSM-5* with the Si/Al ratio of 100 and 23, respectively, which were synthesized by sodium silicate. They gave the bands at 380, 515, 802, 1022, 1125,

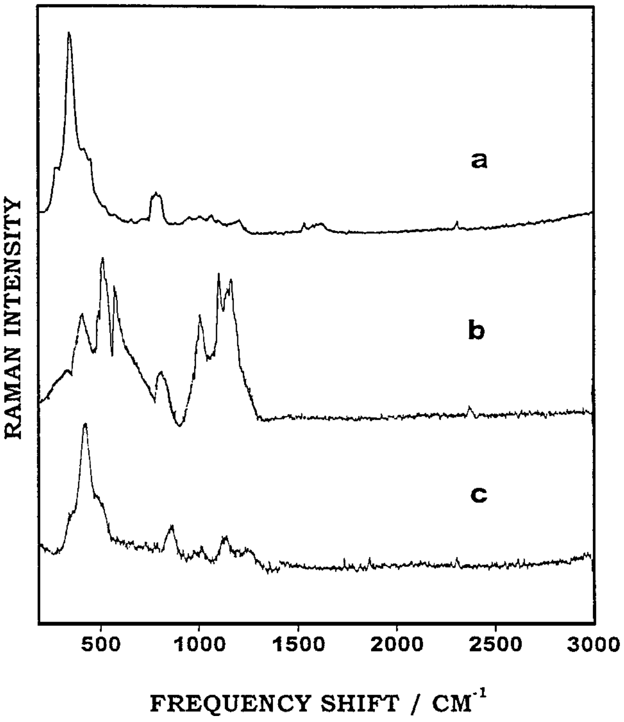

FIG. 1. UV Raman spectra of (a) silicalite-I, (b) Fe-ZSM-5, and (c) a mechanical mixture of silicalite-I with Fe_2O_3, which were prepared from fumed silica as a silicon source.

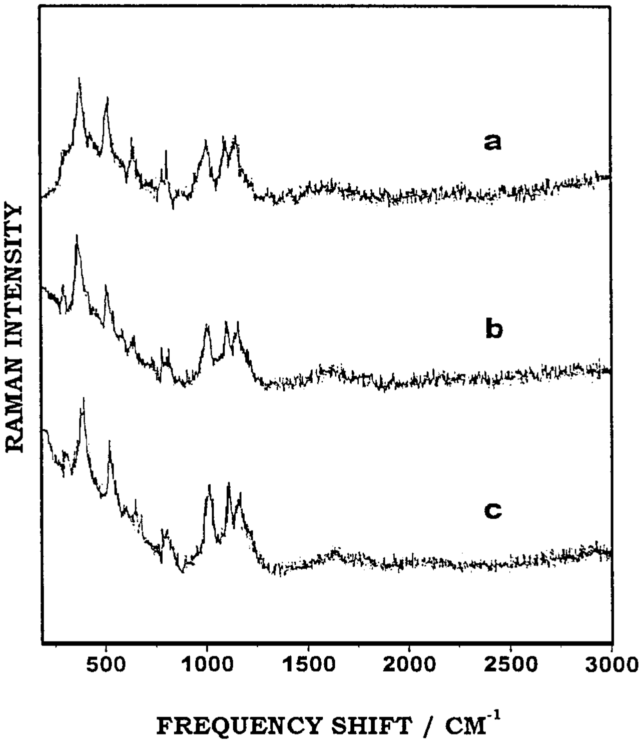

FIG. 2. UV Raman spectra of (a) silicalite-I* and ZSM-5* with Si/Al ratio of (b) 23 and (c) 100 prepared from sodium silicate as a silicon source.

