DISPROPORTIONATION OF ALKANES VIA MOLECULAR REDISTRIBUTION AND MOLECULAR AVERAGING

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In this paper the disproportionation of alkanes via molecular redistribution (MR) and molecular averaging (MA) is discussed. MR/MA chemistry consists of three steps occurring in one single catalyst bed over a bifunctional catalyst system: dehydrogenation of alkanes to olefinic intermediates, metathesis (disproportionation) of these olefin species and hydrogenation of the metathesis products to alkanes. MR/MA represents a unique and rare example of bifunctional heterogeneous catalysis while there are many examples of acid components being one of the bifunctional elements with a metal, e.g., in reforming, hydrocracking and isomerization reactions. MR/MA chemistry provides simple processes which can be accomplished otherwise only via combinations of other existing chemistries. In this paper, we will use MR of pentanes as an example to demonstrate one industrial application of the MR chemistry.

Keywords: Alkane disproportionation; Molecular redistribution and molecular averaging.

The disproportionation of alkanes to lower and higher analogues is an important reaction from the industrial point of view. In attempts of achieving this goal, many catalysts have been investigated in the past, as exemplified by aluminium chloride/hydrogen chloride[1], zeolites[2], and molecular redistribution/molecular averaging (MR/MA) catalysts[3,4]. Among these and other approaches, MR/MA exhibits many unique and superior features in terms of environmentally benign operations and high activity, selectivity, stability and regenerability of the catalysts. MR/MA chemistry was discovered and explored by Chevron researchers in the 1960's and 1970's[3,4]. This chemistry has been recently rejuvenated for a variety of new applications to meet today's demands to make advance in product-generating technologies and environmental protection[5–14]. Here we will use MR of pentanes as an example to demonstrate one industrial application of the MR chemistry.

Olefin metathesis (or disproportionation) chemistry[15,16] does not work directly for alkanes due to the nature of the saturated C–C bonds of al-

kanes. To make alkane disproportionation possible, the MR/MA chemistry uses a bifunctional catalyst containing both dehydrogenation/hydrogenation and olefin metathesis functions. As illustrated in Fig. 1, the MR chemistry is explained below using n-pentane as feed and a physical mixture of $Pt/Li/Al_2O_3$ and W/SiO_2 as catalyst where Li cations are used to neutralize the acid sites of Al_2O_3 to minimize the acid catalyzed reactions:

n-Pentane is first dehydrogenated to a small amount of n-pentenes on $Pt/Li/Al_2O_3$, with an equimolar amount of hydrogen co-produced. After the metathesis reactions of n-pentenes to lighter and heavier olefins (e.g., ethylene and propylene as well as n-heptenes and n-octenes) on W/SiO_2, all olefins are hydrogenated (by the small amount of hydrogen produced during alkane dehydrogenation) on $Pt/Li/Al_2O_3$ to alkanes, leading to the formation of ethane and propane as well as n-heptane and n-octane as MR products.

In the net reaction, two molecules of an alkane (n-pentane) are converted to one molecule of one lighter alkane (e.g., ethane or propane) and one molecule of one heavier alkane (e.g., n-heptane or n-octane). Theoretically there is no net loss or gain of hydrogen. The feed is a single species,
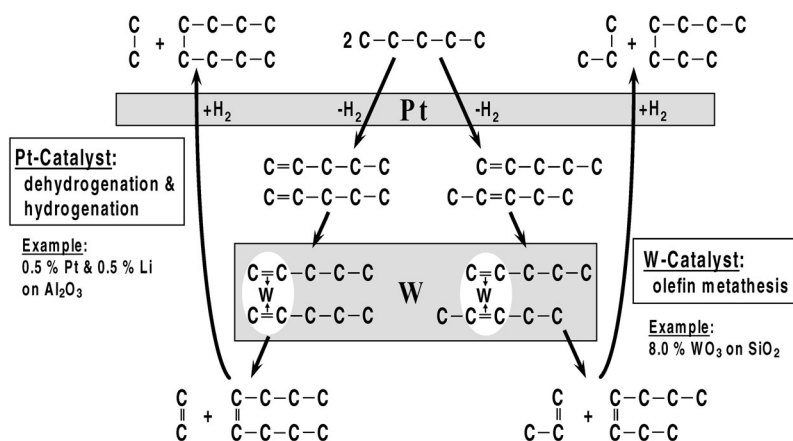

Fig. 1

Illustration of alkane disproportionation of n-pentane to ethane/propane and n-heptane/n-octane via MR over a bifunctional catalyst containing dehydrogenation/hydrogenation and olefin metathesis functions. Note that the intermediate formed on W catalyst is not the real intermediate based on the conventional mechanism of olefin metathesis[15,16]. It is used here only for a simplified illustration of the olefin metathesis reactions on the W catalyst

namely, an alkane. No carrier gas (e.g., H_2 or N_2) is required during the MR reactions. All the reactions occur in a single catalyst bed. The reaction is essentially thermoneutral (neither exothermic nor endothermic).

