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RESEARCH NOTE

Epoxidation of Propylene on NaCl-Modified $VCe_{1-x}Cu_x$ Oxide Catalysts with Direct Molecular Oxygen as the Oxidant

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NaCl-modified VCe_xCu_{1-x} mixed oxide catalysts were found to be effective for propylene epoxidation using molecular oxygen as the oxidant. Hydrogen addition in the feedstock can significantly enhance the PO selectivity and the stability of the catalyst. XPS results also show that Cu^0 may be the active phase for epoxidation.

Key Words: **propylene; epoxidation; Cu catalyst; propylene oxide; XPS.**

INTRODUCTION

Production of propylene oxide (PO) on heterogeneous catalysts with oxygen as oxidant has been attracting both academic and industrial interest. Until now, the major conventional manufacturing methods of PO are the chlorohydrin process and the Halcon process. The chlorohydrin process causes serious environmental pollution, while the latter has the coproduct limitation. Many studies focus on producing PO with novel methods, for example the TS-1/H_2O_2 system (3) and *in situ* generated hydrogen peroxide systems such as palladium- or palladium/platinum-supported titanium silicalite (4, 5), as well as gold supported on titania (6). However, the ideal process is epoxidation of propylene with molecular oxygen. Since the vapor-phase epoxidation of ethylene to its epoxide on silver catalysts was commercialized several decades ago, many attempts have been made to produce PO on silver catalysts, but the PO selectivity is usually very low (1, 2). Recently, modified silver catalysts (7) and Ti-modified silicalites (8) were found to be active for direct epoxidation of propylene. Also, with surface science technology, copper has been found to be a highly effective catalyst for the epoxidation of olefins (9, 10). However, epoxidation on practical Cu catalysts has not been investigated. So, it is necessary to find a new approach to catalysts other than silver and Ti–silicalite for propylene epoxidation.

In the present study, we report that NaCl-modified VCe_xCu_{1-x} catalysts are quite effective for propylene epoxidation. They may be a potential alternative to silver catalysts. It is also found that H_2 addition in the feedstock can significantly improve the PO selectivity and the stability of the Cu catalyst.

EXPERIMENTAL

VCe_xCu_{1-x} ($x = 0$–1.0) mixed oxide was prepared by the sol–gel method. Citric acid was added to the V_2O_5 suspension in distilled water under heating until the $V_2O_5$was totally dissolved. Then a mixed solution of $Ce(NO_3)_3 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ with a certain molar ratio was added. Then citric acid with equimolar amounts of the metal ions was added to the mixture. Under continuous heating and stirring, the solution slowly gelled. The gel was dried at 120°C for several hours, then calcined at 500°C for 4 h. The NaCl-modified catalyst was prepared by impregnating the as-prepared mixed oxide with the NaCl solution. After being dried at 120°C for 12 h, the catalyst was calcined at 400°C for 3 h, then reduced by H_2 at 300°C for another 2 h. Cu–NaCl(20) catalyst was prepared by thermal decomposition of $Cu(NO_3)_2 \cdot 3H_2O$ to CuO, then impregnated with NaCl. All the catalysts were reduced by H_2 at 300°C for 2 h.

The catalytic epoxidation of propylene was carried out in a microreactor system under atmospheric pressure. Air was used as oxidant. Before reaction, the catalyst was reduced by H_2 for 30 min at 250°C. Reaction products were analyzed with online GC analysis. Two GCs were used: a GC920 with an FID detector and PEG-20M capillary column and a GC7890II with a TCD detector and Porapak Q packed column, the PEG-20M with 30°C as initiate temperature and Porapak Q with 60°C. The method of carbon balance was used.

