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Catalytic Ring Opening of MCH and MCP Over Ir Containing USY and HZSM-5 with the Same SiO_2/Al_2O_3 Ratio

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Abstract Selective ring opening (SRO) of methylcyclohexane (MCH) and methylcyclopentane (MCP) over 0.9 wt% Ir supported on USY and HZSM-5 catalysts with same SiO_2/Al_2O_3 ratio were compared in a fixed-bed reactor. Temperature of 250–300 °C, H_2 pressure of 30 bar, WHSV of 1.8 h^{-1} and H_2/feed molar ratio of 40 were used for SRO. The catalysts were synthesized by impregnation method and characterized by BET, H_2-chemisorption, H_2-TPR, XRD, HR-TEM and NH_3-TPD. 0.9 % Ir/USY catalyst converted 52 % of MCH into 28.6 % of ring opening products selectively, and it gave exclusively 67.4 % of ring opening products selectivity at higher 97 % conversion of MCP. In essence, the obtained catalytic results indicated superior catalytic activity for 0.9 wt% Ir/USY catalyst compared to 0.9 wt% Ir/HZSM-5 catalyst. These catalysts exhibit their stability, as well as activity even after 10 h of reaction time.

Keywords Ring opening · Iridium catalysts · Acidity · Bifunctional catalysts · Cyclic compounds

1 Introduction

The demand for diesel fuel and gasoline is expected to increase over the next decade and at the same time environmental concerns have imposed stricter specifications on transportation fuels, such as gasoline and diesel, in order to reduce harmful emissions from exhaust gases. The removal of polynuclear aromatics from diesel fuel has become a focus of intense research due to the stringent environmental legislation associate with clean fuel. Selective ring opening (SRO) of naphthenic rings is the optimum process for reducing the aromatic content of light cycle oils (LCOs) in order to improve diesel quality and consequently its value [1]. The main goal of this research was to study the ring opening (RO) of a model mono-ring compound, namely methylcyclohexane (MCH) and methylcyclopentane (MCP), using a bifunctional catalyst [2]. Aromatic saturation (ASAT) is a potential route to low aromatics and reduced density but it cannot achieve the required cetane number even though it maintains the high molecular weight. Hydrocracking on the other hand increases the cetane number significantly but the molecular weight decreases greatly. The best alternative is SRO of polynuclear aromatics. SRO of naphthenes is one of the most viable processes to produce transportation fuels with high octane/cetane numbers from bitumen derived crude and heavy oils. SRO is defined as opening of naphthene rings without loss of reactant molecular weight and cetane number can be improved significantly [3–5].

Generally, SRO of naphthenes is complex process and therefore, catalysts play an important role in increasing the reaction rates and yield optimization of targeted products [5, 6]. In some cases, catalysts are bifunctional relying on a combination of acid and metal catalysis. Although opening of the ring can be accomplished on either acid or metal catalysts, the combination of the two functions is much more effective than each of them alone [6, 7]. The acidic function promotes the isomerization of six-membered ring structures into the five member, facilitating consequently RO on the metal function. Zeolites are frequently used as a heterogeneous catalysts in petrochemical industry [8]

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because of their crystallinity, high surface area, adsorption capacity, and uniform pore size distribution (PSD) which enable shape selectivity [9].

There are some reports found for RO of naphthenic compound, in which they mentioned Ir as a RO metal of particular interest [1, 4, 10–15]. SRO is generally carried out on certain noble metals and their hydrogenolysis ability increase in the order of Pt < Pd < Ru < Rh < Ir supported on Al_2O_3, SiO_2, and zeolites [1, 13]. Owing to its intrinsically high hydrogenolysis activity, Ir is an active-component of the catalysts employed for upgradation of heavy petroleum fractions, its supremacy is clearly illustrated by several patents [10, 11]. In our previous work an iridium catalyst supported on USY zeolite has been evaluated for hydrotreating of LCO to reduce its aromaticity and improve its cetane index [15]. Another attractive property of Ir is that when it introduced into a hydrocarbon refining catalyst, formation of carbonaceous deposits gets tempered and deactivation markedly slow down [13]. Iridium-based catalysts are more active and selective for breaking unsubstituted C–C bonds in five membered ring compounds compared to platinum, ruthenium, and rhodium catalysts [13, 14]. McVicker et al. [1, 11], reported the high RO activity of Ir catalysts on six-member ring naphthenics. They pointed out the propensity of Ir to cleave C–C bonds via the dicarbene mechanism. On Ir catalysts, this path was found to be independent of particle size and dispersion, but it is strongly dependent on the type of support used [4].

