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Acidity generation on mechanically mixed ZrO_2–ZnO catalysts

Wenzhong Zhang [a], Haiyou Wang [b], Yuanyan Liao [b] and Yuanqi Yin [a,1]

[a] *Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences,*
Lanzhou 730000, PR China
[b] *State Key Laboratory for Physical Chemistry of Solid Surface, Xiamen University,*
Xiamen 361005, PR China

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Lewis acid sites are generated by mechanical mixing of ZrO_2 and ZnO. These sites may be the coordinatively unsaturated metal ions, on which adsorbed pyridine cannot be desorbed during the multiple scans on a laser Raman spectroscope; but physisorbed pyridine and its adspecies on Brønsted acid sites desorb easily under laser irradiation.

Keywords: ZrO_2–ZnO binary oxide; laser induced pyridine desorption; Lewis acidity generation; coordinatively unsaturated metal ions

1. Introduction

Metal oxides such as ZnO and ZrO_2 etc. are possible bifunctional catalysts [1]. They have been used in many reactions as powerful catalysts [2]. As generally accepted, both the acidity and basicity of ZnO and ZrO_2 are weak. Thus much efforts have been made by different groups to study binary metal oxides [3] on which acidity might be generated. A hypothesis for predicting the generation of acid properties by binary oxides has been put forward by Tanabe et al. [3]. According to Tanabe's hypothesis, ZrO_2–ZnO should not provide new acidity when these two oxides are mixed. In our study of CO hydrogenation on mixed oxides, such as on mechanically mixed ZrO_2–ZnO with various metal atom ratios, ethylene was selectively formed on one of the binary oxides (the Schultz–Flory law of FT synthesis was not obeyed) [4]. We have inferred that surface acidity plays an important role in CO hydrogenation to olefins. This letter focuses on the surface acidity on both single and binary oxides characterized by means of LRS (laser Raman spec-

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[1] To whom correspondence should be addressed.

troscopy) after pyridine adsorption following the method described by Lu et al. [5]. It was discovered for the first time that new, stronger Lewis acid sites were generated on mechanically mixed ZrO_2 and ZnO catalysts in contradiction to the hypothesis of Tanabe et al. The coordinatively unsaturated metal ions are considered to be the Lewis acidic sites in the discussion.

2. Experimental

Analytically pure ZrO_2 and ZnO were used. Three binary oxides were prepared by mechanical mixing of these two oxides with metal atom ratios of 1 : 3 (Zr25-Zn75), 1 : 1 (Zr50-Zn50), and 3 : 1 (Zr75-Zn25). All these binary oxides and the two single oxides were calcined at 500°C fog 6 h, and were kept in a desiccator for later use. Every sample (either binary or single) was pressed into a disc with a thickness of 1 mm and a diameter of 12 mm. This disc was kept at 150°C for 3 h before mounting to the sample holder of the LRS instrument (Ramalog-5). The 5145 Å line from a Spectra Physics laser was used with a power of 100 mW. The disc was wetted with about 0.05 ml of pyridine (pre-dehydrated with Na_2SO_4), and then was quickly mounted on the sample holder. Later the sample was subjected to laser irradiation for 10 scans in the range of 900–1100 cm^{-1} with a resolution of 2 cm^{-1} (every scan required about 65 s). The first two scans were omitted. The 3rd to 7th scan were summed up to produce one spectrum (a) of the sample, the sum of 8th to 10th scan was taken as another spectrum (b). The latter scan was considered as a spectrum of the adsorbed pyridine remaining on the sample after laser induced desorption. By comparing the spectra the difference bands can be assigned to weakly adsorbed pyridine.

The sample was also characterized by FTIR spectra and ESR.