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TABLE 1

Effect of Different Catalysts on Catalytic Performance

Catalyst	Propylene conv. (%)	PO formation rate (μmol g^{-1} h^{-1})	Selectivity (%)				
			Aldehyde	PO	Acetone	Acrolein	CO$_x$
Cu–NaCl(20)	1.50	0	0	0	0	73.6	26.4
VCe–NaCl(20)[a]	0	0	0	0	0	0	0
VCe$_{0.98}$Cu$_{0.02}$–NaCl(20)	0.30	41.4	18.5	6.9	17.1	27.4	30.1
VCe$_{0.9}$Cu$_{0.1}$–NaCl(20)	0.70	119.3	20.5	8.6	9.9	25.3	36.2
VCe$_{0.5}$Cu$_{0.5}$–NaCl(20)	0.26	165.3	10.1	32.6	18.6	12.8	25.9
VCe$_{0.2}$Cu$_{0.8}$–NaCl(20)[b]	0.19	162.5	5.6	43.4	11.1	18.2	21.7
VCu–NaCl(20)	0.19	85.6	0	22.9	0	26.6	50.5
VCe$_{0.2}$Cu$_{0.8}$	0.22	21.5	8.4	5.0	0	56.7	29.9
VCe$_{0.2}$Cu$_{0.8}$–NaCl(20)[c]	0.32	0	5.1	0	0	58.3	36.6
CeCu–NaCl(20)	0.60	77.3	0	6.5	0	18.3	75.2

Note. Reaction temperature, 250°C; $C_3H_6 : O_2 = 10 : 1$; S.V. $= 1.5 \times 10^4$ h^{-1}.

[a] NaCl loading (weight percent) referred to the VCe catalyst.

[b] The number in parentheses is the NaCl loading (weight percent) referred to Cu.

[c] Not reduced by H_2.

RESULTS AND DISSCUSION

The catalytic performances on the mixed oxide catalysts are summarized in Table 1. For the Cu–NaCl(20) catalyst, no PO is formed; acrolein with 73.6% selectivity is the only organic product. Since the metallic Cu is easily oxidized and the cuprous oxide is active for the oxidation of propylene to acrolein (11), it is possible that the Cu species in Cu–NaCl(20) becomes cuprous oxide under reaction conditions. The VCe–NaCl(20) catalyst is not active for the reaction, and as a result, little CO$_x$ is produced. For the VCe$_{1-x}$Cu$_x$–NaCl(20) family, it is found that catalytic performance is strongly dependent on the Cu content in the catalysts. With Cu added to the mixed oxide, the catalyst shows the activity and selectivity necessary for the epoxidation. For VCe$_{0.98}$Cu$_{0.02}$–NaCl(20), PO is formed although the selectivity is low (6.9%), and the main product is CO$_x$. When the Cu content in the catalyst increases, the PO formation rate and selectivity to PO rise significantly. For VCe$_{0.9}$Cu$_{0.1}$–NaCl(20), 8.6% PO selectivity and 119.3 μmol g^{-1} h^{-1} PO formation rate are obtained, while for VCe$_{0.5}$Cu$_{0.5}$–NaCl(20), PO selectivity is 32.6%. The PO selectivity reaches its maximum (43.4%) for VCe$_{0.2}$Cu$_{0.8}$–NaCl(20). These results imply that the added Cu in VCe$_{1-x}$Cu$_x$ is the active phase for propylene epoxidation; moreover, the active Cu species is relatively more stable than that in Cu–NaCl(20). A further increase in Cu content results in a drop in PO production. VCu–NaCl(20) gives 22.9% PO selectivity. CeCu–NaCl(20) catalyst also shows activity to the propylene epoxidation; however, the PO selectivity is low (6.5%), possibly due to total oxidation of propylene on CeO$_2$. It can be deduced that the coexistence of V and Ce in the catalyst plays an important role in epoxidation. In the absence of either V or Ce, the separated CuO/V$_2$O$_5$ or CuO/CeO$_2$ is formed.

The unpromoted VCe$_{0.2}$Cu$_{0.8}$ catalyst produces some PO, but with much lower PO selectivity (5.0%), while 56.7% acrolein selectivity is obtained. Compared with VCe$_{0.2}$Cu$_{0.8}$–NaCl(20), NaCl is a more effective promoter for epoxidation. For the unreduced VCe$_{0.2}$Cu$_{0.8}$–NaCl(20) catalyst, no PO is produced, and only 58.3% selectivity to acrolein is obtained. Since the Cu species exists as Cu^{2+} or Cu^{+} in the unreduced catalyst, it can be deduced that the reduced Cu species is responsible for epoxidation.

