[Note]

Aerobic Oxidation of Propene over Amorphous Zirconia Impregnated with Titanium Sulfate

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Direct propene oxidation with molecular O₂ was performed at 428 K under atmospheric pressure over titanium sulfate-modified zirconia (STi/Z) and sulfated-zirconia (SZ) catalysts, which were prepared by direct impregnation of Ti^{IV} sulfate and ammonium sulfate solution onto amorphous zirconia, respectively. The 7.5%STi/Z catalyst exhibited the highest propene conversion (5.6%) under the experimental conditions. C₃-Oxygenates such as propene oxide (PO) and acetone were detected as products with C₄-C₆ hydrocarbons. The catalytic performances depended on the amounts of surface sites for NH₃ adsorption, which could be associated with sulfate content, calcination temperature and reaction time. Molecular oxygen forms oxygenates, and reduces carbonaceous deposits.

1. Introduction

Direct propene oxidation with molecular oxygen to form oxygenated products such as propene oxide is of growing interest, but few studies have investigated these oxidation reactions at moderate temperature (< 473 K) with O₂, in the absence of co-feed or pre-adsorbed reactive compounds such as H₂, H₂O₂, NO_x, MeOH, etc. Propene conversion is in the range of 0.4 to 1.9% over catalysts containing 0.1–30 wt% of nitrates or nitrites of alkali, alkali-earth and silver, supported on Me-silicate (Me: Ti, Ga, Cr, Zr, V, and Ni)^{1)–3)}; acidic compounds such as nitrate and chloride could be important in propene activation in such reactions.

Our research program on oxidation or oxidative dehydrogenation of lower hydrocarbons has already showed the excellent performance of Li-doped sulfated zirconia in the oxidative coupling of methane⁴⁾ and oxidative dehydrogenation of ethane⁵⁾. These findings stimulated the use of zirconia-based catalysts for propene oxidation with gaseous oxygen. This study investigated the catalytic performances of sulfated-zirconia (SZ)^{6),7)} and titanium sulfate-modified zirconia (STi/Z) for the aerobic oxidation of propene.

2. Experimental

Amorphous zirconia (Z) and sulfated-zirconia (SZ) were prepared according to a method previously described⁴⁾. Z was impregnated with ammonium sulfate (6 wt%), followed by drying and calcination at 773

K for 3 h to form 6%S-773/Z catalyst. STi/Z catalysts were obtained by impregnation of Z with the desired amounts (*x*: 5.5% or 7.5 wt%) of Ti(SO₄)₂ solution (30%). Then, the sample was dried and calcined in air at high temperature (θ : 773 K or 973 K) for 3 h. This method provided catalysts of the formula *x*STi- θ /Z, (STi as Ti(SO₄)₂). In addition, Ti-modified Z was prepared by impregnation of Z with Ti(O-*i*Pr)₄ in isopropanol (with about 1 cm³ H₂O) for 5 h at 343 K and finally calcined at 773 K for 3 h to give 1.5%Ti-773/Z. All chemicals were purchased from Wako Pure Chemical Industries, Ltd.

Adsorption-desorption of ammonia was carried out using Multitask TPD (Bel Japan, Inc.) automatically monitored and equipped with a quadrupole mass spectrometer for ammonia species detection. The sample was pretreated at 773 K for 1 h under He flow (50 ml min⁻¹). Then, after cooling to 373 K, ammonia adsorption onto the surface was achieved by pulse injection to saturation, followed by 1 h evacuation. The value *m/z* = 16 was assumed as the most representative mass of NH₃ fragmentation in the ionization chamber. TPD was run from 373 to 1073 K (8.8 K min⁻¹).

Catalytic activity was measured under atmospheric pressure at 428 K or 523 K. A tubular fixed-bed reactor (*OD* = 1.25 cm, *L* = 60 cm) was filled with 1.5 g of catalyst powder and quartz sand (4.6 g/g catalyst). Pretreatment was carried out at 398 K under N₂ flow (45 ml min⁻¹) for 1 h. The reactant feed was C₃H₆/O₂/He = 33/13.2/53.8 (vol%). Hydrocarbons and oxygenated compounds were detected by FID with a Shimadzu GC-8A on Porapak T column kept at 403 K.

