SELECTIVE ISOPENTANE FORMATION FROM CH_3OH ON A NEW ONE-ATOMIC LAYER ZrO_2/ZSM-5 HYBRID CATALYST

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A new one-atomic layer ZrO_2/ZSM-5 hybrid catalyst was prepared by using the repeated reactions between $Zr(OC_2H_5)_4$ and of the OH groups of the external surfaces of ZSM-5, followed by calcination. The one-atomic layer ZrO_2 attached on the ZSM-5 surface was characterized by means of X-ray diffraction, X-ray fluorescence and EXAFS. The ZrO_2 overlayer is suggested to epitaxially grow on the ZSM-5(001) plane in a [111] direction of tetragonal ZrO_2. The one-atomic layer ZrO_2/ZSM-5 is a unique catalyst which produces selectively isopentane from CH_3OH.

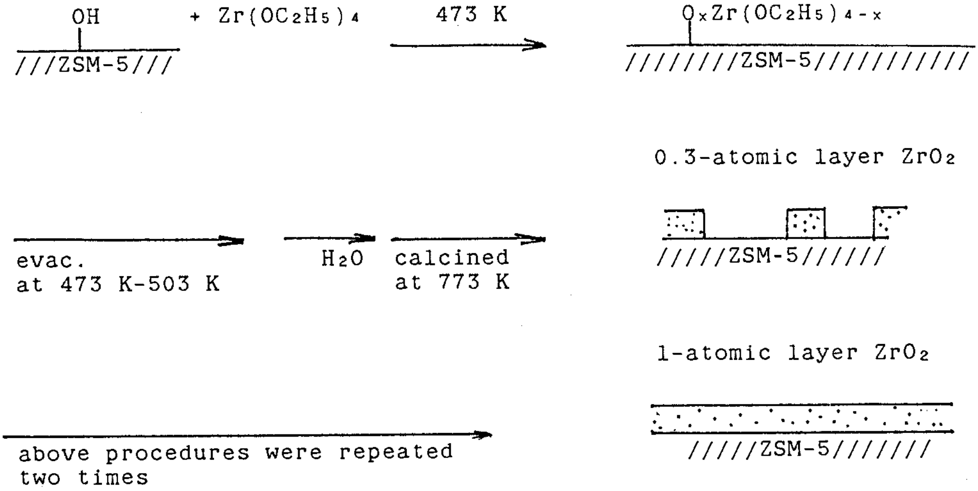
1. Introduction

ZSM-5 is known as a good MTG catalyst which yields mainly C_5–C_{10} hydrocarbons from methanol [1]. Methanol is also converted predominantly to C_2–C_4 products on ZSM-5 when it is ion-exchanged with alkali earth metal, transition metal, boron or phosphorus [2]. While ZSM-5 itself and the modified ZSM-5 catalysts showed a sharp cutoff at C_{10} in hydrocarbon product distribution and a narrow C-number distribution, it is still difficult to selectively obtain a particular hydrocarbon from methanol. We have synthesized the ultrathin layers (one–three-atomic layers) of La_2O_3, TiO_2, SiO_2 and Nb_2O_5 which are chemically bound on ZSM-5 external surface [3] or SiO_2 surface [4][5]. The ultra-thin overlayer/support systems have been demonstrated to have unique catalyses entirely different from those of the corresponding physically-mixed catalysts because they possess new and unique structures, arrangements and coordinative unsaturation around active metal sites [3–5]. Thus one-atomic metal-oxide layers on suitable supports may provide potential preparations of a new class of catalysts. The characteristic catalysts may also give important information on the essential factors and properties closely related with catalysis. In this letter we report the preparation of a new ZrO_2 one-atomic overlayer/ZSM-5 hybrid catalyst, its characterization with EXAFS and the selective catalysis for methanol conversion to isopentane.