Petroleum distillates contain a complex mixture of multi-membered ring naphthenes, which often have multiple alkyl substituents and which may be joined to one another or fused to aromatic rings. The RO of five membered ring structures into alkanes occurs faster and more selectively than that of six membered rings. It is therefore important for the above mentioned reasons to provide additional insight into the role played by the catalyst in the ring-contraction reaction of naphthenes and formation of open-chain alkanes. The selection of MCP and MCH as a model molecule for the evaluation of ring-opening activity was motivated by its relative simplicity, these molecules can undergo the reactions like ring contraction (RC), RO, ring enlargement (RE), and cracking. Therefore, it is interesting to know and compare the cetane number of each of the different products of MCP and MCH SRO reactions and also it important to determine the general applicability of different catalyst and reactions conditions for the improvement of cetane number of product using these model feeds [5, 16]. Literature survey for SRO of MCH and MCP are summarized in Table 1.

In our previous work the effects of structural and acid–base properties of different supports for Ir as, silica, γ-alumina and USY zeolites on conversion and selectivity for RO of MCP and MCH was studied [2]. The surface properties were slightly modified by the addition of potassium and its effect was evaluated.

In this paper, our main goal is to study the acidity and pore structure effect of supports USY and HZSM-5 for Ir, on conversion and RO selectivity in RO of MCH and MCP. It is widely accepted that the RO of naphthenic on acidic catalysts proceeds via a RC step in which the six-member ring is converted into a five-member ring before opening [17].

2 Experimental

2.1 Catalyst Preparation

The support materials USY and HZSM-5 with same SiO_2/Al_2O_3 molar ratio of 80 were obtained from Zeolyst International. 0.9 wt% Ir was loaded on both zeolites by simple impregnation method by use of $IrCl_3 \bullet 3H_2O$ (Tokyo chemical). After impregnation, the catalysts were filtered, and placed in oven at 100 °C overnight for drying and calcined them at 500 °C for 4 h in air.

2.2 Catalyst Characterization

BET surface area, pore size and pore volume measurements of the catalysts were determined from physical adsorption of N_2 using liquid nitrogen by an ASAP2420 Micromeritics adsorption analyzer (Micromeritics Instruments Inc). Prior to the measurements all the samples were degassed at 250 °C for 2 h to remove the adsorbed moisture from catalysts surface. The surface area and PSD were calculated from the BET and BJH equations, respectively, by using instrument software.

The acidity of the catalysts were measured by temperature programmed desorption of ammonia (NH_3-TPD) using (Autochem II 2920 chemisorption analyser, Micromeritics Instruments Inc) equipped with TCD detector. 0.1 g catalyst was placed in an adsorption vessel and heated to 450 °C in He flow for 1 h with rate of 10 °C/min. Later it was cooled to 100 °C in He flow, at this temperature 0.15 % NH_3 in He was passed through the sample for 1 h. NH_3 desorption was studied from 100 to 600 °C with heating rate of 10 °C/min under He flow.

Temperature programmed reduction (H_2-TPR) was used to examine the metal to support interaction and to find out the reduction temperature of Ir in both catalysts. Same instrument was used for TPR (Autochem II 2920 chemisorption analyser, Micromeritics Instruments Inc), which was used for NH_3-TPD. 0.2 g of catalyst was place in sample holder and pretreated it at 100 °C for 2 h. Temperature programmed reduction were performed in the temperature range of 50 to 800 °C with a heating rate of