3. Results and discussion

Figs. 1–3 are the spectra of pyridine adsorbed on pure ZrO_2, ZnO and Zr50-Zn50 samples. From fig. 1, it is obvious that there are three bands at 992, 998 (shoulder peak), and 1032 cm^{-1}. The bands at 992 and 1032 cm^{-1} can be assigned to the ring-breathing vibrational mode of physisorbed pyridine according to ref. [6]. The band at 998 cm^{-1} is the ring-breathing vibration of pyridine adsorbed on Brønsted acid sites. There is no band at 1018 cm^{-1} in fig. 1 which is the ring-breathing vibrational mode of pyridine adsorbed on Lewis acid sites. In fig. 2a, there are the same three bands as that of fig. 1. From fig. 2b it can be seen that these three bands all disappeared after seven scans which takes approximately 7.5 min. This means that both physisorbed and Brønsted acid site adsorbed pyridine on ZnO are very weakly adsorbed and can be easily desorbed under laser irradiation. When the laser was turned to another spot on the same ZnO disc, no bands could be

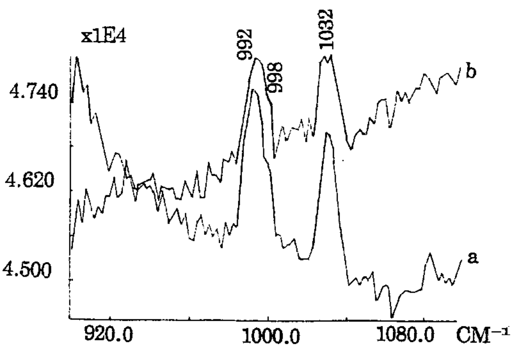


Fig. 1. LRS spectra of pyridine adsorbed on ZrO$_2$. (a) 3rd to 7th scans, (b) 8th to 10th scans.

detected. This may indicate that the heat produced by the laser irradiation was transferred to the disc of ZnO and resulted in pyridine desorption all over the disc. Another explanation might be that pyridine adspecies on ZnO migrate from other parts of the disc to the laser spot and desorb. By considering the fact that ZnO is a good semiconductor, the first explanation seems more reasonable in our opinion. On ZrO$_2$, however, physisorbed pyridine still remains in spite of extensive laser desorption (fig. 1b); the explanation may be that pyridine adspecies migrate to the laser spot slowly, physisorbed pyridine will desorb incompletely in 7.5 min if the sample disc is a poor heat conductor (in fact, the intensities of the bands of adsorbed pyridine decrease with exposure to the laser for a longer time; in addition, as a ceramics, ZrO$_2$ is not a good heat conductor). In fig. 3a there are four bands at 992, 998, 1018 and 1032 cm^{-1}. The existence of the band at 1018 cm^{-1} indicates that there is Lewis acid site adsorbed pyridine. By comparing fig. 3 with the other two figures, it is possible to conclude that new Lewis acid sites are generated on the binary oxide. Fig. 3b shows that laser induced pyridine desorption also occurs on the binary oxide, physisorbed and Brønsted acid site adsorbed pyridine were desorbed after seven scans. This suggests that there is an oxide–oxide interaction between ZrO$_2$ and ZnO. The experiments with Zr25-Zn75 and Zr75-Zn25 catalysts

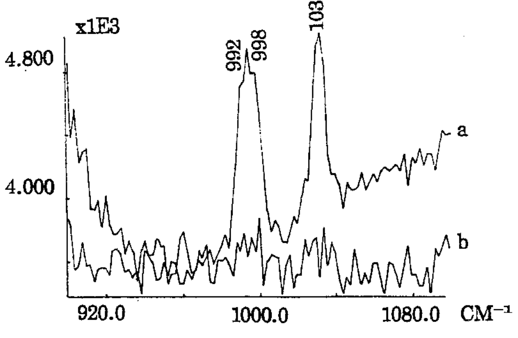


Fig. 2. LRS spectra of pyridine adsorbed on ZnO (a) 3rd to 7th scans, (b) 8th to 10th scans.