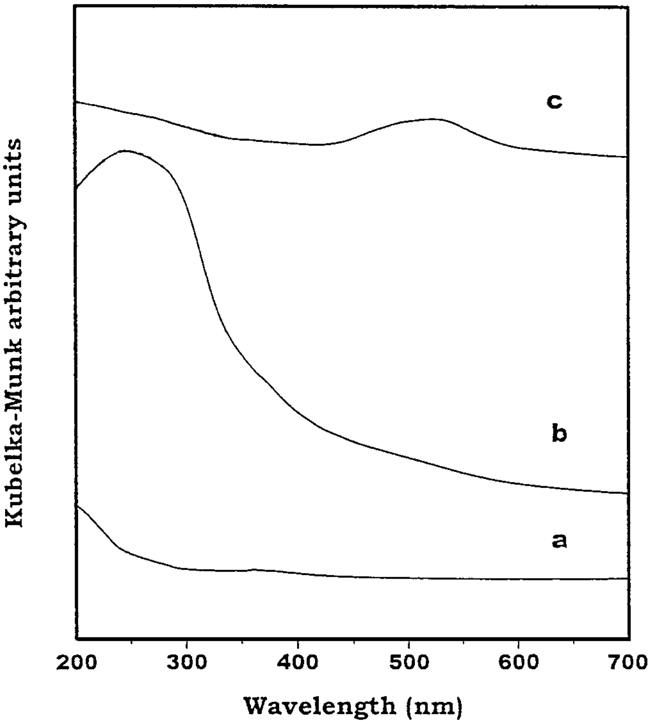

FIG. 3. UV-visible diffuse reflectance spectra of (a) silicalite-I, (b) Fe-ZSM-5, and (c) a mechanical mixture of silicalite-I with Fe_2O_3 prepared from fumed silica as a silicon source.

and 1175 cm^{-1}. Similarly, the bands at 380 and 802 cm^{-1} are assigned to the framework symmetric stretching vibration of a five-membered building unit in MFI-type zeolites (12, 17, 18), and the bands at 515, 1022, 1125, and 1175 cm^{-1} are related to the contribution of the iron impurity. Furthermore, we observed that the intensity of the bands at 515, 1022, 1125, and 1175 cm^{-1} in Fig. 2 was much weaker than those in Fig. 1b, suggesting lower amount of iron atoms in the framework of MFI-type zeolite.

Figure 3 shows UV/visible diffuse reflectance spectrum of silicalite-I, Fe-ZSM-5, and a mechanical mixture of Fe_2O_3 with silicalite-I, which were prepared from fumed silica. Silicalite-I has no bands in the 200–700 nm region, while Fe-ZSM-5 shows a strong absorption band centered at 240–250 nm. The band at 240–250 nm may be assigned to the $d\pi$–$p\pi$ charge-transfer transition between the iron and oxygen atoms in the framework of Fe–O–Si in zeolite (19, 20). Similar phenomena have been observed in Ti–O–Si species of TS-1 (10, 21, 22). Figure 3c shows UV/visible diffuse reflectance spectrum of mechanical mixture of Fe_2O_3 with silicalite-I, and it exhibits an absorption band at 500 nm, indicating that there is no strong absorption band in the UV region (below 300 nm). Figure 4 shows UV/visible diffuse reflectance spectra of silicalite-I* and ZSM-5* with Si/Al ratio of 23 and 100, which were prepared from sodium silicate. We can see that all samples have no obvious absorption bands at 240–250 and 500 nm, suggesting that the UV/visible DRS technique is insensitive to a trace amount of iron atoms in zeolites.