It seems that keeping the Cu species in its low valence is very important for propylene epoxidation, and addition of H$_2$ in the feedstock should have some positive effects. Figure 1 shows the effect of H$_2$ on catalytic performance. Without hydrogen in the feedstock, PO selectivity increases in the first 45 min, which suggests that an induction period is needed. PO selectivity reaches a maximum (62.2%) at 45 min, after which it declines dramatically; in the meantime, the selectivity to acrolein rises. This may be caused by the further oxidation of Cu species to its higher valence state. PO selectivity remains stable (25.8%) after the reaction for 4 h. Since propylene occurs in large excess in the feedstock and is also a reducing agent, the stable PO selectivity may result from the balanced Cu surface oxidized by O$_2$ and reduced by propylene.

With $C_3H_6 : O_2 : H_2 = 10 : 1 : 1$, there is also an induction period, as in the nonhydrogen mixture. The maximum PO selectivity (77.8%) is higher than in that without H$_2$. Although the PO selectivity drops slightly after 45 min, it remains stable at ca. 70% for 9 h. In the case of Au/TiO$_2$ or Pt/TS-1 systems, a H$_2$/O$_2$ mixture is a prerequisite for the reaction; the peroxide species form during the H$_2$/O$_2$ interaction with the catalyst, leading to PO production. In this case, PO can be produced even without any hydrogen; addition of hydrogen can increase the PO selectivity. A separate experiment shows that with $C_3H_6 : O_2 : H_2 = 10 : 1 : 0.4$, the PO selectivity is lower than that with $C_3H_6 : O_2 : H_2 = 10 : 1 : 1$ and it declines with time on stream; however, the decline is much slower than with $C_3H_6 : O_2 = 10 : 1$. Compared to propylene, H_2 has a stronger reducing capability; the role of H_2 in the feedstock is to keep the Cu species at its low valence.

In order to confirm the Cu state in the catalyst, XPS spectroscopy was employed. Figure 2 lists the Cu $2p_{3/2}$ spectroscopies of $VCe_{0.2}Cu_{0.8}$–NaCl(20) under different conditions. For the unreduced catalyst, Cu $2p_{3/2}$ could be deconvoluted into two contributions, with binding energies of 933.1 and 935.3 eV. The former can be assigned to Cu^{2+} (12, 13), and the latter may be related to another state where Cu species coordinate with V and Ce. Also, the oxidized Cu species could be identified by the satellite peaks at 941.7 and 944.1 eV (14). After reduction by hydrogen at 300°C for 2 h, the disappearance of the satellite line and the simultaneous shift of the principle Cu $2p_{3/2}$ peak to a lower binding energy (932.8 eV) show that the copper species is reduced Cu^0. However, since the binding energies of Cu^+ and Cu^0 are very close, the peak at 932.8 eV may also contain some influence of Cu^+. After a 1-h reaction without any hydrogen in the feedstock, the principle peak can be apparently split into two peaks, with binding energies of 932.8 and 934.9 eV, where the latter can be assigned to oxidized copper species. Considering the reappearance of the satellite peak at 941.8 eV, it can be deduced that the oxidation of Cu^0 species occurred. In the meantime, the fact that acrolein selectivity rose after the 1-h reaction indicates that although the Cu^0 species still exists in the catalyst, the concentration of the Cu^+ species increased compared to the reduced one.