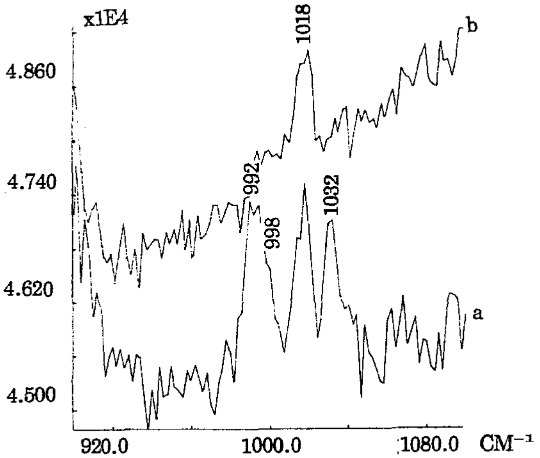


Fig. 3. LRS spectra of pyridine adsorbed on Zr50-Zn50 binary oxide. (a) 3rd to 7th scans, (b) 8th to 10th scans.

show almost the same results as obtained on Zr50-Zn50, but with a slightly different ratio of Lewis sites to Brønsted sites calculated from the peak intensity ratio I_{1018}/I_{998}.

However, Tanabe et al. [7,8] had shown by the IR spectra of pyridine adsorption that both ZnO and ZrO_2 have only Lewis acidic sites and their acid amounts are very small [7,9]. It seems that our results (figs. 1 and 2) are contrary to that of Tanabe et al. However, the bands of pyridine adspecies almost disappeared on ZnO when it was calcined in air at 500°C [8]. In our case, ZnO was also calcined in air at 500°C. Thus it is reasonable that there is no band of Lewis acid adsorbed pyridine in fig. 2. For ZrO_2, the absence of the band at 1018 cm^{-1} might be explained as that LRS is less sensitive than IR to adsorbed species, especially when amounts are small and noise of the spectrum is high.

To verify these explanations, ZrO_2, ZnO and all these three catalysts were characterized by IR spectra after pyridine adsorption. Bands in the region of 1400–1620 cm^{-1} are detected on both ZrO_2 and ZnO when more than 150 scans are taken by FTIR. There are bands with rather high intensity in the same wave number region on all three catalysts after only 30 scans (fig. 4). These results reveal that the amount of acid on mixed oxides is increased, which is in accordance with the results of amine titration of ZrO_2–ZnO [9].

Now, the question will arise, how the Lewis acid sites were generated. The study of various supported binary oxides by Dumesic et al. [10] showed that Lewis acid sites are coordinatively unsaturated metal ions which were not considered in Tanabe's hypothesis. The hypothesis is based on certain assumptions about the structure of the mixed oxide, e.g., the coordination of the oxygen anions is dictated by the structure of that oxide component present in greater concentration and the prediction of acid type is based on electrical charge balance. It seems that we can get

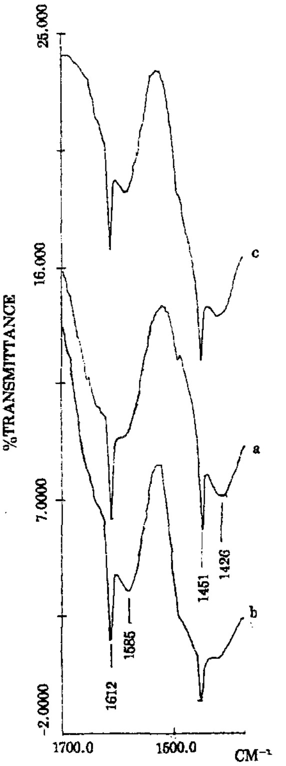


Fig. 4. IR spectra of pyridine adsorbed on binary oxides. (a) Zr25-Zn75, (b) Zr50-Zn50, (c) Zr75-Zn25. Every sample was preadsorbed at 150°C, purged with He at 150°C for 1 h and evacuated at r.t. to 10^{-3} Torr for 1 h.