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Fig. 1 Typical NH₃-TPD Curve for 7.5%STi-773/Z Catalyst

Propene, permanent gas, and CO_x were detected by TCD, using a Shimadzu GC 14B equipped with Porapak Q and molecular sieves MS-5A columns (383 K). The reaction products were also analyzed by mass spectrometer. Initial activities of catalysts were checked by GC analyses started 2-6 min after reaching the reaction temperature. The conversion and the selectivity were estimated on the basis of the number of carbon atoms in compounds: Conversion(%) given by $10^2(\sum \alpha_i P_i)/3N_0$; Selectivity(%) for a product i given by $10^2(\alpha_i P_i)/\sum \alpha_i P_i$. The yield (%) is $10^{-2}(\text{Conversion} \times \text{Selectivity})$. The factors N_0 , P_i and α are the propene amount flowed into the reactor, the partial pressure and the number of carbon in a product i .

3. Results and Discussion

Figure 1 illustrates a typical thermogram of ammonia desorption for 7.5%STi-773/Z catalyst. The effective ammonia desorption took place between 373 K and 948 K. The total amounts of NH₃ adsorption of the studied catalysts (**Table 1**, column (373-948 K)) were

in the order: 7.5%STi-773/Z > 5.5%STi-773/Z > 6%S-773/Z > 5.5%STi-973/Z > Z > 1.5%Ti-773/Z. **Table 1** also exhibits the amount of NH₃ adsorbed at temperatures between 550 K and 948 K (column (550-948 K))*¹⁾. However, the order of the amounts are approximately the same as that of the column (373-948 K).

The catalytic performances are summarized in **Table 2**. No product was formed through the reactor in the absence of catalyst. Propene undergoes mono-oxygenation as well as dimerization, dimerization-cracking, and oligomerization-cracking. The products such as C₃-oxygenates (PO, acetone, *i*-PrOH), and C₄-C₆ hydrocarbons were detected by GC-analyses. However, the C₃-oxygenates such as PO and acetone were not major products and C₄-C₆ hydrocarbons predominated. Deep oxidation to CO_x did not occur at the conditions of propene/O₂ ratio of 2.5 at 428 K. Sulfate-containing catalysts were possibly active for the reaction (**Table 2**, Runs 3, 4 and 9), whereas the Z and 1.5%Ti-773/Z⁸⁾ catalysts were not active (**Table 2**, Runs 1 and 2)¹⁰⁾. The order of reactivity should be consistent with that of the amounts of NH₃ adsorbed (compare **Tables 1** and **2**). In fact, when the amounts of NH₃ desorbed increased (**Table 2**: Run 7 < Run 9 < Run 4 < Run 3), the order of propene conversion was Run 7 < Run 9 < Run 4 > Run 3 (**Table 2** and **Fig. 2**). As a result, for 7.5%STi-773/Z (**Table 2**, Run 3), the propene conversion was 5.6%, which was comparable with those previously reported at reaction temperatures below 473K*²⁾. The order of selectivity to C₃-oxygenates was Run 7 < Run 9 = Run 4 > Run 3 (**Table 2**). **Figure 3** shows the evolution of total selectivities for (C₄ + C₅), C₆, C₃-oxygenated compounds and propene conversion as a function of the contents of Ti(SO₄)₂ (STi/Z catalysts) or SO₄²⁻ (SZ catalysts). The 2%S-773/Z and 2.5%STi-773/Z catalysts favor dimer-

Table 1 Quantitative Estimation of Acid Sites on Ti-Modified SZ and SZ Catalysts by NH₃-TPD

