Removal of Ethylene over KMnO$_4$/Al$_2$O$_3$-SiO$_2$

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Ethylene gas (C$_2$H$_4$) is an odorless and colorless gas which widely exists in nature, especially where plants and plant products are stored. Even in trace amounts, it can accelerate the ripening and aging process of fruits, vegetables, and floral product. Therefore, these properties of ethylene are not desirable for the packaging and long-term storage of such agro-products. Oxidants such as KMnO$_4$,[1-3] hypochlorites,[4] TiO$_2$,[5,6] etc., have been used to remove ethylene from storage rooms. Various metals ions, especially Ag,[7,8] Cu,[9] and Pd,[10,11] either alone or mixed and supported on porous inorganic or organic materials, have been used as a renewable and safe way to remove ethylene, even when it is present at very low concentration. Various inorganic solids, viz. zeolites,[12] zirconias,[13] clays,[14] silicas,[15] aluminas,[16] and organic materials, viz. resins,[17,18] polymers,[19] and carbons,[20] have been extensively used as supporting materials for the above-mentioned metal ions. However, up to now, KMnO supported on silica-alumina is the most important adsorbent in use worldwide. In this work, we have synthesized various materials by using sodium metasilicate and sodium aluminate, and found that their ethylene adsorption capacity was not only related to the KMnO$_4$ content, but also to the Si/Al molar ratio and the process used for the fabrication of the support.

Experimental Section

Sodium metasilicate (Acros Organics Co.) solution is mixed with sodium aluminate (Kanto Chemical Co.) solution to produce the silica-alumina carrier by adding an appropriate amount of sulfuric acid to render the pH of the solution neutral. After filtration, followed by drying the deposit or further calcining it at 550 °C for 4 hours, KMnO$_4$ solution was added and then the water was evaporated while stirring to obtain the powdered samples. Four samples were produced with different Si/Al ratios using different production processes. Table 1 lists the sample preparation details and the data for the ethylene adsorption. XRD was measured by Rigaku D/MAX-3B diffractometer for which Cu-Kα radiation is employed. SEM images were obtained by Jeol JSM840-A microscope. The difference between SA181 and SA182 is only in the drying process of their supports, and the difference between SA175 and SA176 is the use of calcination. Catalytic removal tests were carried out at 20-22 °C in a stainless steel column (i.d. 8 mm; length, 300 mm) fitted to a GC (HP5890) with FID. In the middle of column, 0.8 g of catalyst in the form of powder was placed. The total flow rate of gas (2000 ppm ethylene balanced with air) was adjusted to 10 mL/min. Water vapor was supplied via bypass route to feed gas prior to its reach of the reactor, where the relative humidity is about 40-50%. The peak areas of GC were integrated using HP Chem Station Revision A.09.03 software.

Results and Discussion

The SEM image in Figure 1(a) (SA175) is different from that of Figure 1(b) (SA176). The image of SA176 shows that it has a very loose structure and a more developed porosity compared with SA175, which allows the former to be impregnated with KMnO$_4$ easily and consequently, the KMnO$_4$ should be dispersed on the surface of or incorporated into SA176 evenly. However, in the case of SA175, the KMnO$_4$ was only dispersed on its surface loosely, and the KMnO$_4$ particles are almost separated from the support. Moreover, the larger particle size results in a relatively slow removal rate and low removal quantity. Broad peaks centered at $2\theta = 14.5, 28.0, 38.3, 49.1$ were observed from the

Table 1. Preparation parameters of varous catalysts and their catalytic activity for ethylene oxidation

Sample Name	Starting materials	Si/Al	Drying temp. (°C)	Calcin. cond.	KMnO$_4$ Content (%)	Removal quantity[a]
SA175	Na$_2$SiO$_3$ + NaAlO$_2$	1:5	110	550 °C, 5 h	15.7	5.38 (77.4%)*
SA176	Na$_2$SiO$_3$ + NaAlO$_2$	1:5	110	No	18.2	7.91 (97.8%)*
SA181	Na$_2$SiO$_3$ + NaAlO$_2$	30:1	30	No	20.1	1.90 (21.3%)*
SA182	Na$_2$SiO$_3$ + NaAlO$_2$	30:1	110	No	19.2	3.82 (44.8%)*

