Propane Oxidative Dehydrogenation over Nickel Supported on Sulfated Zirconia

Shaobin Wang, Kazuhisa Murata, Takashi Hayakawa, Satoshi Hamakawa, and Kunio Suzuki
Department of Surface Chemistry, National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305

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Excellent performance for the oxidative dehydrogenation of propane is achieved over lithium promoted nickel supported on sulfated zirconia, giving propylene selectivity of 50% at propane conversion of 20%.

The oxidative dehydrogenation (ODH) of light alkanes ($<C_6$) is an attractive alternative for producing alkenes since it does not present either thermodynamic limitations or the typical catalyst deactivation of the conventional dehydrogenation process. At present, there exists a growing interest in finding active catalysts at temperatures lower than 600 °C capable of diminishing the total combustion products. In most recent literature much effort has been devoted over V-Mg-O and Mo-Mg-O catalysts.[1,2] Few previous studies of alkane ODH reactions have focused on zirconia supported oxides catalysts.[3,4] We first reported here the catalytic performance of Ni-ZrO_2 systems in selective oxidation of propane.

The fresh ZrO_2 was prepared by a two-step method.[5] The sulfated zirconia (SZ) with 6 wt% sulfate (6SZ) was prepared by wetness impregnation with $(NH_4)_2SO_4$ at appropriate concentration, dry at 105 °C and calcination at 700 °C for 3 h. Ni-based catalysts or promoted with LiCl were also prepared by impregnation described above, in which NiO loading was kept at 5 wt%. The catalysts of 0.5 g with 1.0 g quartz sand were tested in a fixed-bed, alumina tubular reactor operated at atmospheric pressure between 500 and 600 °C. The feed was a mixture of 10 vol % propane, 10 vol % oxygen, and the balance nitrogen. The flow rate was 60 ml/min at room temperature. The reactants and reaction products were alternately analysed on-line by two Shimadzu GC-8A gas chromatographs equipped with a thermal conductivity detector and a flame ionic detector. A Porpack Q column for separating hydrocarbons and a molecular sieve column for CO, CO_2, N_2 and oxygen were both used. The homogeneous contribution was tested with the empty reactor. These runs showed no activity below 620 °C. The results were very similar with and without the use of quartz particles. The conversion and product A selectivity are defined as: Conv. = (moles of propane consumed/moles of propane in feed) × 100 %; Sel. = 100 % × (moles of product A/moles of propane consumed)/R_c, where R_c is the ratio of the number of carbon atoms in propane to the number of carbon atoms in product A. In all runs, a carbon balance of 100 ± 5 % was obtained.

The property and catalytic behaviour of supports, fresh ZrO_2, ZrO_2 calcined at 700 °C for 3 h, sulfated zirconia, and Ni-based catalysts, at 600 °C are presented in Table 1. It is seen that ZrO_2 and sulfated zirconia are active for ODH of propane reaction. However, the major products for the reaction are carbon oxides. The selectivities towards propylene and olefins (ethylene and propylene) are around 10% and 20%, respectively for all three catalysts. Calcined zirconia and SZ shows lower propane conversion than that of fresh ZrO_2. This is probably due to the decreased surface area. The total conversion order of three catalysts is the same as that of their surface area variation. However, a comparison of conversion per surface area for three catalysts shows a sequence of ZrO_2(700) > 6SZ > ZrO_2(fresh). This is probably due to the different chemical structure of ZrO_2 presented in catalysts. Further work is required. XRD measurements indicate that three zirconia samples show different structure. The fresh zirconia is amorphous with a little tetragonal phase. The main phase of sulfated zirconia is monoclinic with a larger amount of tetragonal phase. However, calcined zirconia exhibits only monoclinic phase. This suggests that sulfation of zirconia inhibits the transformation of tetragonal ZrO_2 to monoclinic phase. This phenomenon has been reported by several other researchers.[6,7] Fernades and Volta[8] have reported that catalysts prepared on tetragonal or on monoclinic ZrO_2 showed different catalytic behaviour during the ODH of propane.

