Marked Size Effect of Zinc Oxide Particles Supported on Silica in Propene–Deuterium Addition and Exchange Reactions

Shuichi Naito,*[a] Mistutoshi Tanimoto[b] and Mitsuyuki Soma[c]

[a] *Research Centre for Spectrochemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113, Japan*
[b] *Department of Chemistry, Faculty of Science, Shizuoka University, 836 Ohya, Shizuoka 422, Japan*
[c] *The National Institute for Environmental Studies, 16-2, Onogawa, Tsukuba, Ibaraki 305, Japan*

Small particles of ZnO trapped between silica particles exhibit a marked size effect on the reaction rates as well as on the reaction intermediates of the propene–deuterium addition and exchange reactions.

Several studies on the particle size effect of supported metal catalysts on the activity and selectivity of catalytic reactions have been reported.[1–4] However, such effects for supported metal oxide catalysts have so far not been investigated in detail.[5] In this communication, we report on the C_3H_6–$^2H_2$ and C_3H_6–$C_3{}^2H_6$ reactions over unsupported and silica-supported ZnO catalysts; microwave spectroscopy was used to determine the structure of the reaction intermediates.[6] We have found that very small particles of ZnO trapped within the space between silica particles exhibited remarkably different catalytic behaviour from that of larger particles or unsupported ZnO.

Catalysts were prepared by impregnating aqueous solutions of zinc acetate [$Zn(MeCO_2)_2 \cdot 2H_2O$, Wako Chemicals] onto SiO_2 (Aerosil 300, Nippon Aerosil, surface area 300 $m^2\ g^{-1}$), followed by calcination at 673 K. Unsupported ZnO catalyst

Table 1 Initial rates of propene–deuterium reactions over various ZnO catalysts and their characterization by XPS

	XPS analysis		Reaction rates ($\times 10^{-8}$ mol s^{-1} per g of ZnO)		
			C_3H_6–$^2H_2$ (403 K)^b		C_3H_6–$C_3{}^2H_6$ (403 K)^c
	Dispersion	Zn2p$_{3/2}$/eV^a	Propane	[$^2H_1$]propene	[$^2H_1$]propene
Unsupported ZnO		1022.0	0.8	1.8	1.7
ZnO : SiO$_2$					
1 wt%	0.24	1023.4	48	17	0.9
10 wt%	0.40	1023.4	4.2	5.4	3.6
20 wt%			2.3	5.1	5.2
Zn(OAc)$_2$: SiO$_2$					
1 wt%	0.30	1023.5			
10 wt%	0.85	1023.4			

[a] For the calibration of the binding energy, Au 4f$_{7/2}$ (84.0 eV) was used as a reference. [b] $P_{C_3H_6}$ = 3.3 kPa; $P_{^2H_2}$ = 6.7 kPa. [c] $P_{C_3H_6} = P_{C_3{}^2H_6}$ = 3.3 kPa.

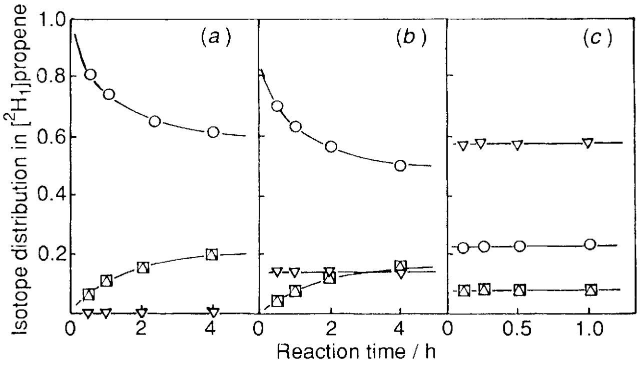

Fig. 1 Isotopic distribution of monodeuteriopropene formed during the C_3H_6–$^2H_2$ reaction over various ZnO : SiO$_2$ catalysts at 403 K: (*a*) 20 wt%, (*b*) 10 wt%, (*c*) 1 wt%. ○: CH_2=CH–$CH_2{}^2H$, ▽: CH_2=C^2H–CH_3, □: *cis*-CH^2H=CH–CH_3, △: *trans*-CH^2H=CH–CH_3

was also prepared by the decomposition of zinc acetate at 673 K. The catalyst (1 g) was placed in a U-shaped glass reactor, which was connected to a closed gas circulation system. The products were analysed by gas chromatography and their deuterium content was determined by mass spectroscopy. The amounts of the various isomers of monodeuteriopropene were determined by microwave spectroscopy.

Dispersed Zn(OAc)$_2$ and ZnO were characterized by X-ray photoelectron spectroscopy (XPS), as summarized in Table 1. Dispersion on silica caused the Zn 2p$_{3/2}$ peaks to shift 0.4 eV upwards from that of the unsupported ZnO. The atomic ratio of Zn : Si on the surface was estimated from the corrected peak area of Zn 2p$_{3/2}$ and Si 2s and used to derive the dispersion of Zn(OAc)$_2$ and ZnO on silica (the ratio of surface Zn atoms to bulk Zn atoms, which is obtained by assuming that each component consists of homogeneous spherical particles and that XPS intensity is proportional to the surface area).