Samples	Loaded species [wt%]		T calcination [K]	A _{BET} [m ² /g]	Amounts of NH ₃ adsorbed [μmol/m ²]	
	Ti ^{IV}	SO ₄ ²⁻			373 K-948 K ^{a)}	550 K-948 K ^{b)}
ZrO ₂	0	0	573	256	0.205	0.143
1.5%Ti-773/Z	1.5	0	773	182	0.154	0.107
7.5%STi-773/Z	1.5	6	773	117	1.367	0.726
5.5%STi-773/Z	1.1	4.4	773	175	0.446	0.244
5.5%STi-973/Z	1.1	4.4	973	110	0.293	0.160
6%S-773/Z(6SZ)	0	6	773	158	0.336	0.211

a) Total amounts of NH₃ desorbed at temperatures between 373 K and 948 K.

b) Amounts of NH₃ desorbed at temperatures between 550 K and 948 K.

*¹⁾ In order to exclude the effect of "1-peak"⁹⁾, the amounts of NH₃ adsorbed at 550-948 K was taken for convenience.

*²⁾ Generally, the conversion of propene is reported to be approximately 2% or less¹⁾⁻³⁾.

Table 2 Performances of Catalysts

Catalytic activity		Run 1	Run 2	Run 3	Run 4	Samples ^{a)}		Run 6	Run 7	Run 8	Run 9
		ZrO ₂ (Z)	1.5%Ti-773/Z	7.5%STi-773/Z	5.5%STi-773/Z <i>t</i> = 2 min ^{b)}	5.5%STi-773/Z <i>t</i> = 80 min	5.5%STi-773/Z Pretreated at 723 K	5.5%STi-973/Z	7.5%STi-773/Z Reacted without O ₂	6%S-773/Z (6SZ)	
Conversion	[%]	0	0	5.6	3.4	1	0.02	1.5	1.5	2.8	
Temperature ^{c)}	[K]	523	523	428	428	428	428	428	428	428	
Selectivities	[%]										
<i>i</i> -Butane				18.7	13.8	2.7	0	3.3	14.1	13.6	
ΣButenes ^{d)}				7.8	9	11.2	4.4	6.4	8.3	8.5	
<i>i</i> -Pentane				13.6	12.3	1	0	3.2	13	11.8	
ΣPentenes				13.2	13.8	14.3	12.2	11	16.6	16.4	
ΣC ₆				37.3	41.2	56.3	78.5	66.7	38.6	39.7	
C ₃ -oxygenates		0	0	8.8	9.1	12.4	4.7	7.7	7.7	9.1	
PO ^{e)}				5.1	5.8	7.6	3.5	3.1	4.5	5.5	
Acetone				2.2	1.7	3	—	3.5	1.6	1.9	
<i>i</i> -Propanol				1.5	1.6	1.8	1.2	1.1	1.6	1.7	
%C ^{f)}				3.1	3	1.2	—	1.4	4.5	4.5	

Reaction conditions

Catalyst: 1.5 g, C₃H₆: 10.5 ml STP min⁻¹, O₂: 4.2 ml STP min⁻¹, He balance: 16.1 ml STP min⁻¹, *P* = 1 atm.

a) S: Sulfate ions, STi: Ti sulfate (containing 20 wt% of Ti), SZ: sulfated zirconia. b) Time-on-stream at constant reaction temperature (428 K). c) Reaction temperature. d) Overall butene isomers. e) PO: propylene oxide. f) Lost carbon as deposits: shortfall of C (outlet of the reactor) compared to C atoms in the feed.

Fig. 2 Proposed Mechanism Illustrating the Possible Reactions of Propene over Titanium Sulfate-modified Zirconia (STi/Z)

ization leading to the formation of C₆. As the contents of Ti(SO₄)₂ or SO₄²⁻ are increased, oligomerization and subsequent cracking became pronounced and, thus, the selectivities to C₄ + C₅ are higher than C₆, and C₃-oxygenate formation was also increased (Figs. 3 and 2). Thus, the surface sites for NH₃ adsorption were probably effective for oligomerization and cracking of propene as well as for C₃-oxygenate formation (Fig. 2)^{6),10)}.