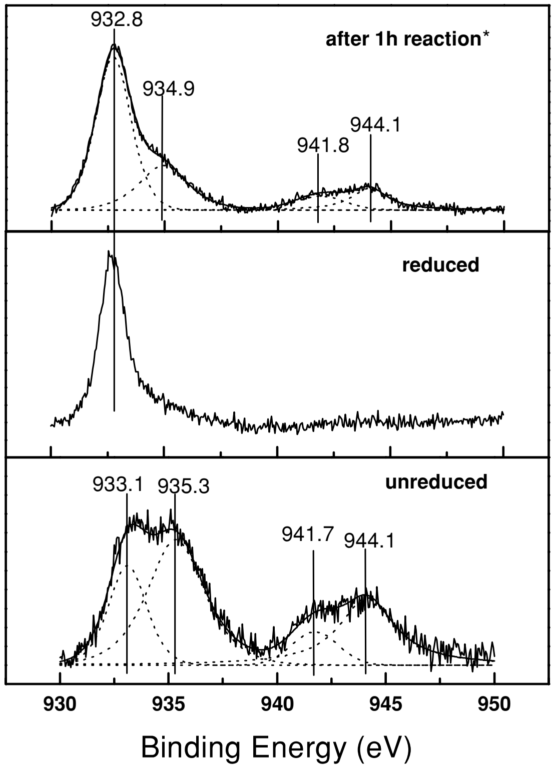

FIG. 2. XPS spectra of Cu 2p of $VCe_{0.2}Cu_{0.8}O$–NaCl(20) catalysts. *, 215°C reaction temperature; $C_3H_6 : O_2 = 10 : 1$; S.V. $= 6.0 \times 10^4\ h^{-1}$.

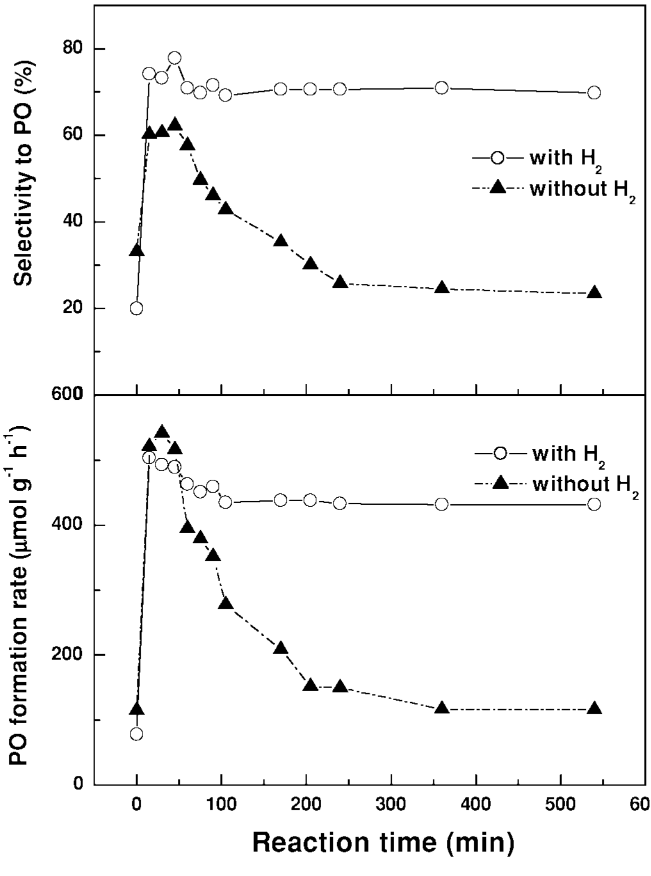

FIG. 1. Effects of H_2 addition on the catalytic performance of $VCe_{0.2}Cu_{0.8}$–NaCl(20) catalysts. Reaction temperature, 215°C; $C_3H_6 : O_2 : (H_2) = 10 : 1 : (1)$; S.V. $= 6.0 \times 10^4\ h^{-1}$.

CONCLUSION

In conclusion, NaCl-modified $VCe_{1-x}Cu_x$ catalysts are active and selective for propylene epoxidation using molecular oxygen as the oxidant. H_2 in the feedstock can increase the PO selectivity and keep the catalyst stable. The effect of H_2 is that it can reduce the Cu species and keep it at its low valance. Under certain reaction conditions, 70% PO selectivity is obtained for $VCe_{0.2}Cu_{0.8}$–NaCl(20) catalyst. XPS data of Cu $2p_{3/2}$ indicate that Cu^0 may be the active phase for propylene epoxidation. However, given the induction period in the reaction, it is possible that a proper intermediate state of oxidation is required.

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