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Direct Conversion of Ethane to Ethylene Oxide over Ni–Ag–O Catalyst

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Ethylene oxide was directly synthesized by oxidation of ethane over Ni–Ag–O catalyst with ethane conversion of 10% and ethylene oxide yield of 1.2% at 310 °C. NiO_x and Ag in the catalyst favor ethane activation and the formation of ethylene oxide, respectively.

Since ethylene oxide (EO) is a raw material for glycol, polymer, and many chemical products,[1,2] the epoxidation of ethylene to EO is industrially important.[3,4] The industrial process is carried out exclusively using silver catalysts supported on inert alumina from feed ethylene.[5,6] On the other hand, ethylene is mainly produced by the thermal pyrolysis of ethane or naphtha, a process that operates under severe conditions, which is highly energy consuming.[7,8] Thus it would be desirable to have a method by which ethylene oxide could be directly synthesized via a one-step reaction from ethane under mild reaction conditions.

Although the oxidative dehydrogenation of ethane to ethylene in the presence of a suitable catalytic material constitutes the most attractive alternative to steam cracking, the reaction temperature is generally not lower than 400 °C.[9–12] For the epoxidation of ethylene to ethylene oxide, however, such a high reaction temperature easily causes further oxidation of product to CO_x. It obstructs the probability of combining the two reactions, namely, oxidation dehydrogenation of ethane to ethylene and epoxidation of the intermediate ethylene to ethylene oxide.

In our previous work, nanosized NiO exhibited considerable low-temperature catalytic performance for oxidative dehydrogenation of ethane to ethylene below 300 °C.[13] The adsorptive electrophilic oxygen species was considered to be the active species involved in the reaction, which differs from the reduction of transition-metal oxide over other bulk catalysts.[14]

Herein we report on a one-step reaction that ethylene oxide is directly synthesized by oxidation of ethane over NiO-doped Ag catalyst (Ni–Ag–O).

Ni–Ag–O catalyst was prepared by a hydrothermal method using $Ni(NO_3)_2 \cdot 6H_2O$ and $Ag(NO_3)_4 \cdot 5H_2O$. The selected molar ratio of Ni to Ag was 1/19 by the investigation of the dependence of catalytic behavior on Ni content. Stoichiometric urea solution was added to the mixture solution of nickel and silver nitrate. The mixture was transferred into a Teflon-lined stainless steel autoclave and aged at 100 °C for 20 h. The resulting solid was filtered and washed with deionized water and absolute ethanol. Then it was dried at 110 °C for 10 h, followed by calcination at 400 °C for 4 h in air. For comparison purposes, pure NiO and Ag were prepared by the same method.

The XRD patterns of these samples (not shown) indicate that broader diffraction peaks corresponding to NiO are observed on the pure NiO sample, suggesting small particle size and large surface area, which is consistent with SEM observation and BET result, respectively. XRD patterns of the fresh and used Ni–Ag–O catalysts only show the presence of large Ag particles, but no peaks related to NiO was observed, owing to low content or high dispersion.

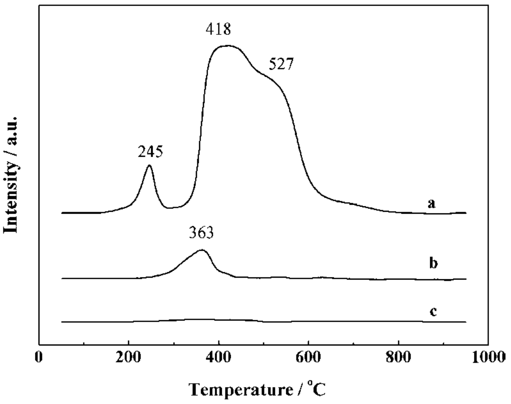

Figure 1. H_2-TPR profiles of the catalysts: (a) NiO, (b) Ag–Ni–O, (c) Ag.

Figure 1 shows H_2-TPR profiles of the catalysts. The profile of pure NiO catalyst shows two main reduction peaks at 245 and 418 °C, attributed to reduction of Ni_2O_3 to NiO and NiO to Ni, respectively. A shoulder peak at 527 °C might be ascribed to the reduction of NiO of different size. For Ni–Ag–O catalyst, only a small reduction peak at about 363 °C is observed, which corresponds to the reduction of NiO_x which interacts with Ag. This result indicates that the addition of Ag decreased the reduction of NiO_x. There is no detection of any XRD peaks that could be related to phases of solid solution of Ag and NiO_x. This is probably a result of the very low extent of metal ion infiltration. Nevertheless, it can be speculated that NiO_x has interaction with Ag by hydrothermal method from TPR results.

The catalytic test was carried out in a fix-bed quartz tubular reactor, using 0.1 g of the catalyst. A gas mixture of 12.5% ethane, 12.5% oxygen, and 75% nitrogen passed through the catalyst bed, with a flow rate of $40\,mL \cdot min^{-1}$. The reactants and products were analyzed using an on-line gas chromatograph equipped with a TCD detector attached with a porapak Q and a 5 Å molecular sieve column.