The activity decreased with time-on-stream (compare Table 2, Runs 4 and 5). Probably, the number of species such as hydroxyl groups, the presence of which was confirmed by *in situ* diffuse reflectance FT-IR spectra, was decreased. In fact, when the reaction was carried out on 5.5%STi-773/Z catalyst after pretreatment at 723 K under N₂ for 1 h, the propylene conver-

Fig. 3 Catalytic Performances as a Function of Loaded Sulfate Ions for SZ Catalysts or Loaded Titanium Sulfate (STi) for STi-Modified Z Catalysts

sion was extremely low (0.02%) (Table 2, Run 6). Also, the catalyst 5.5%STi-973/Z (calcined at 973 K) was found to be less active than 5.5%STi-773/Z catalyst (compare Table 2, Runs 4 and 7). With decreased activity, C₆ selectivity was increased, and C₄ and C₅ selectivities were decreased. Since thermogravimetric analysis has showed the stability of sulfate species on zirconia surface up to 873 K, the change in these activities and selectivities at 428 K could be associated with deep dehydroxylation rather than the decomposition of surface sulfate.

When the amounts of adsorbed NH₃ increased (Table 2: Runs 7, 9, 4 and 3), the selectivities for satu-

rated hydrocarbons such as isobutane and isopentane also increased, whereas selectivities for olefins decreased. Hydrogen from surface OH groups^{*3)} over the catalyst possibly participated in such alkane formation. In fact, after 80 min reaction, the selectivities to alkanes were decreased (compare **Table 2**, Runs 5 and 4). Also, the alkane selectivities were dramatically decreased after pretreatment at 723 K (**Table 2**, Run 6) or calcination at 973 K (Run 7).

Beyond the involvement of oxygen in the reaction mixture, molecular oxygen was also effective to decrease the carbonaceous deposits on the acid surface. The amounts of carbon atoms lost on the catalyst surface as coke are estimated in the **Table 2** (see bottom column). Comparing STi/Z samples, the deposits increased with the increase in surface sites for NH₃ adsorption. The reaction performed in the absence of O₂ (**Table 2**, Run 8) led to the highest carbon deposits (4.5%). Co-Feeding of O₂ with propene (see Run 3) reduced this value to 3%.

4. Summary

The present investigation of the reactivity of propene in the presence of molecular oxygen showed that STi-modified Z and SZ catalysts activate propene at 428 K. In this process, propene conversion was about 5.6%, which is comparable to previous results at reaction tem-

peratures below 473 K. The order of the activities was STi-modified Z > SZ > Ti/Z; and apparently accords with the amounts of surface sites for NH₃ adsorption, which could be associated with sulfate content, calcination temperature and reaction time. C₃-Oxygenates such as propene oxide (PO) and acetone were detected as products with C₄-C₆ hydrocarbons. Molecular oxygen contributes to oxygenates formation, and also reduces carbonaceous deposits.

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*3) The presence of the surface OH group was confirmed by *in situ* diffuse reflectance FT-IR spectra.

要 旨

硫酸チタン修飾アモルファスジルコニア触媒上でのプロペン気相酸化反応

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硫酸チタン修飾ジルコニアおよび硫酸根ジルコニア触媒を用いて、分子状酸素の存在下でプロペンの反応を 428 K、常圧で行った。用いた触媒は、それぞれ硫酸チタンまたは硫酸アンモニウムをアモルファスジルコニアに含浸して調製した。とりわけ硫酸チタン修飾ジルコニア (STi/Z) では、用いた条件下で最高プロペン転化率 (5.6%) が得られた。生成物としては、プロペンオキシド (PO) やアセトンなどの C₃-含酸素化合物

とともに、C₄-C₆炭化水素が得られた。表面の NH₃吸着サイト量が触媒活性と関係しているようであり、このサイトは硫酸根濃度、焼成温度および反応時間に依存していることが推定された。酸素の役割として、C₃-含酸素化合物の生成だけでなく、炭素析出量を制御するという効果もあることが併せて分かった。

Keywords

Aerobic oxidation, Titanium sulfate, Zirconia, C₃ oxygenates, Propene