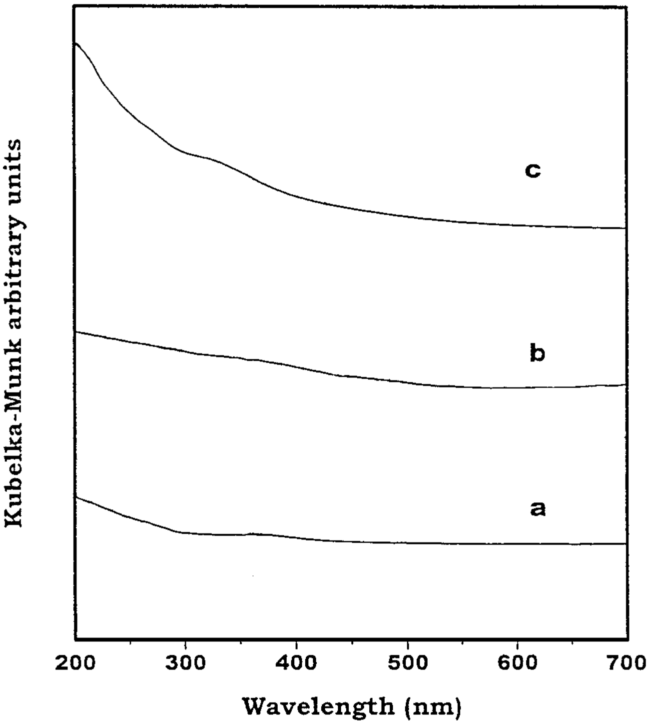

FIG. 4. UV-visible diffuse reflectance spectra of (a) silicalite-I* and ZSM-5* with Si/Al ratio of (b) 23 and (c) 100 prepared from sodium silicate as a silicon source.

ESR spectra of silicalite-I and Fe-ZSM-5 prepared from fumed silica as a silicon source were also made, and the Fe-ZSM-5 sample shows one resonance signal at $g = 4.3$, which is assigned to the Fe^{3+} ions in the tetrahedral coordination of ferrisilicate framework (5, 23–26). In contrast, the sample of silicalite-I does not exhibit any obvious signals associated with the Fe^{3+} species. ESR spectra of silicalite-I* and ZSM-5* samples prepared from sodium silicate as a silicon source were recorded, and there are no signals assigned to the iron species. It seems that ESR spectroscopy is unable to characterize the trace amount of iron species in the zeolites, and the ESR signals associated with iron species are observed only for the Fe-ZSM-5 with a relatively large amount of iron atoms.

In the UV/visible diffuse reflectance spectrum of Fe-ZSM-5 (Fig. 3), there is a typical absorption band centered at 240–250 nm, while no electronic absorption band is found for silicalite-I. The band at 240–250 nm results from the charge-transfer transition between iron and oxygen atoms in Fe-ZSM-5. The UV laser line at 244 nm, the excitation for UV Raman spectroscopy, is just in the band region 240–250 nm. As we know, excitation occurs within an electronic absorption band—resonance excitation, the electronic transition, and the vibrational transition are excited at their natural frequency of oscillation. As a result, the induced dipole moment becomes much larger, leading to a large increase in the intensity of the Raman scattering. This "resonance" Raman scattering intensity can increase by as much as 10^8 times, which means that vibrational Raman spectra of samples can be selectively observed if the samples are excited with frequencies of light selectively absorbed by the sample (27). Therefore, Raman bands at 516, 580, 1026, 1126, and 1185 cm^{-1} observed for Fe-ZSM-5 can be reasonably attributed to the resonace Raman bands of iron species in the sample.

Furthermore, we observed that the UV Raman spectrum of silicalite-I is the same as that of a mechanical mixture of Fe_2O_3 with silicalite-I (Fig. 1c). This means that no resonance Raman phenomenon is observed for Fe_2O_3. This is in good agreement with the UV/visible diffuse reflectance spectrum in Fig. 3c, which shows no evidence of electronic absorption bands in the 200–300 nm region for Fe_2O_3. The iron atoms in the nonframework of MFI-type zeolite could not be detected by the UV Raman spectroscopy, but the UV Raman spectroscopy could selectively identify the iron atoms in the framework of MFI-type zeolite.

In contrast, other techniques such as ESR and UV/Vis DRS are insensitive to a trace amount of iron atoms in the framework of zeolites.

CONCLUSION

The iron atoms in the framework of MFI-type zeolites are selectively identified using UV resonance Raman spectroscopy because of the resonance Raman effect and the avoidance of fluorescence interference from zeolite samples. This technique is very sensitive to the framework iron atoms with trace amounts, while other techniques such as XRD, ESR, and UV/Vis DRS are unable to obtain information on trace amounts of iron atoms in the zeolite samples.

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