Table 1 Literature survey for SRO of MCH and MCP

Feed	Catalyst	Reaction (T/ °C)	Pressure (bar)	Selectivity (%)	Conversion (%)	Ref.
MCH	Ir/Al_2O_3	275	28.5	87	15.5	[1]
	Pt/Al_2O_3	350		5	6.6	
	Ni/Al_2O_3	310		12	2.3	
	Ru/SiO_2	310		42	17	
	H-β	220	atm.	12	–	[3]
	Ir/H-β	220		50.1	69.5	
	Ir/SiO_2	220		9.9	58.9	
	Ir/Al_2O_3	220		23	48	
	Pt/HY + Ir/SiO_2	280	20	84.93	90.1	[6]
	Pt/HY	260		2.4	29.9	
	Ir/SiO_2	320		38	49	
	Pt/mordenite	320	20	13	71	[26]
	Pt/ZSM-5	320		12	75	
	Pt/ZSM-23	320		13	69	
	Ir/USY	300	30	28.6	51.6	This work
	Ir/HZSM-5			11.8	38.1	
MCP	Ir/Al_2O_3	310	28.5	99	52	[1]
	Pt/Al_2O_3	350		97	10.4	
	Ni/Al_2O_3	310		80	17.8	
	Ru/Al_2O_3	310		42	17	
	Pt/hydrotalcite	350	atm	96.5	60.9	[23]
	Rh/HY	200	0.069	66	7.7	[24]
	Rh/SiO_2	200		88	79.1	
	Rh–Pt/SiO_2 (60 % Pt–40 % Rh)	360	0.159	21.1	3.9	[25]
	Ir/USY	300	30	66.4	97.6	This work
	Ir/HZSM-5			45.5	83.4	

10 °C/min at 800 °C hold for 30 min. The hydrogen consumption was monitored by a TCD.

The X-ray diffraction analysis has been done in Rigaku D/Max-3c diffractometer, equipped with anode and Cu K_α radiation. The morphology and metallic dispersion of catalyst has been determined by transmission electron microscope (TEM, JEOL JEM-2010). The metal dispersion in different catalysts was estimated from H_2-chemisorption measurements using (Autochem II 2920 chemisorption analyser, Micromeritics Instruments Inc).

2.3 Catalyst Activity Measurement

The RO of MCH and MCP were carried out in fixed-bed reactor using temperature range of 250–300 °C, H_2 pressure of 30 bar, WHSV of 1.8 h^{-1} and H_2/feed molar ratio of 40. In a typical experiment, catalysts were pelletized, crushed and sieved to 500 mesh size; about 0.5 g of catalyst was loaded in the reactor. Before starting the reaction, the catalysts were reduced at 200 °C with H_2 flow (20 cc/min) for 1 h at atmospheric pressure. The optimum temperature for reduction was adopted form TPR analysis. Products were analyzed by online GC (DS Chrom 6200, Donam Instruments Inc) equipped with a FID detector and DB-1HT capillary column (Alltech, USA) (30 m × 0.2 mm × 0.5 μm), using helium as a carrier gas. GC conditions are, FID temp. of 250 °C, injector temperature of 250 °C, Oven program: holding for 5 min at initial temperature of 45 °C, increased to final temperature of 200 °C with heating rate of 10 °C/min, and hold it for 10 min. Identification of GC peaks were accomplished by GC–MS analysis by Agilent HP 5973 GC–Mass Spectrometer (Agilent Technologies, USA) with Chem-Station MSD software using DB-1HT fused capillary column (30 m × 0.25 mm × 0.1 μm). The same GC conditions were used for the separation. The mass spectrometer was operated in an electron impact ionization (EI) mode at ionization energy of 70 eV in the mass range (m/z) of 30–500 amu.

The conversion of MCH and MCP leads, to produce large amount of hydrocarbons with more than 20 peaks being usually observed in the GC. In order to simplify the discussion, reaction products were grouped as follows,

Products of MCH:

(i) RC: DMCP = (1,1-dimethylcyclopentane + 1,2-dimethylcyclo pentane + 1,3-dimethylcyclopentane), ethylcyclopentane;
(ii) RE : >C7 hydrocarbons;
(iii) Cracking (CR): butane, isobutane, 3-methylbutane, methylcyclopentane, 2-methylcy clopentane, 3-methylcyclopentane, *n*-hexane, <C7
(iv) RO: DMPs = (2,2-dimethylpentane + 2,3-dimethylpentane + 2,4-dimethylpentane), MHs = (2-methylhexane + 3-methylhexane), *n*-heptane.

Products of MCP:

(i) RE: cyclohexane (CH) and benzene (Bz);
(ii) Cracking (CR): <C6
(iii) RO: 2-methylpentane (2MP), 3-methylpentane (3MP), *n*-hexane.

The conversion of MCH and MCP was calculated using the following equations, where

$$\text{Conversion } C\,(\%) = 100 \times [\text{Area (initial)} - \text{Area (final)}]/\text{Area (initial)}$$

Area (initial) designates the peak area of feed before reaction and Area (final) designated the peak area for products after reaction.