2. Preparation of a ZrO_2 one-atomic overlayer / ZSM-5 hybrid catalyst

The ZrO_2 one-atomic layer/ZSM-5 hybrid catalysts were prepared by taking advantage of the reaction between $Zr(OC_2H_5)_4$ and the OH groups of ZSM-5 external surface, followed by calcination as shown in scheme 1, similarly to the previously reported way [3,4]. $Zr(OC_2H_5)_4$ vapor (vapor pressure 133 Pa at 473 K) was interacted with the 473 K-pretreated ZSM-5(Toso Co.) at 473 K. Since the molecular size of the $Zr(OC_2H_5)_4$ was larger than the pore size (0.52 nm × 0.56 nm), $Zr(OC_2H_5)_4$ can react with the OH groups located at the external surface and thus it was expected to stay at the external surface. After the reaction, unreacted $Zr(OC_2H_5)_4$ was evacuated at 473 K and then the sample was heated to 503 K to complete the reaction. The sample was then exposed to water vapor at room temperature to convert the OC_2H_5 ligands to OH groups, followed by calcination at 773 K in air. The loading of ZrO_2 in the sample thus obtained was determined by X-ray fluorescence by using several standard ZrO_2/ZSM-5 samples with known amounts of ZrO_2. The coverage of ZrO_2 deposited by one attachment-reaction was estimated to be about 1/3 atomic layer where 1.7 wt%(Zr/ZSM-5) is denoted as one-atomic layer based on the external surface area of ZSM-5(15 m^2/g and the ZrO_2 2-dimensional unit cell size (0.13 nm^2). Therefore, the above procedure was repeated to obtain the hybrid system covered with more amounts of ZrO_2. As a result we obtained a full monolayer coverage of ZrO_2 (one-atomic layer ZrO_2) by carrying out the attaching reaction by three times as shown in scheme 1.

The reduction of the pore size and volume of ZSM-5 was not observed after the three-times attachment treatments judging from the rates of adsorption of the toluene, o- and p-xylenes and the amounts of adsorbed pentane and benzene. No



Scheme 1. Preparation of one-atomic layer ZrO_2.

X-ray diffraction (XRD) pattern corresponding to ZrO_2 crystal was observed with the one-atomic layer catalyst. In contrast, equal amount of ZrO_2 supported onto ZSM-5 by an impregnation method using $ZrCl_4$ aqueous solution showed the ZrO_2 XRD pattern.

3. Characterization

Zr K-edge EXAFS spectra were measured to obtain the information on the local structure around Zr atom in the overlayer [5]. Figure 1 shows the Fourier transforms of the EXAFS oscillation for ZSM-5-attached ZrO_2 catalysts together with those for monoclinic ZrO_2 [6] (purchased from Soekawa Co.) and tetragonal ZrO_2 [7,8] (prepared by calcination of $Zr(OH)_4$ at 773 K precipitated from $Zr(NO_3)_2$). Further analysis was carried out with the curve fitting techniques using the theoretical phase shift and amplitude functions [9]. The coordination numbers for ZrO and Zr–Zr bounds were obtained on the basis of the Nb–O bond in $YNbO_4$ and Zr–Zr bond in Zr metal, respectively. Table 1 shows the

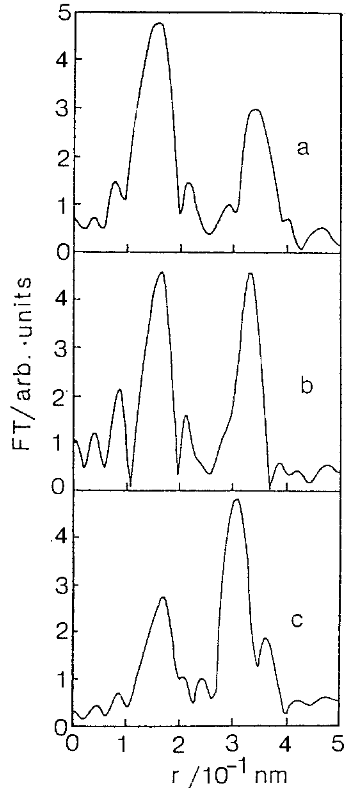


Fig. 1. Fourier transforms of Zr K-edge EXAFS of (a) 1-atomic layer ZrO_2 attached on ZSM-5, (b) tetragonal ZrO_2, (c) monoclinic ZrO_2.

