Chinese Chemical Letters Vol. 11, No. 7, pp. 649–652, 2000

Modifying NaY Zeolite with Metal Oxide by Microwave Irradiation: Influence on the Adsorption and Decomposition of *N*-nitrosamines

Li Li MA, Bin SHEN, Jian Hua ZHU*, Jia Rong XIA, Qin Hua XU

Chemistry Department, Nanjing University, Nanjing 210093

Abatract: Coating MgO or ZrO_2 on zeolite NaY accelerated decomposition of *N*-nitrosodimethylamine and *N*-nitrosopyrrolidine, resulting from variation of the surface state such as generation of basic sites.

Keywords: Zeolite NaY, MgO, ZrO_2, N-nitrosamines, cigarette smoke.

Smoke is a grave problem everywhere in the world causing serious health problems, because carcinogenic compounds exist in cigarette smoke. A cigarette containing zeolite can become a catalytic converter and help to eliminate substantial amount (50% and more) of carcinogenic compounds in cigarette smoke[1-2]. However, addition of commercial zeolite with sodium ion would disturb the original taste of cigarette. Substitution with exchanged zeolite could avoid this disadvantage[1], but the exhaust solution produced in exchanging process would cause new environment pollution. Recently coating zeolite with metal oxide under microwave irradiation has been proven to be a novel way for preparation of functional materials[3], since no any pollutant liberated during the process and all of the guest could be utilized for modifying the host without any waste. Moreover, the resulting composite seemed to keep the character of zeolite but had no negative influence on the taste of the cigarette[2]. Suspicions exist on the coated zeolite, however, concerning what influence would be caused on the adsorption and decomposition of *N*-nitrosamines over zeolite. This prompts us to perform an investigation by use of temperature-programmed surface reaction (TPSR).

MgO, ZrO_2 and ZnO were coated on zeolite NaY by microwave irradiation[3], and the coating amount kept 5 wt.-%. *N*-nitrosodimethylamine (NDMA) and *N*-nitrosopyrrolidine (NPYR) were purchased from Sigma and the solutions prepared by dissolving 5mL *N*-nitrosamines in 100 mL methylene chloride. Adsorption was performed in a fixed-bed microreactor filled with 5mg zeolite at 593K, while solution of *N*-nitrosamine was pulse injected in the amounts of 2μL each time in a flow of hydrogen. Gaseous effluent was analyzed by an on-line Varian 3700 gas chromatograph and the decrement in the solute/solvent ratio was utilized to calculate the amount of *N*-nitrosamine adsorbed on zeolite. In TPSR experiment sample was activated at 773K and adsorbed *N*-nitrosamine at 313K [4]. While the sample was heated to 773K at a rate of 10K/min, the liberated NOx was detected by colorimetric method [5] and represented the amount of *N*-nitrosamine decomposed.

NPYR with five-membered ring and NDMA with chain structure are carcinogenic compounds existing widely in tobacco smoke and beer along with bacon. As seen in **Figure 1**, most of NDMA or NPYR could be selectively adsorbed from methylene chloride solution at 593K. Unlike the sample modified with MgO, coating ZnO or ZrO_2 decreased adsorption of NPYR on zeolite NaY, especially when the total amount of injection exceeded 0.8 mmol/g. For adsorption of NDMA coating MgO or ZnO on zeolite NaY had no influence, decrement was observed when the zeolite was coated with ZrO_2. It is clear that the property and dispersion of guest oxide strongly influenced the adsorption of *N*-nitrosamine on host zeolite. On the other hand, different adsorption behavior of NDMA and NPYR on the modified zeolite could also be tentatively attributed to their molecular size. With a bigger molecular dimension (0.56nm), NPYR was hindered much more seriously than NDMA (0.45nm) to diffuse through the narrowed channel of zeolite NaY by coating oxide.

Figure 2 shows the influence of coating oxide on the decomposition of NPYR or NDMA over zeolite NaY. NOx desorption appeared in the range of 563K-733K on NaY, and about 0.26 mmol/g of NPYR was decomposed. Coating ZrO_2 on NaY caused a high temperature desorption of NOx emerging at 773K, and the decomposed amount increased to 0.56 mmol/g. Addition of MgO on NaY made the maximum temperature (T_{max}) of NOx desorption increased slightly from 593K to 613K, and more NPYR (0.35 mmol/g) was degraded. About 0.21 mmol/g of NDMA decomposed on zeolite NaY in the range of 593K-723K. Same amount of NDMA was fragmented on 5%ZrO_2/NaY but the T_{max} changed from 653K to 633K while a new desorption of NOx emerged above 713K. 5%MgO/NaY sample could decompose more NDMA (0.23 mmol/g) than the parent zeolite, but the T_{max} was similar. Contrarily, the decomposed NDMA on 5%ZnO/NaY was about one third of that on NaY at the same temperature (653K), although zinc dust in acetic acid was the most common agent for denitrosation[6].

Accelerated decomposition of NDMA or NPRA over MgO/NaY can be attributed to existence of basic sites on zeolite surface, since cleavage of *N*-nitrosamines could occur in basic solution[7]. ZrO_2 had usual catalytic function because it had both acidic and basic properties[8]. When *N*-nitrosamine was adsorbed on ZrO_2/NaY, existence of both acidic and basic sites on the surface would be helpful for conversion of the carcinogenic compound owing to its intrinsic factor. With the extensive delocalization of the unshared electron pair and the π electrons of the N=O group, *N*-nitrosamines could be fragmented in either acid or basic environment[9]. Clearly coating ZrO_2 on zeolite also accelerated decomposition of *N*-nitrosamines, though further investigation is required to explore the mechanism.