Products selectivity S of a product ‘i’ was calculated using Area %, where

$$\text{Area } (\%) = 100 \times [\text{Actual area (product)}i/\text{Area (total)}]$$

$$\text{Selectivity } S\,(5) = 100 \times [\text{Area }\%\,(\text{product})i/\text{Conversion }(\%)]$$

3 Results and Discussion

3.1 Catalysts Characterization

The structural properties of the catalysts determined by N_2 adsorption are well summarized in Table 2. BET surface area of Ir/USY catalyst is found to be 759 and 406 m^2/g for Ir/HZSM-5 catalyst. Surface area of Ir/USY catalyst is higher than that of Ir/HZSM-5 catalyst with similar SiO_2/Al_2O_3 mol ratio and with same 0.9 wt% of metal loading. The total pore volume and pore size followed the same trend. The pore size and pore volume of Ir/USY catalyst were 27.48 Å and 0.52 cm^3 respectively and for Ir/HZSM-5 catalyst, pore size 21.78 Å and pore volume 0.22 cm^3 were observed, which is less than that of Ir/USY catalyst. The isotherm of Ir/USY and Ir/HZSM-5 catalyst exhibits a large uptake of N_2 at a very low relative pressure ($P/P_o = 0.02$), and a hysteresis loop at higher pressures. These two properties are characteristic of microporous and mesoporous materials. Obtained BET results can says that both catalyst exhibits low external surface area of 84 m^2/g for Ir/USY and 45 m^2/g for Ir/HZSM-5 which correspond to 10–11 % of total surface area. The micropore surface area (S_{micro}) and micropore volume (V_{micro}) of both the catalyst showed similar trend as total surface area, total pore volume and pore size. Theses BET results clearly showed that the micropore properties of both catalysts are preserved well. The external surface area (S_{exter}) also higher on Ir/USY as compared to Ir/HZSM-5 catalyst. Mesopore structures that can be influence the interaction between zeolite and iridium and the catalytic performance of the zeolite based hydrocracking catalyst. Kubicka et al. [13] showed that, use of large-pores zeolites favors the ring-opening reaction by limiting deactivation due to coke deposits.

Table 2 Surface properties of 0.9 % Ir/USY and 0.9 % Ir/HZSM-5 catalyst

Catalyst	SiO_2/Al_2O_3 ratio	BET area (m^2/g)[a]	*t*-Plot external surface area (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)[b]
0.9 % Ir/USY	80	759	83.44	27.48	0.52
0.9 % Ir/HZSM-5	80	406	42.93	21.78	0.22

[a] Calculated by the BET method

[b] Calculated from nitrogen adsorption branch at $P/P_o = 0.9$

The H_2-TPR profiles for the 0.9 % Ir/USY and 0.9 % Ir/HZSM-5 catalysts were illustrated in Fig. 1. Both catalysts exhibited a single major peak near at 200 °C, corresponding to the reduction of Ir oxide to metallic Ir, as previously observed [2, 18]. 0.9 % Ir/USY catalyst displayed their H_2 consumption peak at 180 °C and for 0.9 % Ir/HZSM-5 catalyst, peak observed at 170 °C, little shift in

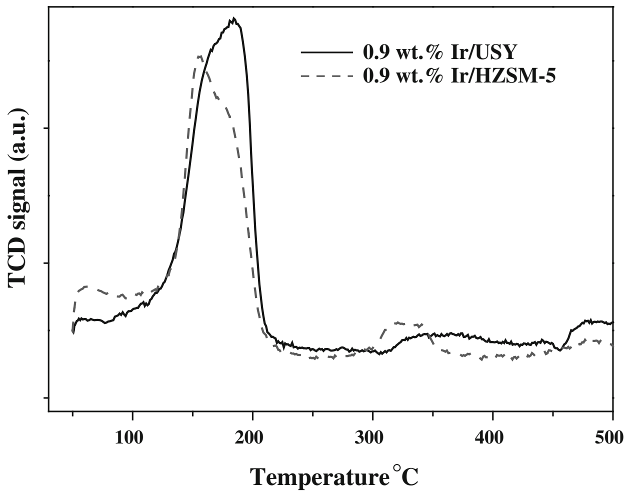

Fig. 1 H_2-TPR profiles of Ir catalysts supported on USY and HZSM-5 zeolite supports

Table 3 Acidity of 0.9 % Ir/USY and 0.9 % Ir/HZSM-5 catalyst

Catalyst	Total acidic strength (μmol/g)	Weak[a]	Medium[b]	Strong[c]
USY	487	44	170	273
0.9 % Ir/USY	388	115	94	179
HZSM-5	315	78	178	59
0.9 % Ir/HZSM-5	290	161	97	32