Table 1
The curve fitting analysis of the Zr K-edge EXAFS spectra

	Zr–O		Zr–Zr	
	N	*r*/nm	*N*	*r*/nm
ZrO_2/ZSM5				
0.3 atomic layer	3.0(5)	0.206(3)	3.0(7)	0.369(3)
0.7 atomic layer	3.5(5)	0.205(3)	4.1(8)	0.369(3)
1.0 atomic layer	3.0(5)	0.206(3)	3.1(7)	0.369(3)
2.0 atomic layer	3.0(5)	0.206(3)	7.0(1.5)	0.366(3)
Zr/SiO_2				
0.5 atomic layer	3.5(4)	0.207(3)	1.0(3)	0.347(3)
ZrO_2				
tetragonal	4.2(3)	0.207(3)	7.2(1.5)	0.365(3)
	(4	0.2065	12	0.3667) *
monoclinic	2.0(3)	0.214(3)	6.8(1.0)	0.343(3)
	(7	0.2159	7	0.3454) *

Theoretical phase shift and amplitude functions were used.
* The averaged values derived from X-ray crystallographical analysis.

curve fitting results of the hybrid catalysts. The bond distances for the standard samples (monoclinic and tetragonal ZrO_2) derived from EXAFS agree with those determined from X-ray crystallography within the errors of 0.003 nm. The smaller coordination numbers derived from the EXAFS analysis might be due to the static disorder. The Zr–O and Zr–Zr bond lengths of one-atomic layer ZrO_2 was close to those in tetragonal ZrO_2 rather than the monoclinic ZrO_2, indicating the formation of a tetragonal ZrO_2-like structure. The bond distances in 0.3-, 0.7-, 1-atomic layers on ZSM-5 were almost the same. The coordination numbers for Zr–O and Zr–Zr bonds were observed to be 3.2 ± 0.3 and 3.5 ± 0.6, respectively. These results suggest that the local structures similar to tetragonal ZrO_2 have already been formed at the 0.3 atomic layer supported on ZSM-5 external surface and the two-dimensional islands have grown to form the one-monolayer on ZSM-5 with an increase of ZrO_2 coverage. The Zr–Zr coordination number increased from 3.1 for the one-atomic layer ZrO_2/ZSM-5 to 7.0 in the 2-atomic layer ZrO_2/ZSM-5 a little less than that in the bulk ZrO_2. In contrast to the $<$ 1-atomic layer samples, the formation of 3-dimensional islands of ZrO_2 is indicated with the 2-atomic layer ZrO_2/ZSM-5. The Zr–Zr distance in the 0.3–1 atomic layer ZrO_2 was 0.004 nm longer than that in tetragonal ZrO_2 bulk, while the 2-atomic layer ZrO_2/ZSM-5 showed almost the same distance as the bulk as shown in table 1. There are crystallographically two different types of Zr–Zr distances in the ZrO_2 tetragonal crystal. One is 0.364 nm along [100] direction and the other is 0.368 nm along [111] direction. The Zr–Zr distance observed in the 1-atomic layer ZrO_2 agrees with the distance in a [111] direction of tetragonal ZrO_2 crystal. Thus the Zr–Zr bonding is suggested to be formed along the [111] direction on the ZSM-5 external surface. After the completion of the full monolayer of ZrO_2, the three dimensional ZrO_2 islands grow on the one atomic layer ZrO_2. On the other hand, the structure of one-atomic layer ZrO_2 supported on SiO_2 prepared in the similar way was more similar to monoclinic ZrO_2 structure because Zr–O and Zr–Zr distances were close to those of monoclinic ZrO_2 rather than those of tetragonal one as shown by the EXAFS analysis. As a result, on the ZSM-5 external surface the ZrO_2 one-atomic layer may grow epitaxicially in a [111] direction of tetragonal ZrO_2, where the formation of three-dimensional ZrO_2 islands/particles was not observed below a monolayer coverage of ZrO_2.