a possible explanation, if we assume coordinatively unsaturated metal ions being generated by mechanical mixing of ZrO_2 and ZnO. In fact, an oxygen vacancy exists on ZnO [11], the Zn^{2+} ion adjacent to oxygen vacancy is a coordinatively unsaturated metal ion, and it might be a Lewis acid site [12]. This consideration was supported by the fact that the bands of adsorbed pyridine disappeared on ZnO after calcination in air at 500°C [8]. Calcination at high temperature in air will completely eliminate oxygen vacancies, so it is possible that the respective sites will disappear. ESR was used to study whether or not there are new oxygen vacancies after mixing of ZrO_2 and ZnO. Fig. 5 shows that ZrO_2–ZnO gives a signal with sharp peak at $g = 1.960$ (which is the characteristic signal of localized electron [11]). This signal is sensitive to the sample pretreatment at elevated temperature with or without air. There is a signal at $g = 1.962$ on ZnO; its intensity is very low compared to that of ZrO_2–ZnO sample under the same pretreatment conditions. However, there is no such signal on ZrO_2, but a signal with $g = 1.958$ appears when ZrO_2 is evacuated at high temperature such as 450°C and it disappears when it is

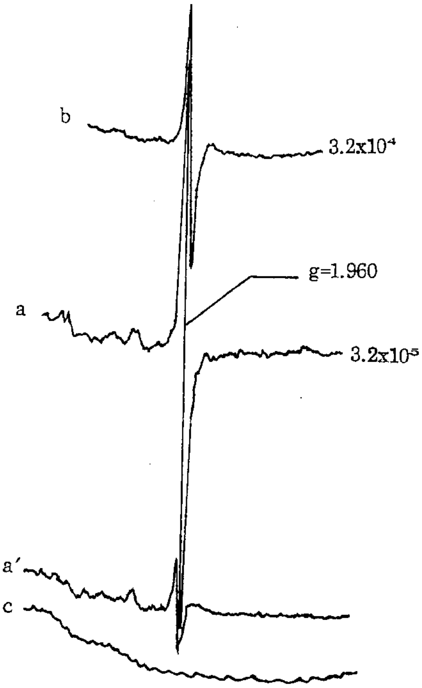
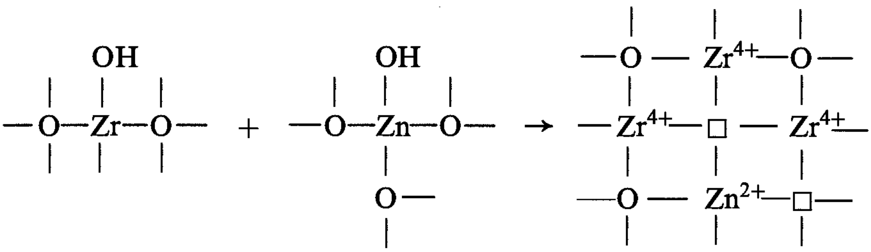


Fig. 5. ESR signals of various oxides. (a) Zr50-Zn50 catalyst pretreated in air at 150°C and purged with He at r.t., followed by evacuation at r.t. to 10^{-3} Torr. (a′) Zr50-Zn50 catalyst treated in air at 350°C, evacuated at r.t. to 10^{-3} Torr. (b) ZnO pretreated as in the case (a). (c) ZrO_2 pretreated as in the case (a).

heated in oxygen at 350°C. All these results suggest that there are newly generated oxygen vacancies on the binary oxide. The metal ions adjacent to them might be considered as Lewis acid sites.