[a] Calculated from the NH_3 amount desorbed in the 100–270 °C

[b] Calculated from the NH_3 amount desorbed in the 270–400 °C

[c] Calculated from the NH_3 amount desorbed in the 400–600 °C

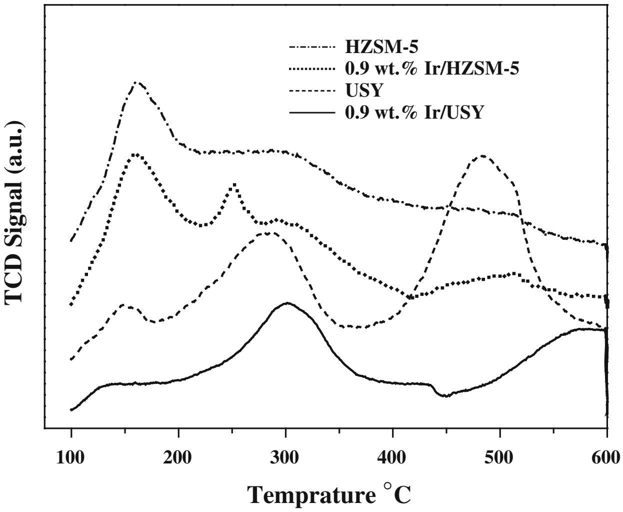

Fig. 2 NH_3-TPD profiles of Ir catalysts supported on USY and HZSM-5 zeolite supports

reduction temperature has been observed. In our investigation, we found that reduction peak appears at low temperature which shows weak interaction of Ir metal with support, and thus it indicates that good dispersion of Ir metal on both zeolite supports [18].

The NH_3-TPD results of acidity are shown in Table 3 and NH_3-TPD profiles of both catalysts have been shown in Fig. 2. Total acidic strength and its distributions into weak, medium and strong are determined by measurement of total amount of NH_3 chemisorbed at different temperature. Peaks assigned at low and high temperatures could be attributed to NH_3 desorbed from weak and strong acid sites [19]. Generally peak observed in range of 100–270 °C and 270–400 °C is due to weak and medium acidic strength respectively.

It is clearly seen that bare USY and HZSM-5 zeolites contains a large amount of acidic sites than that impregnated with Ir. As we previously observed [2, 15] impregnation with Ir, results in a loss of acidic sites as shown in Table 3, which may indicate blocking of pores during Ir impregnation process. In 0.9 % Ir/USY catalyst, broad desorption peaks were observed in the temperature range of 400–600 °C showing the presence of strong acidic sites which is higher than that of Ir/HZSM-5 catalyst. The total acidic strength of 0.9 % Ir/USY is 349 μmol/g and for 0.9 % Ir/HZSM-5 is 291 μmol/g has been found. The strong acidic strength for 0.9 % Ir/USY catalyst is found to be 97 μmol/g, which is three times higher than that of Ir/HZSM-5 catalyst, and with weak and medium acidic strength of 115 and 94 μmol/g respectively was observed. The weak acidic strength of 161 μmol/g and medium of 97 μmol/g were found in Ir/HZSM-5 catalyst.

These characterization results indicate that 0.9 % Ir/USY catalyst exhibit high acidity with good Ir dispersion on support. It has been previously reported that selective hydrogenation of alycyclic compound depends on the strong acidic site of the support [2, 20].

In XRD pattern (not given here) of both the catalysts, loading of Ir did not show any crystalline phase related to the iridium and also no distinct decrease in the relative crystallinity of both supports has been observed. Diffraction peak for Ir was not observed in diffraction pattern, likely due to high dispersion of Ir nano particle as well as due to the low loading of metal (0.9 wt%).

The result of XRD analysis, concerning highly dispersed metal particles with a small size, were confirmed by HR-TEM analysis. The HR-TEM micrographs of reduced 0.9 % Ir/USY and 0.9 % Ir/HZSM-5 catalysts are shown in Fig. 3. By thorough examination of the images of both catalysts revealed that both catalysts possessed high dispersion of metallic Ir, having average particle size of 2–3 nm. From H_2-chemisorption of both catalysts we observed that H_2/Ir value (derived from hydrogen uptakes) >1 which indicates high iridium dispersion, as typically observed by other researchers working with supported Ir catalysts [4, 12]. At the same metal loading and same metal dispersion, catalyst behavior depends on acidic properties of supports.