Table 1 lists the catalytic activities of the catalysts at 290 °C. It is found that the pure Ag catalyst was ethane inactive from the reaction. At the reaction temperature over Ag catalyst C_2H_4 could be epoxidized to ethylene oxide. It is known that catalysts based on Ag are effective for ethene to ethylene oxide. The adsorption electrophilic oxygen species on the catalyst was thought to be the epoxidative species of the C=C double bond. Nevertheless, the species cannot activate the C–H bond of ethane. The oxygen species on the surface of NiO catalyst is more active

Table 1. Catalytic performance of the catalysts for ethane oxidation[a]

Catalyst	Conv./%	Sel./%			Yield/%
	C_2H_6	C_2H_4O	C_2H_4	CO_2	C_2H_4O
NiO	20.8	—	42.5	57.5	—
Ag	—	—	—	—	—
NiO + Ag[b]	17.5	—	6.8	93.2	—
Ni–Ag–O	6.2	13.1	10.1	76.8	0.8

[a]Reaction conditions: $T = 290\,°C$, O_2:C_2H_6:N_2 = 1:1:6. [b]Mixture of NiO and Ag.

toward ethane and oxidative dehydrogenation reaction occurs. Over pure NiO catalyst only C_2H_4 and overoxidation product, CO_2, were obtained without any ethylene oxide. When a mechanical mixture of NiO and Ag is used as the catalyst, it showed similar C_2H_6 activity as the pure NiO catalyst, but with lower C_2H_4 selectivity and no C_2H_4O is product. It is obvious that the process directly from ethane to ethylene oxide cannot be realized just by mechanically mixing NiO and Ag catalysts.

Unlike the pure NiO or the mixed NiO + Ag, over the Ni–Ag–O C_2H_4O was produced along with C_2H_4 and CO_2 as the products of ethane oxidation. NiO_x in Ni–Ag–O is crucial in the activation of ethane, despite of its low content. The dehydrogenation product, C_2H_4, was epoxidized on the surface of Ag. On the other hand, Ag which has interaction with NiO_x plays a key role in separation of NiO_x and, therefore, prevents further oxidation of C_2H_4O to some extent.

Figure 2 presents the catalytic performance of ethane oxidation over Ni–Ag–O catalyst with different reaction temperatures. It is found that ethane conversion increases with increasing reaction temperature, while the C_2H_4O selectivity decreases. The maximum ethylene oxide yield of 1.2% is obtained at 310 °C with ethane conversion of 10.2%. The stability of Ni–Ag–O catalyst was investigated at constant reaction conditions (T = 310 °C) for 48 h. Ethane conversion and ethylene oxide yield maintained their initial values for the entire time span of the experiment, which indicates the high stability of the catalyst.

The effect of contact time on the catalytic performance of Ni–Ag–O catalyst is also investigated. The results shown in Figure 3 indicate that the shorter contact time favors the selectivity to C_2H_4, whereas that to C_2H_4O increases with increasing contact time. However, with further increasing contact time (>0.15 s·g·mL^{-1}) the C_2H_4O is further oxidized to CO_2, and C_2H_4O selectivity decreases again. This observation suggests that C_2H_4 is probably the primary products, with C_2H_4O as the secondary products from the consecutive oxidation of C_2H_4 over the Ni–Ag–O catalyst.

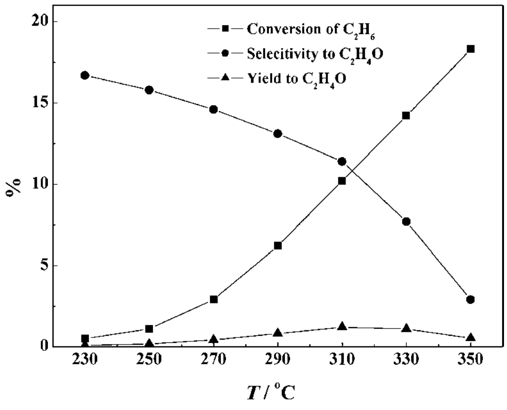

Figure 2. Catalytic performance of Ni–Ag–O catalyst with reaction temperature.

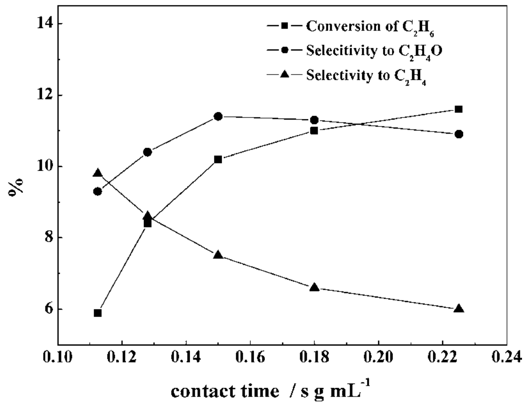

Figure 3. Effect of contact time on the performances of Ni–Ag–O catalyst (Reaction temperature: 310 °C).

In summary, ethylene oxide could be directly synthesized from ethane over Ni–Ag–O catalyst, with ethane conversion of 10% and ethylene oxide yield of 1.2% at 310 °C. The decreased reduction of NiO_x in catalyst suggests that there is an interaction between NiO_x and Ag, which contributes to the separation of active sites on the NiO_x surface and the formation of ethylene oxide. Further research is in progress.

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