Influence of Starting Solution in Preparation of V_2O_5/TiO_2 Catalysts for Selective Oxidation of Benzene

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The selectivity in benzene oxidation over V_2O_5/TiO_2(rutile) was drastically changed with starting solutions in the preparation of catalysts, although V_2O_5/TiO_2(rutile) prepared from oxalic acid solution of NH_4VO_3 selectively oxidized benzene to maleic anhydride, only a total oxidation proceeded over those prepared without oxalic acid.

V_2O_5/TiO_2 catalysts are well known to be effective for the selective oxidation of o-xylene[1,2] and the reduction of nitrogen oxide with ammonia,[3] which can be found extensively in industrial application. Since the catalytic activity and selectivity often vary significantly with preparation method and type of support, the effect of these factors has been extensively examined.[4-7] Impregnation is the most popular method for the preparation of V_2O_5/TiO_2 catalysts; however, starting materials, procedure and preparation conditions may affect the catalytic performances.

We have started a project on the preparation of V_2O_5/TiO_2 catalysts under the organization of the Committee on Reference Catalyst of the Catalysis Society of Japan. A similar project named "EUROCAT OXIDE" has been carried out by European scientists with the aim of distribution of *standard* V_2O_5/TiO_2 catalysts.[8] In our project, for the aim of the standardization of preparation method, nine kinds of V_2O_5/TiO_2 catalysts were prepared in five individual laboratories and then examined their structure and catalytic reactions. As a part of the results from this project, we have found a strong influence of starting solution on the selectivity of benzene oxidation, and will report it in this communication.

Two kinds of TiO_2 in the Reference Catalysts named JRC-TIO-3 (rutile phase, 49.5 m^2g^{-1} specific surface area) and JRC-TIO-4 (anatase phase > 60%, 50.1 m^2g^{-1} specific surface area) were used as supports, since they have almost the same surface area but different crystal phase.[7] V_2O_5/TiO_2 catalysts were prepared by impregnation of TiO_2 with NH_4VO_3 solution. The preparation conditions are summarized in Table 1. The prescribed amount of NH_4VO_3 was dissolved in water, nitric acid or oxalic acid solution. After addition of TiO_2, the solution was evaporated with stirring until it became a pasty cake or a powder. The solid thus obtained was dried and then calcined at the prescribed temperature. V_2O_5 contents measured by Inductive Coupled Plasma (ICP) were ranging from 4.7 to 5.5 wt%, which were nearly equivalent amount of the theoretical monolayer coverage.[5,6] Surface area of the catalysts was ranging from 36.0 to 45.0 m^2g^{-1}.

Oxidation of benzene was carried out in a conventional continuous-flow apparatus at atmospheric pressure. A mixture of 2.2% benzene, 20% oxygen diluted with nitrogen was fed to 0.1 g of catalyst at a flow rate of 100 cm^3min^{-1}. The catalytic tests were carried out at the reaction temperature from 573 to 633 K. The products were analyzed by on-line gas chromatography. Maleic anhydride (MA), CO, CO_2 and a little amount of benzoquinone were produced, and a good carbon balance was confirmed for all the catalytic run.

Figure 1 shows the selectivity to MA with the conversion of benzene. In the case of TIO-4 support, the formation of MA was observed in all the catalysts, and the selectivity to MA was in the following sequence; C > D > A > B. In contrast, the effect of the preparation conditions on the selectivity to MA was significant in the case of TIO-3 support : Although VT3-C, D and E showed moderate selectivity to MA, MA was not detected and only CO and CO_2 were formed over VT3-A and B.

The dependence of the selectivity to MA on the preparation method can be summarized as follows;

TIO-4 support : C > D > A > B
TIO-3 support : C = D = E >> A, B =0 .

Table 1. Preparation conditions of V_2O_5/TiO_2 catalysts

			Starting Solution		Treatments		
Catalyst	Support	Method	Solution	NH_4VO_3/mol dm^{-3}	Evaporation	Drying	Calcination
VT3-A	TIO-3	A	water	0.0361	water bath	383 K, 18 h	773 K, 5 h
VT4-A	TIO-4				5 h	in air	in air
VT3-B	TIO-3	B	nitric acid	0.0392	water bath	398 K, 12 h	773 K, 3 h
VT4-B	TIO-4		pH=4.0		12 h	in air	in air
VT3-C	TIO-3	C	oxalic acid	0.735	water bath	383 K, 12 h	723 K, 12 h
VT4-C	TIO-4		1.0 mol dm^{-3}		3 h	in air	in air
VT3-D	TIO-3	D	oxalic acid	0.0630	evaporator	343 K, 2 h	773 K, 3 h
VT4-D	TIO-4		0.43 mol dm^{-3}		2 h	in vacuo	in oxygen
VT3-E	TIO-3	E	oxalic acid	0.0551	water bath	373 K, 24h	773 K, 3 h
-	-		0.32 mol dm^{-3}		3 h	in air	in oxygen

