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Formation of C_3 Hydrocarbons from Methane Catalyzed by Na^+ Doped ZrO_2

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Sodium doped ZrO_2 was studied as the methane activation catalyst and found to be highly active at low temperature giving C_3 hydrocarbons as main products. Among the catalysts tested, 4.3 mol% Na^+ doped ZrO_2 showed the best conversion (18.2%) and selectivity (59.0%) for the formation of C_2 and C_3 hydrocarbons at 873 K; the yield of C_3 was 7.5% with ratio 3.3 of propane/propene.

In recent years, a large number of attentions have been focused on the oxidative coupling of methane. Although many kinds of catalyst systems were reported,[1] it needed high reaction temperatures to get the satisfactory activity and selectivity, in the vicinity of 1000 K or higher. Zirconium oxide is a noteworthy material as catalyst or catalyst support: that is, an acid-base bifunctional catalyst,[2] the selective formation of isobutene from $CO-H_2$,[3] the generation of superacid character by the addition of sulfate ion or tungsten oxide,[4] the property of superionic conductor,[5] and a support of Ag electrode for the oxidative coupling of methane.[6] In the present work, we studied the catalytic action of zirconium oxide for the oxidative coupling of methane and found that Na^+ doped ZrO_2 is active for the selective formation of C_3 hydrocarbons, even at the temperature range lower than 873 K.

The catalysts were prepared by impregnation method from $Zr(OH)_4$ and Na_2CO_3. $Zr(OH)_4$ was obtained by hydrolyzing $ZrOCl_2 \cdot 8H_2O$ with aqueous ammonium hydroxide, washing, drying at 373 K, and powdering the precipitates (20-32 mesh). The hydroxide was impregnated with aqueous sodium carbonate followed by evaporating water, drying, and treating at reaction temperarure for 2 h in $He-O_2$ stream in a reactor (quartz glass tube, O.D. 6 mm) before reaction. The reaction was carried out in a conventional flow method at atmospheric pressure; the reaction conditions were as follows: catalyst weight, 0.2 g; composition of reaction gas, $He:O_2:CH_4=5:1:4$; total flow rate, 100 $ml \cdot min^{-1}$. The products were analyzed by G.C. (Porapak R-2 m, Active carbon-1 m, R.T.). All data were calculated by carbon unit base.

The reaction of methane was performed at 823-1023 K; the results are shown in Table 1. ZrO_2 itself showed a little activity to form hydrocarbons; CO and CO_2 were mainly produced (Exp. No. 1). However, the treatment with sodium ion enhanced largely the activity of ZrO_2 for the formation of hydrocarbons with the restraint of formation of CO and CO_2. The catalytic activity and selectivity were raised as Na^+ content increased; the highest activity was given by the addition of 4.3 mol% Na^+ (Exp. No. 4). Other catalysts, containing more than

4.3 mol% Na^+, showed almost same activity and selectivity. The catalysts were sufficiently active at 873 K, low temperature for the activation of methane catalyzed by solid materials.[1] Selectivities were almost constant in spite of the rising of reaction temperature.

The present catalyst produced a considerable amount of C_3 hydrocarbons which have not been formed over other catalysts;[1] the amount of C_3 was larger than that of C_2 over all catalysts examined in this study except ZrO_2. The composition of C_3 hydrocarbons was 77% of propane and 23% of propene under the conditions of Exp. No. 4. As for the C_2 hydrocarbons produced, the most part was ethane.

Activities as well as selectivities were maintained constant in most cases up to 95 min from the first period of reaction. With regard to the crystalline structure of the catalyst, the 4.3% Na^+ doped material (873 K) showed the presence of tetragonal ZrO_2 without the crystallization of Na_2O; it is considered that Na^+ was highly dispersed and taken into the ZrO_2 lattice. The role of Na^+ on the catalytic action is under investigation.

Table 1. Catalytic activity and selectivity of Na^+ doped ZrO_2 for the activation of methane

Exp. No.	Reaction temp/K[a]	Na^+ cont. /mol%	Conv./%	Selec./%	Composition / %				
					CH_4	C_2	C_3	CO	CO_2
1[b]	973	0.0	25.2	14.9	74.8	2.1	1.6	10.4	11.0
2	873	0.7	12.5	43.9	87.5	1.4	4.1	1.5	5.5
3	873	2.9	14.1	46.1	85.9	1.1	5.4	0.5	7.1
4	873	4.3	18.2	59.0	81.8	3.2	7.5	0.4	7.1
5	873	12.5	17.9	55.4	82.1	2.8	7.2	0.7	7.4
6	873	15.6	17.2	56.5	82.8	2.9	6.8	0.6	6.9
7	823	4.3	2.5	0.0	97.5	0.0	0.0	0.7	1.8
8	973	4.3	16.5	60.1	83.5	3.5	6.4	0.4	6.2
9	1023	4.3	14.3	61.7	85.7	2.6	6.3	0.5	5.0

All data were obtained at processing time 95 min.

a): Measured by a thermocouple attached to the outside of reaction tube.

b): Reaction gas composition, $He:O_2:CH_4=3:2:3$, total flow rate 40 $ml \cdot min^{-1}$.

References

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