The initial rates of propane and [$^2H_1$]propene formation in the C_3H_6–$^2H_2$ and C_3H_6–$C_3{}^2H_6$ reactions over unsupported and various silica-supported ZnO catalysts are listed in Table 1, which indicates a remarkable dependence of the rate upon the amount of ZnO loading. In the C_3H_6–$^2H_2$ reaction, the rates of both propane and [$^2H_1$]propene formation over 1 wt% ZnO : SiO$_2$ were much larger than those over 10 wt% catalyst. Higher loading decreased both reaction rates toward those over unsupported ZnO. In the C_3H_6–$C_3{}^2H_6$ reaction, on the other hand, the rate of [$^2H_1$]propene formation increased gradually as the loading increased.

It has been reported that over unsupported ZnO, hydrogen addition to propene takes place *via* an associative mechanism through n- and sec-propyl intermediates, whose reverse reaction to form monodeuteriopropene is prohibited. Hydrogen exchange of propene takes place *via* an independent dissociative mechanism through π-allyl intermediate.[7–10] The same results were obtained over 20 wt% ZnO : SiO$_2$ in the present study. The rate of the [$^2H_1$] propene formation in the C_3H_6–$^2H_2$ and C_3H_6–$C_3{}^2H_6$ reactions indicates that both reactions proceed through the common π-allyl reaction intermediate. Microwave spectroscopic analysis of the monodeuteriopropene formed in these reactions confirmed this as shown in Fig. 1(*a*), where CH_2=CH–$CH_2{}^2H$ was the major initial product at the initial stage of the exchange reaction. The different rate over 20 wt% ZnO : SiO$_2$ and unsupported ZnO may be explained in terms of the surface area of respective ZnO particles.

A completely different result was observed over 1 wt% ZnO : SiO$_2$ catalyst. The rate of [$^2H_1$]propene formation in the C_3H_6–$^2H_2$ reaction was one order of magnitude larger than that in the C_3H_6–$C_3{}^2H_6$ reaction, suggesting different reaction intermediates in the two reactions. On the other hand, similar temperature dependences of the rates of propane and [$^2H_1$]propene formation in the C_3H_6–$^2H_2$ reaction indicate that both addition and exchange processes proceed *via* an associative mechanism through the same propyl intermediates. As shown in Fig. 1(*c*), microwave spectroscopic analysis of the monodeuteriopropene disclosed that the n-propyl intermediate is the most active species, from which the CH_2=C^2H–CH_3 is predominantly formed. In the case of 10 wt% catalyst, the isotopic distribution shown in Fig. 1(*b*) exhibited a mixed feature of (*a*) and (*c*), indicating that the amount of the active n-propyl species decreased with the increasing loading amount.

The very high dispersion (0.85) in 10 wt% Zn(OAc)$_2$: SiO$_2$ suggests formation of a zinc acetate monolayer on the silica surface. Calcination of the catalyst decreased the dispersion (0.40), which indicated sintering of the acetate monolayer to ZnO particles with 40–50 Å diameters. In contrast, the rather small dispersion (0.30) of the 1 wt% Zn(OAc)$_2$: SiO$_2$ catalyst is peculiar, when we consider the formation of an acetate monolayer even at the 10 wt% impregnation. Moreover, little sintering was observed following calcination (0.24).

Since the spherical silica particles in Aerosil (70 Å diameter) are known to have few micropores, the only reasonable explanation for these results would be as follows: at the initial stage of impregnation, zinc acetate may be trapped preferentially within the space between the spherical silica particles and would give less intense XPS peaks than those on the 'outer' surface of combined silica particles. The remarkably rapid formation of propane and [$^1H_1$]propene in the C_3H_6–$^2H_2$ reaction may proceed in these particular active sites, where n-propyl adsorbed species can act as stable intermediates. As the amount of impregnated acetate is increased, this structure may be destroyed to form a monolayer and larger ZnO particles were formed on the silica surface after calcination.

In the case of the C_3H_6–$C_3{}^2H_6$ reaction, the isotopic distribution pattern of monodeuteriopropene was similar to that in Fig. 1(*a*) over all the catlayst investigated. Accordingly, this reaction proceeds *via* a dissociative mechanism through π-allyl intermediate irrespective of the particle size of the ZnO. The increase in the reaction rates with loading suggests that larger ensembles of ZnO are required for the stabilization of π-allyl adsorbed species.

Received, 3rd July 1992; Com. 2/03514F

References

1 M. Boudart, *Adv. Catal.*, 1969, **20**, 153.
2 M. Boudart, *J. Mol. Catal.*, 1985, **30**, 27.
3 G. A. Somorjai and J. Carrazza, *Ind. Eng. Chem., Fundam.*, 1986, **25**, 63.
4 B. Sen and M. A. Vannice, *J. Catal.*, 1991, **130**, 9.
5 S. Naito and M. Tanimoto, *Chem. Lett.*, 1990, 2145.
6 S. Naito and M. Tanimoto, *J. Catal.*, 1986, **25**, 63.
7 A. L. Dent and R. J. Kokes, *J. Am. Chem. Soc.*, 1970, **92**, 6718.
8 S. Naito, Y. Sakurai, H. Shimizu, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, 1971, **67**, 1529.
9 A. C. Dent and R. J. Kokes, *J. Am. Chem. Soc.*, 1970, **92**, 1092.
10 S. Naito, T. Kondo, M. Ichikawa and K. Tamaru, *J. Phys. Chem.*, 1972, **76**, 2184.