*The KMnO$_4$ utility efficiency is calculated according to the reaction stoichiometry: C$_2$H$_4$ + 4MnO$_4^-$ − 4H$^+$ = 2CO$_2$ − 4MnO$_2$ + 4H$_2$O. [a]The figures in parentheses mean the utilization degree of KMnO$_4$.
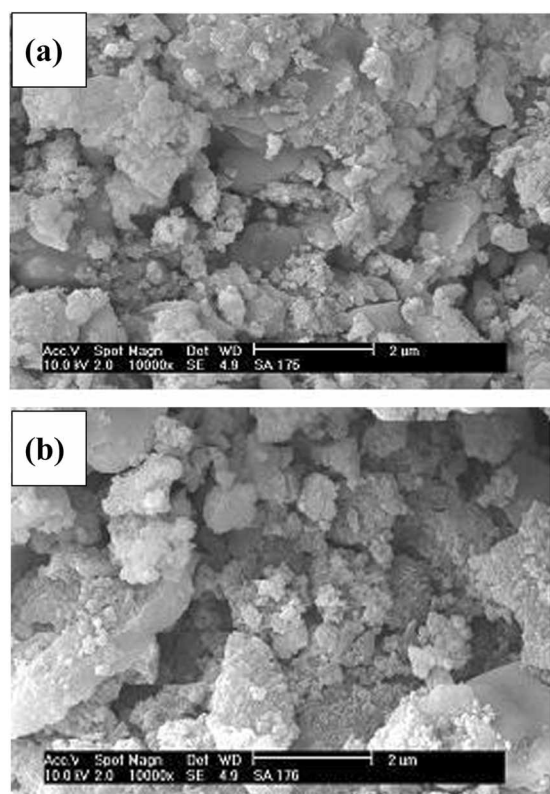
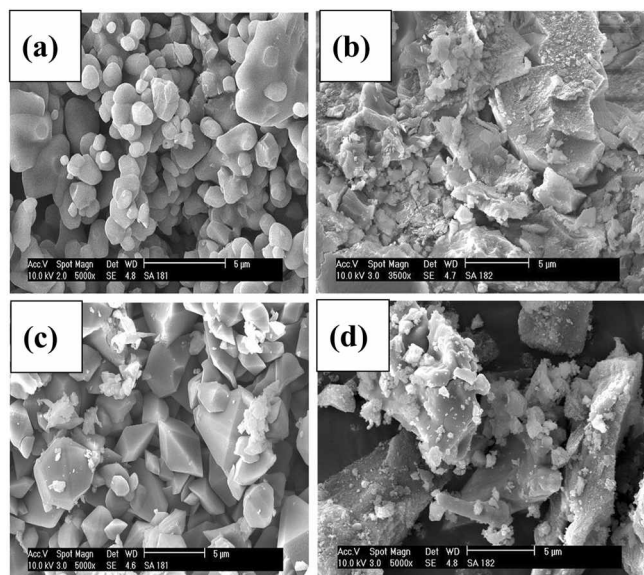**Figure 1**. SEM images of (a) SA175 and (b) SA176.

Figure 2. SEM images of (a) support of SA181, (b) support of SA182, (c) SA181 and (d) SA182.

XRD pattern of SA175 indicating the formation of silica-alumina. As shown in Figure 2, the SEM image of support of SA181 is different from that of SA182. The particles of the support of SA181 show spheroid, ellipsoid and other anomalous shapes with different sizes, and a slippery surface. These kinds of particles make it difficult for a large amount of KMnO₄ to be evenly employed. The particles of support of SA182 have multifarious sizes and a rough
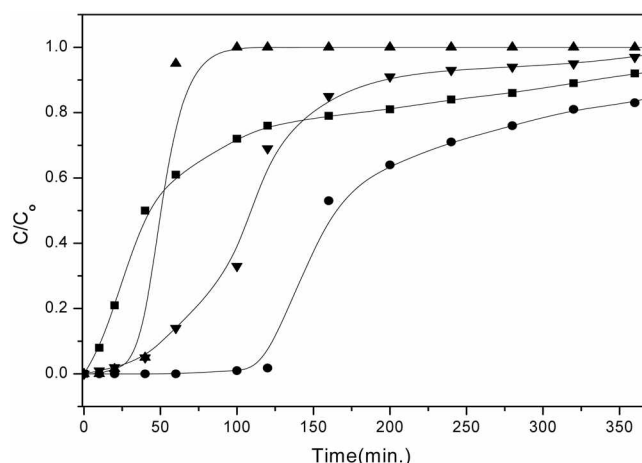

Figure 3. The breakthrough curves of ethylene oxidation by SA175, SA176, SA181 and SA182 at an ethylene flow rate of 10 mL/min. ■ SA175, ● SA176, ▲ SA181 and ▼ SA182. C₀ and C indicate ethylene concentration before and after reaction, respectively.