The formation of oxygen vacancies might be explained as follows: When two oxides were put together and calcined at high temperature, the hydroxyl either from ZrO_2 or from ZnO will be dehydrated, especially at the boundary of these two oxides; as a result, mixed metal–oxygen species will be formed. According to the electron neutrality theory, an oxygen vacancy will be formed when low valence metal ions coordinate to high valence metal ions, which can be shown by the following:



$$\begin{array}{c} \mathrm{OH} \\ |\quad|\quad| \\ -\mathrm{O}-\mathrm{Zr}-\mathrm{O}- \\ |\quad|\quad| \end{array} + \begin{array}{c} \mathrm{OH} \\ |\quad|\quad| \\ -\mathrm{O}-\mathrm{Zn}-\mathrm{O}- \\ | \\ \mathrm{O}- \\ | \end{array} \rightarrow \begin{array}{c} |\qquad|\qquad| \\ -\mathrm{O}-\mathrm{Zr}^{4+}-\mathrm{O}- \\ |\qquad|\qquad| \\ -\mathrm{Zr}^{4+}-\square-\mathrm{Zr}^{4+}- \\ |\qquad|\qquad| \\ -\mathrm{O}-\mathrm{Zn}^{2+}-\square- \\ |\qquad|\qquad| \end{array}$$

Apparently, if a Zn^{2+} ion coordinates to a Zr^{4+} ion through oxygen anions, four coordinatively unsaturated metal ions will be formed, which may act as Lewis acid sites. It can be predicted that the acid strengths on Zn^{2+} and Zr^{4+} will be different. In fig. 4, there are two bands at 1451 and 1426 cm^{-1}, and two bands at 1612 and 1585 cm^{-1}. These bands reflect two kinds of Lewis acid sites as explained by Dumesic et al. [10]. The bands at 1585 and 1426, 1612 and 1451 cm^{-1} can be assigned to coordinatively unsaturated Zn^{2+}, Zr^{4+} respectively. The formation of coordinatively unsaturated metal ions as new Lewis acid sites was supported by the results on WO_x/TiO_2 obtained by Knözinger et al. [13].

4. Conclusion

It seems possible to conclude that coordinatively unsaturated metal ions are produced through interaction of ZrO_2 and ZnO just by mechanical mixing of these two oxides; thus, the stronger Lewis acidity is generated on ZrO_2–ZnO binary oxides. Also it seems reasonable that the formation of new Lewis acid sites is one of the reasons for the synergistic effect between ZrO_2 and ZnO [4].

Acknowledgement

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References

[1] K. Tanabe, in: *Proc. 9th Int. Congr. on Catalysis*, Vol. 5, eds. M.J. Phillips and M. Ternan (The Chemical Institute of Canada, Ottawa, 1988) p. 85.
[2] K. Maruya, A. Inabam, T. Maehashi, K. Domen and T. Onishi, J. Chem. Soc. Chem. Commun. (1985) 487.
[3] K. Tanabe, T. Sumiyoshi, K. Shibata, T. Kiyouya and J. Kitagawa, Bull. Chem. Soc. Japan 47 (1974) 1064.
[4] W. Zhang, R. Gao, G. Su and Y. Yin, in: *10th Int. Congr. on Catalysis*, Preprint Book (1992) P354.
[5] X. Yang, W. Lu, B. Zhao and Q. Chen, Chinese Petrochem. Tech. 5 (1991) 340.
[6] E. Payen et al., Appl. Spectry. 36 (1982) 30.
[7] Y. Nakano, T. Iizuka, H. Hattori and K. Tanabe, J. Catal. 57 (1979) 1.
[8] K. Tanabe, L. Ishiya, I. Matsuzaki, I. Ichikawa and H. Hattori, Bull. Chem. Soc. Japan 45 (1972) 45.
[9] K. Shibata, T. Kiyoura, J.I. Kitagawa, T. Sumiyoshi and K. Tanabe, Bull. Chem. Soc. Japan 46 (1973) 2985.

[10] G. Connell and J. Dumesic, J. Catal. 102 (1986) 216.
[11] A. Hausman, Physik. Z 86 (1970) 237.
[12] C. Morterra and G. Cerrato, Catal. Lett. 10 (1991) 357.
[13] F. Hilbrig, H. Schmelz and H. Knözinger, *10th Int. Congr. on Catalysis*, Preprint Book (1992) O93.