As expected, coating MgO or ZrO_2 did not weaken the function of zeolite NaY for eliminating *N*-nitrosamines in cigarette smoke while a decrement emerged in the case of coating ZnO, but the taste of cigarette was obviously improved[10]. Based on all facts mentioned above, it is clear that novel shape-selective functional composites can be prepared through the surface coating process by microwave irradiation, and the resulting materials will play more and more important role in the field of public health and environmental protection.

Figure 1. Adsorption of (left) NPYR or (right) NDMA on (a)NaY, (b)5%MgO/NaY, (c) 5%ZnO/NaY and (d)5%ZrO_2/NaY samples at 593K.

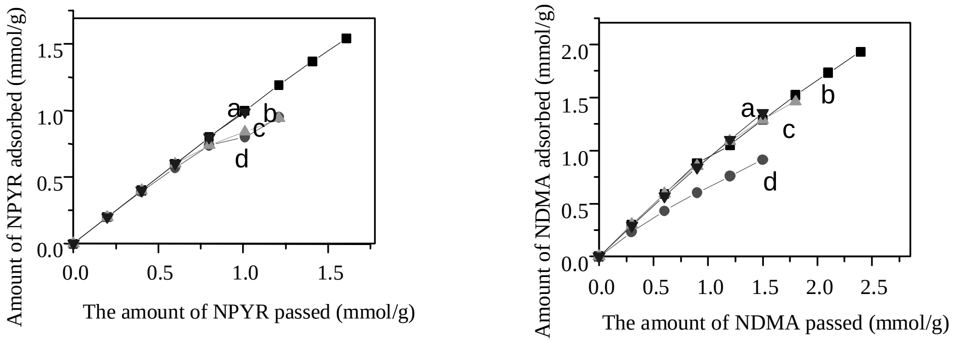
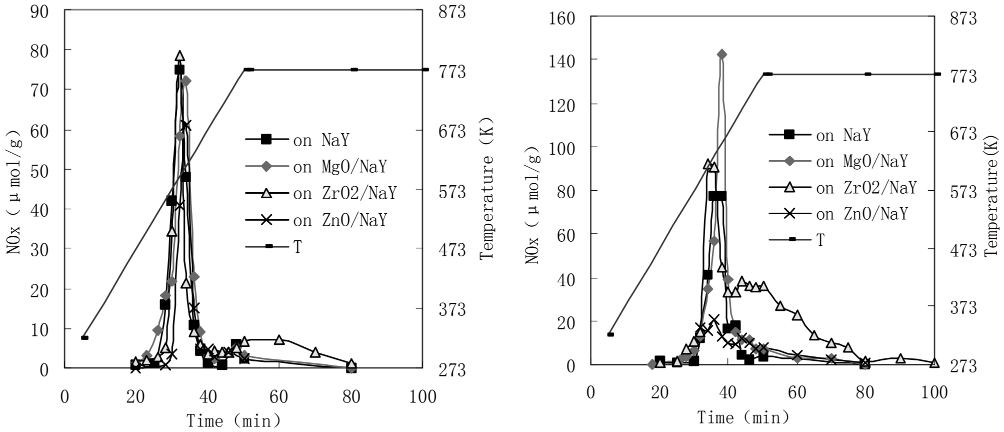


Figure 2. TPSR profiles of (left) NPYR or (right) NDMA on NaY zeolites before and after modified by oxide of 5 wt.%.



Acknowledgments

The National Natural Science Foundation of China (29773020) and National Advanced Materials Committee of China supported this work. Financial supports from Analysis Center of Nanjing University are also gratefully acknowledged.

References

1. M.W. Meier, J. Wild, F. Scanlan, EP 0740907A1, **1996**.
2. B. Shen, J.H. Zhu, Y. Chun, J.R. Xia, Q.H. Xu, *Jinshu Gongneng Cailiao,* **1998**, *6*, 224.
3. Y. Wang, J.H. Zhu, J.M. Cao, Y. Chun, Q.H. Xu, *Micropr. Mesopr. Mater.*, **1998**, *26*, 175.
4. L.L. Ma, B. Shen, J.H. Zhu, Q.H. Xu, *Chin. J. Catal.*, accepted.
5. B.E. Saltzman, *Anal. Chem*., **1954**, *26*, 1949.
6. J-P. Anselme, in "*N-nitrosamines*", Am. Chem. Soc., Washingdon, **1979**. p11.
7. R.N. Loeppky, C.T. Gnewuch, L.G. Hazlitt, W.A. Mckinley, *ibid.* p109.
8. K. Tomishige, T. Sakaihori, Y. Ikeda, K. Fujimoto, *Catal. Lett*., **1999**, *58*, 225.
9. Y.L. Chow, C.J. Colon, *Can. J. Chem*., **1968**, *46*, 2827.
10. J.H. Zhu, B. Shen, F. Wu, Q.H. Xu, CN 98111479.2, **1998**.

Received 1 December 1999
Revised 24 April 2000