4. Selective conversion of methanol to isopentane

The catalytic properties of the 1-atomic layer ZrO_2 attached on ZSM-5 for methanol conversion were examined in a stainless-steel flow system using 1 g of catalyst at 1 and 10 atm. The samples were oxidized at 773 K for 2 h in a flow of dry air and cooled to reaction temperatures under Ar atmosphere. CH_3OH was fed into an Ar flow by a micro-pump and the Ar/CH_3OH ratio in gas volume was controled to be 2 or 16. The products were analyzed by gas chromatography. Table 2 shows the activities and selectivities of the ZSM-5-attached ZrO_2 catalysts for CH_3OH conversion reactions at 1 atm. C_5 hydrocarbons were found to be selectively produced (88.9%) at 623 K on the 1-atomic layer ZrO_2/ZSM-5 catalyst more than 95% of which was isopentane. Under the similar reaction conditions ZSM-5 produced hydrocarbons with a variety of carbon numbers. The 2-atomic layer ZrO_2/ZSM-5 showed a higher conversion rate compared with the 1-atomic layer ZrO_2/ZSM-5, but the selectively toward C_5 products was much low and the product distribution was broad similarly to that observed for ZSM-5 itself. The C_5 selectively decreased with an increase of the total pressure; at 10 atm, 19.6% (573 K) and 8.2% (623 K) as shown in table 3. Under 10 atm conditions, p-xylene was favorately formed (selec. 21.8% at 623 K) on 1-atomic layer ZrO_2/ZSM-5 than on ZSM-5 (12%). The relatively high selectivity for p-xylene formation was also found in the 2-atomic layer ZrO_2/ZSM-5 (22.6% at 673 K). On the other hand, the 1-atomic layer ZrO_2/SiO_2 prepared in a similar way to the ZrO_2/ZSM-5 catalyst showed no catalytic activity for CH_3OH conversion under similar reaction conditions. The 3-atomic layer SiO_2/ZSM-5 was also tested at 1 atm; the catalyst was prepared by the interaction between the $CH_3Si\ (OC_2H_5)_3$ and the external surface OH of ZSM-5 followed by calcination as previously reported [3].

Table 2
The methanol conversion reaction product distributions (total pressure = 1 atm)

	T/K	CH_3OH conv./%	Selectivity/%										
			C_2	C_3	C_4	C_5	C_6	C_6H_6	C_6H_{12}	ArMe	p-$ArMe_2$	o-$ArMe_2$	Ar_8^+
1-atomic layer ZrO_2/ZSM-5	573	10.5	3.9	2.8	0.0	88.9	3.0	0.0	0.0	0.0	0.1	0.7	0.5
	623	13.8	8.4	10.6	0.0	73.5	0.0	0.0	0.0	0.0	1.7	0.3	5.6
2-atomic layer ZrO_2/ZSM-5	623	30.7	11.5	16.0	11.8	13.5	8.2	0.7	0.8	3.8	16.6	4.2	14.8
3-atomic layer SiO_2/ZSM-5	573	42.2	11.0	16.5	0.0	14.4	12.0	0.8	0.7	3.0	16.1	3.8	24.3
ZSM-5	573	25.2	17.1	28.3	0.0	13.4	9.8	1.0	0.9	3.7	14.1	4.0	15.0

Reaction conditions: The catalyst = 1 g, $P = 1$ atm, $Ar/CH_3OH = 2$, $W/F = 310$ g min mol^{-1}.

Table 3
The methanol conversion reaction product distribution (total pressure = 10 atm)

	T/K	CH_3OH conv./%	Selectivity/%										
			C_2	C_3	C_4	C_5	C_6	C_6H_6	C_6H_{12}	ArMe	p-$ArMe_2$	o-$ArMe_2$	Ar_8^+
1-atomic layer	573	35.6	11.7	21.6	11.8	19.6	15.3	4.5	1.6	2.9	4.4	1.4	5.2
ZrO_2/ZSM-5	623	60.7	5.6	21.5	16.7	8.2	2.7	0.0	0.0	3.5	21.8	5.7	14.2
2-atomic layer	570	45.3	11.8	21.7	11.7	21.4	17.3	4.0	1.6	2.2	3.4	1.3	3.6
ZrO_2/ZSM-5	673	85.3	9.4	36.0	1.8	9.4	5.9	1.4	0.0	5.0	22.6	4.0	4.2
3-atomic layer	623	83.5	5.0	15.6	17.2	11.2	7.5	0.3	0.3	4.9	16.4	3.8	17.7
SiO_2/ZSM-5	653	100.0	4.8	19.1	18.6	10.3	6.4	0.1	0.0	5.7	15.9	3.2	15.9
ZSM-5	653	43.9	11.7	30.4	12.4	12.5	3.4	0.2	0.3	1.0	14.6	2.4	11.1
	673	56.8	15.8	33.6	9.6	4.9	4.6	0.4	0.3	4.0	10.2	1.6	15.0