surface on which the KMnO₄ should be dispersed well. After their impregnation with KMnO₄, the difference between SA181 and SA182 was more obvious. Some phase transformation took place during the impregnation of KMnO₄ over SA181, because crystalloids with a very slippery surface were observed in the SEM image of SA181 (Fig. 2(c)) which was not found in the image of the carrier of SA181(Fig. 2(a)). Also, it was clearly observed that the KMnO₄ particles in SA181 were separated from these crystalloids. Therefore, the ethylene removal efficiency of SA182 was higher than that of SA181 (see Table 1), and the KMnO₄ utility efficiency of SA182 (44.8%) was about two times higher than that of SA181 (21.3%). Therefore, it can be inferred that drying at 110 °C in an oven is better than drying at room temperature (SA181 *vs.* SA182) or calcining at 550 °C (SA175 *vs.* SA176). Further comparisons among these catalysts clearly demonstrate that the differences between them are not only limited to their adsorption quantities, but also concern their removal efficiencies. The utilization degree of KMnO₄ of SA175 and SA176 are higher than those of SA181 and SA182. In particular, all of the ethylene adsorption quantities and KMnO₄ utilization efficiency of SA175 and SA176 are more than two times higher than those of SA181 and SA182, which indicates that the Si/Al ratio has a very strong effect on the catalytic activity.

The ethylene abatement efficiency can be clearly understood by studying the breakthrough curves. Figure 3 shows the breakthrough curves of SA175 and SA176 at an ethylene flow rate of 10 mL/min. No ethylene signal was obtained over SA176 until the reaction time was up to 100 min. However, ethylene was detected during the first 10 min over SA175. Therefore, the ethylene removal efficiency was much higher when SA176 was used than when SA175 was used. The contrast between SA181 and SA182 was not as evident as that between SA175 and SA176. At the ethylene flow rate of 10 mL/min, the ethylene removal efficiency and

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Notes

oxidized ethylene quantity over SA182 was higher than that over SA181, but the ethylene signal was detected within 30 min in all of the ethylene oxidation experiments for both samples. As shown in Figure 3, although the ethylene removal capacity of SA182 is higher than that of SA181, the breakthrough curve obtained using SA182 is not lower than that obtained using SA181 during the first 30 min. However, after 30 min, the breakthrough curve obtained using SA181 increases rapidly, and reaches a maximum within 60 min, and the data of the gas signal show that the C/C_o ratios were 0.9929 and 1.000 at the retention times of 60 min and 80 min, respectively.

Conclusion

The ethylene removal efficiency of the $KMnO_4$ based catalysts was strongly affected by the $KMnO_4$ supports which were made using different methods and processes. When the support was made from the mixture of silicate and aluminate sources, the Si/Al ratio, drying process and calcination conditions were found to have a strong effect on their activities. If a wrong method or process was used to synthesize the carrier, it was not possible to obtain a desirable ethylene removal catalyst with high performance, even though the $KMnO_4$ content was high.

References

1. Jin, X.; Jin, X.; Yi, X. *CN Patent* **2000**, 1,364,656.
2. Alvarez, J. B.; Garcia, P. A. *US Patent* **1990**, 4,906,398.
3. Shy, L.; Smith, B.; Eyde, D. *WO Patent* **2005**, 000,369.
4. Kunugiza, T. *JP Patent* **1990**, 02,131,536.
5. Yasuda, M.; Fukunaga,T.; Abe, K. *JP Patent* **1990**, 02,126,935.
6. Sohn, J. R.; Lee, S. H.; Park, W. C.; Kim, H. W. *Bull. Korean Chem.* **2004**, *25*, 657.
7. Maruoka, T.; Maeda, S.; Matsushita, M. *JP Patent* **1989**, 01,148,341.
8. Yang, R. T.; Padin, J.; Rege, S. U. *US Patent* **2002**, 6,423,881.
9. Yamada, S.; Takahashi, K. *JP Patent* **1988**, 63,229,118.
10. Horii, I.; Kuroda, I. *JP Patent* **1990**, 02,004,443.
11. Park, J. N.; Lee, C. W.; Chang, J. S.; Park, S. E.; Sin, C. H. *Bull. Korean Chem.* **2004**, *25*, 1355.
12. Frauchiger, U.; Pfenninger, A. *Eur. Patent Appl.* **2005**, 1,525,802.
13. Seto, T.; Yokoyama, S. *JP Patent* **1990**, 02,172,534.
14. Drean, H. L. *WO Patent* **2000**, 064,577.
15. Hirota, M. *JP Patent* **2002**, 333,266.
16. Ogawa, M.; Matsumoto, M.; Takai, T.; Suzuki, M. *JP Patent* **1989**, 01,279,075.
17. Liu, Y.; Wu, Z.-b.; Su, Y. *Gaoxiao Huaxue Gongcheng Xuebao* **2000**, *14*, 426.
18. Wu, Z.; Han, S.-S.; Cho, S.-H.; Kim, J.-N. *Ind. Eng. Chem. Res.* **1997**, *36*, 2749.
19. Holland, R. V. *WO Patent* **1991**, 9,104,292.
20. Liu, Z. X.; Park, J. N.; Abdi, S. H. R.; Park, S. K.; Park, Y.-K.; Lee, C. W. *Top. Catal.* **2006**, *39*, 221.