Table 1. Catalytic activity of zirconia catalysts for propane oxidation at 600 °C

Catalyst	S_{BET}	Conv.	Sel.			Yield
	m^2/g	%	%			%
		C_3H_8	C_3H_6	CO_x	Olefins*	C_3H_6
ZrO_2(fresh)	220	32.0	9.1	79.3	16.1	2.9
ZrO_2(700)	21	23.2	13.9	76.1	20.7	3.2
6SZ	70	28.3	12.8	72.2	22.2	3.6
Ni/6SZ	44	34.2	18.6	75.5	22.0	6.4
NiLi/6SZ	4.8	20.8	52.1	16.0	77.0	10.8
Ni/Li_2ZrO_3	<1	4.3	64.2	0	87.4	2.8

* including C_2H_4 and C_3H_6.

Ni supported on 6SZ catalyst shows higher activity and propylene selectivity than those of any supports, however, the main products are still carbon oxides. It is noted that Ni/6SZ exhibits higher catalytic activity at low temperatures. Ni/Li_2ZrO_3 shows the least activity, suggesting that Li_2ZrO_3 is not active for ODH propane. NiLi/6SZ exhibits medium propane conversion but much high selectivity towards propylene (over 50%) and olefins (77%). XRD measurements reveal that some of Li_2ZrO_3 formed in NiLi/6SZ catalyst, which accounts for the less propane conversion than Ni/6SZ. Comparison of propylene yields among all catalysts tested, it is found that NiLi/6SZ gives the highest propylene yield. These results are almost comparable to the best values ever reported for vanadium and molybdenum-based catalysts.[2,9]

It has been pointed out that the reaction pathways and product distributions of the oxidative transformation of light alkanes depend on the acid-base properties of the solid catalysts. Generally, basicity promotes the dehydrogenation reaction, while acidity facilitates the formation of oxy-products.[10] NiLi/6SZ shows the highest propylene selectivity probably due to the synergetic effect of acid anion (SO_4^{2-}) and basic cation (Li^+). Sulfated zirconia as a superacid favours the oxidation of alkane. Addition of lithium increases the basic sites for olefin selectivity. Nickel oxide due to its redox property acts as active sites for activation of surface oxygen and propane, resulting in the reaction occurring at low temperatures. Further research is carried out to elucidate the roles of these components.

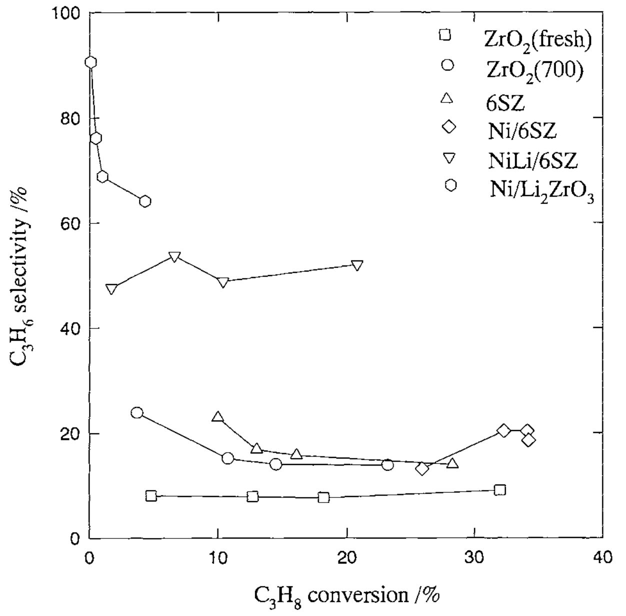

Figure 1. Relationship between propane conversion and selectivity to propylene in ODH of propane.

Figure 1 shows the propylene selectivity as a function of propane conversion for all catalysts. The selectivity over fresh ZrO_2 is lower than 10% and does not change with propane conversion. Calcined ZrO_2, sulfated zirconia and Ni/Li_2ZrO_3 catalysts display the typical behaviour of selectivity decline with an increase in conversion. Although the selectivity of propylene over Ni/Li_2ZrO_3 is high, it decreases faster with increasing conversion. For Ni/6SZ propylene selectivity increases a bit as conversion increases and then keeps at the same level (20%). NiLi/6SZ exhibits the similar propylene selectivity (about 50%) in temperature range of 500-600 °C. This suggests that NiLi/6SZ can keep its propylene selectivity at high propane conversion.

In summary, zirconia and sulfated zirconia as well as NiO-based sulfated zirconia catalysts are effective for propane oxidative dehydrogenation. LiCl promoter increases propylene selectivity and thus resulting in high yield. This catalyst can be a promising candidate for ODH of propane.

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