Reaction conditions: The catalyst = 1 g, P = 10 atm, $Ar/CH_3OH = 16$, $W/F = 54.9$ g min mol^{-1}.

Table 4
The activity and selectivity of the CO hydrogenation reaction

	T/K	CO conv./%	Total hydrocarbon	hydrocarbons selectivity/%								CO_2	$(CH_3)_2O$
				CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5^+		
0.7-atomic layer	573	0.07	100	61.7	14.1	3.9	9.4	3.1	7.8	0.0	0.0	0.0	0.0
ZrO_2/ZSM-5	623	0.13	100	61.4	10.9	7.0	9.2	3.9	4.9	0.0	0.0	0.0	0.0
	673	0.23	100	62.6	10.4	10.2	8.5	3.6	3.3	0.0	1.4	0.0	0.0
1-atomic layer	603	0.04	67.9	72.8	11.9	5.1	6.8	3.4	0.0	0.0	0.0	32.1	0.0
ZrO_2/ZSM-5	543	0.15	75.1	35.1	10.7	3.7	9.9	1.6	21.7	0.6	16.7 [a]	24.7	0.2
	673	0.31	74.3	49.5	15.9	3.2	9.3	1.5	17.2	0.5	3.0	25.5	0.2
2-atomic layer	543	0.11	65.4	63.3	16.0	3.1	13.7	3.1	0.8	0.0	0.0	34.4	0.2
ZrO_2/ZSM-5	593	0.40	65.1	61.5	11.3	7.6	10.4	2.8	5.1	1.3	0.0	34.7	0.2
	643	0.59	68.3	60.7	13.4	9.9	11.1	2.7	2.1	0.1	0.0	31.6	0.1

[a] $C_5H_{10} = 4.7\%$, $C_5H_{12} = 5.7\%$, $C_6^+ = 6.3\%$.

This sample depicted a similar selectivity to that of ZSM-5 though the external SiO_2 layer enhanced the overall reaction rate as shown in table 2.

The unique feature of the 1-atomic layer ZrO_2/ZSM-5 catalyst in product distribution was also observed in CO hydrogenation. Table 4 shows a high selectively toward C_4H_8 hydrocarbons (mainly isobutene) on the 1-atomic layer ZrO_2/ZSM-5, whereas no interesting product distribution was observed with the 2-atomic layer ZrO_2/ZSM-5. ZrO_2 itself has been known to be a catalyst for isosynthesis from $CO + H_2$ [10]; the reaction was accompanied by the formation of a large amount of CO_2. The CO_2 formation was suppressed on the 1-atomic layer ZrO_2/ZSM-5 catalyst which produced mainly hydrocarbons.

The detailed reaction mechanism for the selective formation of isopentane from CH_3OH on the 1-atomic layer ZrO_2/ZSM-5 catalyst is not clear at present, but the specific catalysis must be correlated with the chemical hybrid environments composed of the 1-atomic layer of ZrO_2 and the acidic cavity of ZSM-5. As mentioned before, one-atomic layer of ZrO_2 grows epitaxially on the ZSM-5(001) plane in a [111] direction of tetragonal-like ZrO_2. In an alternative view the coordinatively unsaturated, active [111] plane of tetragonal ZrO_2 may be produced by the misfit between the ZrO_2 overlayer and ZSM-5 external surface and stabilized on the external surface of ZSM-5 by forming the Zr–O–Si (ZSM-5 surface) bonds. The one atomic layer ZrO_2/ZSM-5 hybrid catalyst is possible to generate a unique reaction environment for multifunctional catalysis which is hardly observed with physically-mixed hybrid samples and traditionally-prepared catalysts.

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