While the MR chemistry of alkanes represents an analogy to the self metathesis of an olefin to a lighter and heavier olefin, the MA chemistry proceeds in opposite direction where the reaction between two alkanes of different molecular weights leads to the formation of a broad alkane mixture containing the average, similar to cross metathesis of olefins. For example, the MA between $n-C_6H_{14}$ and $n-C_{16}H_{34}$ leads to a broad mixture containing alkanes ranging from $n-C_7H_{16}$ to $n-C_{15}H_{32}$.

EXPERIMENTAL

The MR/MA catalyst presented in this paper was a physical mixture consisting of (i) 0.5 wt.% Pt and 0.5 wt.% Li on Al_2O_3 and (ii) 8.0 wt.% WO_3 on SiO_2. The catalysts were prepared from the 24–42 mesh particles of Al_2O_3 or SiO_2 bases via impregnation with an aqueous solution of $LiNO_3$ and $Pt(NH_3)_4(NO_3)_2$ or ammonium metatungstate, respectively, by a single step incipient wetness procedure. The volume ratio of the Pt-component to W-component was 5:4. The details are reported in our patents[5–14].

In the microunit experiments, the MR catalyst (4.0 ml total catalyst volume) prepared above was loaded into a 1/4 inch stainless steel tube reactor which was mounted into an electric furnace containing three heating zones. The catalyst mixture was first dried in nitrogen flow (100 cc/min) from room temperature to 204 °C (400 °F) in 1 h and held at 204 °C for another 1 h. The catalyst was then reduced in hydrogen flow (100 cc/min) using a temperature program consisting of 204 to 482 °C (400 to 900 °F) in 1 h and holding it at 482 °C for 12 h. Subsequently the catalyst mixture was purged with a nitrogen flow for about 1 h and cooled to a preset reaction temperature, e.g., 399 °C (750 °F). The nitrogen purge was necessary because the presence of hydrogen during the MR/MA reactions would lower the feed conversion[12–14]. The reactor was pressurized to 13 891 kPa (2000 psig) with nitrogen. The nitrogen was switched then to a hydrocarbon feed (e.g., n-pentane) delivered at a liquid feed rate of 2.0 ml/h in order to start the MR or MA reactions at a LHSV (liquid hourly space velocity) of 0.5 h^{-1}. During the reactions, no carrier gas such as H_2 or N_2 was added into the reactor system; only the hydrocarbon feed went through the catalyst bed. The MR/MA products were analyzed with an on-line GC every hour.

RESULTS AND DISCUSSION

In this publication, we will use MR of pentanes as an example to demonstrate one industrial application of the MR chemistry. Here the refinery pentanes are upgraded via MR[5]. Under new regulations for gasoline in US, MTBE is phased out and replaced by more volatile ethanol. This means that pentanes as volatile components in gasoline have to be displaced to maintain the volatility of the blended gasoline constant. MR disproportionates pentanes to C4- (mainly C4's) and C6+ (mainly C6's) alkanes. C4's are then

converted to alkylate in alkylation process while C6+ alkanes are upgraded to aromatics via reforming or to more branched alkanes via hydroisomerization to boost the octane number of gasoline. This concept is depicted in Fig. 2.

Table I shows the results from the MR reactions of pure n-pentane, pure iso-pentane and a mixture of n-pentane and iso-pentane. The results are highlighted below.

1. Both the total n-pentane/iso-pentane conversion and individual conversions of n-pentane and iso-pentane increase with increasing reaction severity (higher temperature).

2. Pure n-pentane can be very easily converted, as demonstrated by the low reaction temperature 288 °C (550 °F) with a conversion of ~56%. A conversion of up to ~80% can be achieved at 343 °C (650 °F), 13 891 kPa (2000 psig) and 0.5 h^{-1} LHSV. It shows also, as expected, that the MR reactions occur more readily with heavier n-alkanes such as n-pentane than with propane and n-butane. Likewise, n-butane is more reactive for MR reactions than propane[6,12–14].

3. Iso-pentane is also reactive for MR reactions, although its conversion (up to ~54% under the conditions applied in our studies) is lower than that of n-pentane. As reported earlier[6,12–14], isobutane is basically not reactive for the MR reactions because its anticipated MR intermediates can not be formed due to the steric hindrance. Apparently, the longer alkyl chain of iso-pentane possesses more characteristics typical of n-alkanes and facilitates its MR reactions.