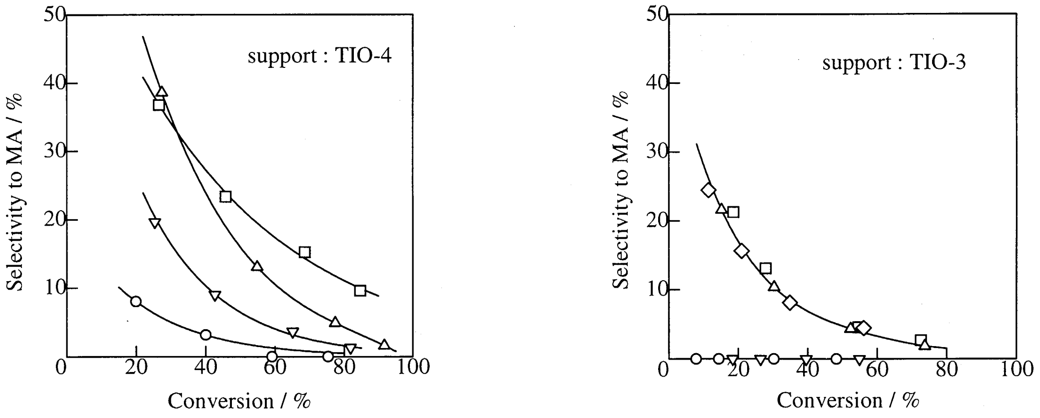

Figure 1. Selectivity to maleic anhydride (MA) with the conversion of benzene oxidation over V_2O_5/TiO_2 catalysts prepared by method (▽)A, (○)B, (□)C, (△)D and (◇)E.

When compared to Table 1, above sequence in the selectivity cannot be related to the conditions in evaporation, drying and calcination. A clear correlation between the selectivity and the starting solution was observed in the case of TIO-3 support. The catalysts prepared from oxalic acid solution (C, D and E) exhibited moderate selectivity to MA, while only total oxidation proceeded over the catalysts prepared from water or nitric acid solution (A and B). This suggests that oxalic acid may play very important role in the preparation of the selective catalysts. The similar trend was also observed in TIO-4. Namely, VT4-C and D exhibited higher selectivity to MA than VT4-A and B; however, the dependence of the selectivity on the preparation method was not drastic.

One may suspect that the dispersion of supported vanadium species is one of the determining factor for the selectivity. The number of the surface V=O species measured by the NARP technique[9] was 2.2-3.3 μmol m^{-2} for the catalysts prepared by the method A and B, and 3.5-4.7 μmol m^{-2} for the other catalysts. This result indicates that the lower dispersion results in the lower selectivity; however, the lower dispersion is not the sole factor for the non-selective oxidation over VT3-A and B because of the production of MA over VT4-A and B. Any qualitative or structural differences of supported vanadium species are expected to be more essential for the selectivity. In Raman spectra, the band assignable to surface amorphous vanadium species was observed in all the catalysts and the band assignable to crystalline V_2O_5 was observed in VT3-A, VT4-A, B and D. The formation of crystalline V_2O_5 was not correlated with the selectivity to MA, the changes in the selectivity should not be due to crystalline V_2O_5 but to qualitative or structural differences in the surface amorphous vanadium species affected by the interaction with TiO_2 supports. The influence of the starting solutions appeared more significantly on TIO-3 (rutile) support than on TIO-4 (mainly anatase) support. Since a good fit of crystallographic patterns at V_2O_5-TiO_2 (anatase) interface has been reported,[10,11] the weak influence of the starting solutions on TIO-4 support may be due to a good interaction of anatase. In the case of V_2O_5-TiO_2(rutile), it can be expected that the difference in the starting solutions resulted in a significant modification of the structure of the surface vanadium species, such as coordination number of oxygen,[6] formation of solid solution,[12] polymerization[13] and so on. The reason for the changes in the selectivity is now under investigation, and will be reported in further publication.

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