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Aromatization of Lower Paraffin with Hybrid Catalysts Containing ZSM-5

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It was pointed out that Ga promote the zeolite-promoted aromatization of lower paraffin by "Reverse Spillover Effect" of hydrogen. A new hybrid catalyst which was comparable to Ga-ZSM-5 for the title reaction was developed on this concept.

It has been found that ZSM-5 type zeolite containing gallium or zinc exhibits high selectivities for the title reaction.[1-5] They are effective in promoting the reaction in the impregnated form,[1-3] ion exchanged form[4] or even when they are incorporated in the zeolite framework.[5] The formation of aromatics is also promoted by adding oxygen in the feed.[6] In the present study a new concept for the role of added Ga or Zn was postulated and a new hybrid catalyst was developed based on this concept.

Hybrid catalysts were prepared by co-grinding the two kinds of catalysts and pressure-molding the mixture to granules.

In Table 1 are shown the results of n-butane conversion obtained on a variety of catalysts including hybrid catalysts. Although the protonic ZSM-5 (H-ZSM-5) was effective for cracking n-butane, the main product was not aromatic hydrocarbons but propane and C_2-C_4 olefins. When 5 mol% oxygen was added to the feed gas, the n-butane conversion on the H-ZSM-5 catalyst increased slightly and the selectivity to aromatic hydrocarbons increased drastically from 8.8% to 16.1%. The formation ratio of hydrogen, which is defined as the mole ratio of hydrogen produced to the consumed n-butane, is much lower in the presence of oxygen in spite of much higher aromatics selectivity, which indicates that hydrogen atoms on the zeolite surface reacted with oxygen to form H_2O and that H-ZSM-5 itself exhibits a high level of aromatic formation if the product hydrogen atoms on the surfaces are effectively removed from the reaction system.

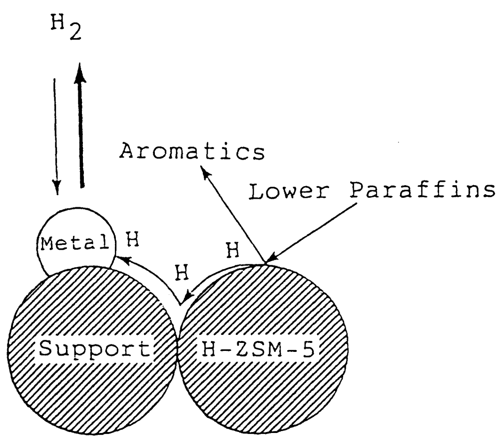

Fig. 1. Model of hydrogen reverse spillover.

A hybrid catalyst composed of H-ZSM-5 and Ga/Al_2O_3 showed cracking activity and aromatic selectivity comparable to those on the Ga-ZSM-5, in spite of the extremely low catalytic activity of Ga/Al_2O_3 for paraffin cracking and olefin aromatization (not shown). The role of added Ga on H-ZSM-5 or Ga/Al_2O_3 in the hybrid catalyst for aromatic formation is most favorably attributed to the removal of hydrogen atoms from the zeolite surface through a "Reverse Spillover" effect as shown in Fig. 1,[7] where Ga acts as the site for the recombination of hydrogen atoms to hydrogen molecules and for its desorption to gas phase.

In order to make the "Reverse Spillover" concept clearer, the catalytic performance of a hybrid catalyst composing H-ZSM-5 and the Ni/SiO_2 was studied. The Ni/SiO_2 was sulfided before use by treating it with a H_2-H_2S mixed gas at 450 °C to suppress its catalytic activity for dehydrogenation or decomposition. Although a Ni-ion exchanged ZSM-5(Ni-ZSM-5) was much less effective than Ga-ZSM-5 in making aromatic hydrocarbons, the hybrid catalyst exhibited even higher activity of n-butane conversion and a comparable selectivity for aromatics to that of Ga-ZSM-5 while the Ni/SiO_2 has little catalytic activity for either n-butane conversion or propylene aromatization (not shown) as was the case for Ga/Al_2O_3. The high performances of the hybrid catalysts should be attributed to the inter-particle transfer of hydrogen atoms from H-ZSM-5 to Ni/SiO_2 and the desorption of the hydrogen atoms as hydrogen molecules through the reverse spillover on the Ni/SiO_2.

Table 1 Conversion of n-butane on a ZSM-5 catalyst[a)]

Catalyst	H-ZSM-5		Ga-ZSM-5	H-ZSM-5 + Ga/Al_2O_3 b)	Ni-ZSM-5	Ni/SiO_2	H-ZSM-5 + Ni/SiO_2 b)
Conversion / %	41.6	50.9[c)]	47.9	47.7	15.7	0.3	47.0
H_2/converted butane / mol ratio	0.3	0.16	1.4	1.3	0.8	-	1.5
Product distribution / carbon %							
C_1+C_2 paraffins	9.6	8.5	9.5	11.0	9.8	-	8.7
C_3H_8	58.6	54.2	52.5	51.7	57.8	-	49.0
C_4H_{10} isomer	3.7	3.5	3.5	3.2	3.0	-	4.9
C_2-C_4 olefins	16.3	15.4	10.0	13.0	20.5	92.3	11.8
C_5+ aliphatics	3.0	2.3	2.5	1.7	3.0	-	2.6
Aromatics	8.8	16.1	22.0	19.4	5.9	7.7	23.0

a) Temperature 450 °C, P_{C4H8} = 20 kPa, P_{N2} = 80 kPa, W/F = 10 g h mol^{-1},
b) Content of 5 wt% Ga/γ-Al_2O_3 or 5 wt% Ni/SiO_2(sulfided) were 20 wt%,
c) Reaction in the presence of 5 vol% of oxygen.

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