4. With the n-pentane/iso-pentane mixture, both the total n-pentane/iso-pentane conversion and individual conversions of n-pentane and iso-pentane range below the conversion of pure n-pentane but above the con-
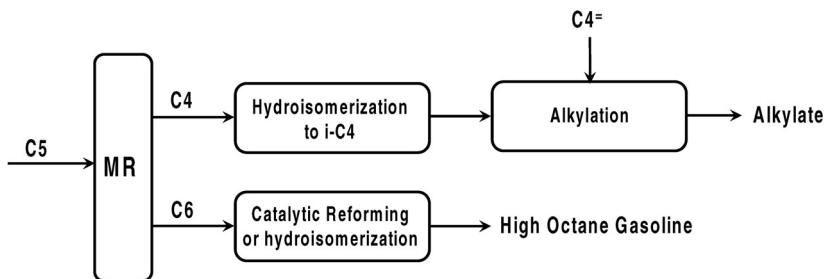

Fig. 2
Upgrade of refinery pentane streams via MR

version of pure iso-pentane. This means that iso-pentane MR is boosted and facilitated by the presence of n-pentane via the cross metathesis reactions between the corresponding olefinic intermediates of n-pentane and iso-pentane. A similar situation was observed with the MR reactions of iso-butane/n-butane and iso-butane/propane mixtures[6,12–14].

5. With pure n-pentane feed, the MR products are basically only n-alkanes. Similarly, the MR products of pure iso-pentane feed are basically

TABLE I
Results from MR of pure n-pentane, pure iso-pentane and n-pentane/iso-pentane mixture at 13 891 kPa (2000 psig), 0.5 h^{-1} LHSV and different temperatures

Feed	Pure n-pentane		Pure iso-pentane		Mixture of n-/iso-pentame	
n-Pentane, wt.%	100		0		43.5	
iso-Pentane, wt.%	0		100		56.5	
Temperature, °C	288	343	343	399	343	399
Total nC5/iC5 conversion, %	56.04	80.52	34.00	53.91	59.50	70.14
nC5 Conversion, %	56.04	80.52	–	–	69.23	80.28
iC5 Conversion, %	–	–	34.00	53.91	52.01	62.33
Yield, wt.%						
Total C2-'s	0.38	1.49	0.58	2.43	1.07	2.63
Methane	0.02	0.19	0.28	1.11	0.10	0.53
Ethane	0.36	1.30	0.30	1.32	0.97	2.10
Propane	6.55	13.93	2.11	5.25	7.50	11.42
Total C4's	17.43	22.07	12.22	14.40	17.71	19.71
n-Butane	17.32	21.75	1.89	3.80	10.93	12.01
iso-Butane	0.11	0.32	10.33	14.60	6.78	7.70
n-Pentane	–	–	0.95	1.65	–	–
iso-Pentane	0.38	0.80	–	–	–	–
Total C6's	13.08	13.24	10.78	12.38	14.10	14.22
2-Methylpentane	0.24	0.55	4.10	6.18	5.51	6.23
3-Methylpentane	0.21	0.47	6.49	5.96	4.32	4.16
n-Hexane	12.63	12.22	0.19	0.23	4.27	3.83
C7+	18.22	29.29	7.36	17.80	19.12	22.15

iso-alkanes. Some small amounts of iso-alkane or n-alkane products are formed from pure n-pentane or iso-pentane feed, respectively. These 'n-to-iso' or 'iso-to-n' reactions are related to the isomerization reactions catalyzed by the acid sites of the $Pt/Li/Al_2O_3$ catalyst which are not completely neutralized by Li cations. These acid catalyzed reactions can be further suppressed, if necessary, by increasing the Li content. It is also to note that the small amount of methane is a by-product caused by hydrogenolysis. As indicated by the mechanism of olefin metathesis, methane is not involved as a product in olefin metathesis reactions and is, therefore, not a MR product.

As reported in our earlier publications[5–14], there are many other industrial applications of MR/MA chemistry. Some examples of them will be also presented at the 2008 Czech and Slovak Symposium on Catalysis.

In summary, MR/MA represents a unique and rare example of bifunctional heterogeneous catalysis consisting of dehydrogenation of alkanes to olefinic intermediates, metathesis (disproportionation) of these olefin species and hydrogenation of the metathesis products to alkanes. MR/MA is carried out in a very simple fashion in one single catalyst bed over a bifunctional catalyst system. As demonstrated in this paper with the MR of pentanes, MR/MR chemistry can be applied in a variety of industrial processes.

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