3.2 Selective RO of MCH and MCP

Ring opening appears to be an attractive process for decreasing the aromatic content of and increasing cetane number of diesel, without significant losses in molecular weight. Within a series of noble metals investigated by Gault [21], Ir displayed the strongest tendency to break unsubstituted C–C bonds; McVicker et al. [1] evaluated that 0.9 wt% Ir/Al_2O_3 catalyst active for the selective production of RO products. They have report 87 % selectivity for RO at 15 % conversion of MCH at 578 K and also received 99 % of RO product selectivity at 52 % conversion of MCP. These authors found higher yields to RO products of MCH, when a high activity hydrogenolysis catalyst, such as Ir/Al_2O_3, is coupled with an acidic zeolite

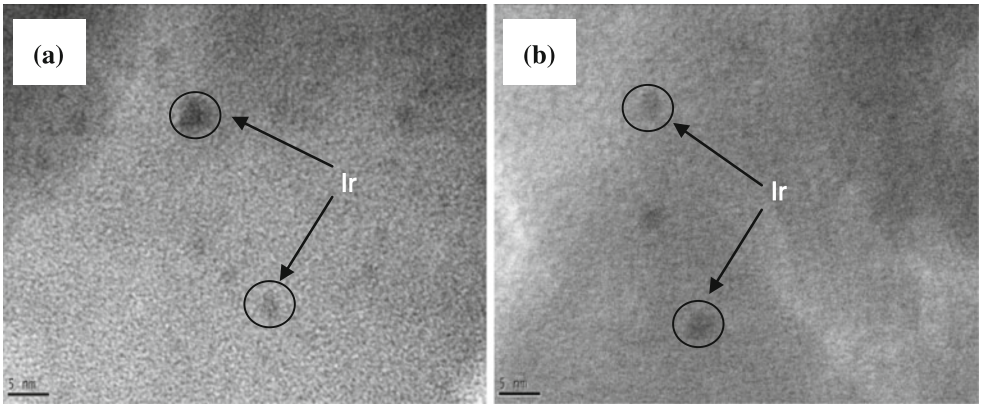

Fig. 3 HR-TEM images of reduced **a** 0.9 % Ir/USY and **b** 0.9 % Ir/HZSM-5

(e.g. ECR-32). In our study we observed little less RO selectivity for both MCH and MCP as compared to reported work [1] but conversion is improved significantly.

In case of MCP we got *n*-hexane along with 2MP and 3MP as a RO products but McVicker et al. [1] observed different products distribution, they got only 2MP, 3MP selectively instead of *n*-hexane. In the case of platinum metal it displays a preference for bond cleavage at the tertiary carbon of MCP, as evidenced by relatively high *n*-hexane selectivity [1]. The RO of MCP can follow two pathways: a non-selective mechanism and a selective mechanism [21]. The non-selective mechanism leads to formation of 2-MP, 3-MP and *n*-hexane, in a statistical distribution of 2:1:2, on highly dispersed particles of Pt. Another pathway for RO was observed, the partly selective mechanism, in competition with non-selective and selective mechanisms. This mechanism was obtained for noble metals dispersed on acidic support and formed *n*-hexane in a high proportion [22]. Galperin et al. [23] observed, in the presence of potassium, platinum bifunctional catalysts behave like monofunctional metallic catalysts which convert MCP through a nonselective RO mechanism with total RO selectivity of around >95 % over the conversion range of 75–80 %. At 200 °C, rhodium is a very efficient hydrogenolysis catalyst, RO is dominating reaction on Rh/HY samples [24].The selectivity towards benzene formation was highest on the Rh–Pt/SiO_2 bimetallic sample, especially at higher temperatures. Selective RO products occurred on all catalysts, resulting mostly in 2 and 3-MP and less *n*-hexane [25].

In present work possible product obtained during hydrocoversion of MCH and MCP are shown in Fig. 4. RO pathway of MCH on both catalysts, shows the same sequence, where the primary products are a mixture of dimethylcyclopentanes and ethylcyclopentane formed by RC of MCH [26]. The primary products undergo RO reactions with formation of *n*-heptanes and isohexanes, further they react to form cracking products. The selectivity and distribution of products from RC and RO reactions are strongly affected by the acidity of zeolites [23]. RO of MCP resulted in formation of *n*-hexane, 2-MP and 3-MP and C_1–C_5 hydrocarbons.

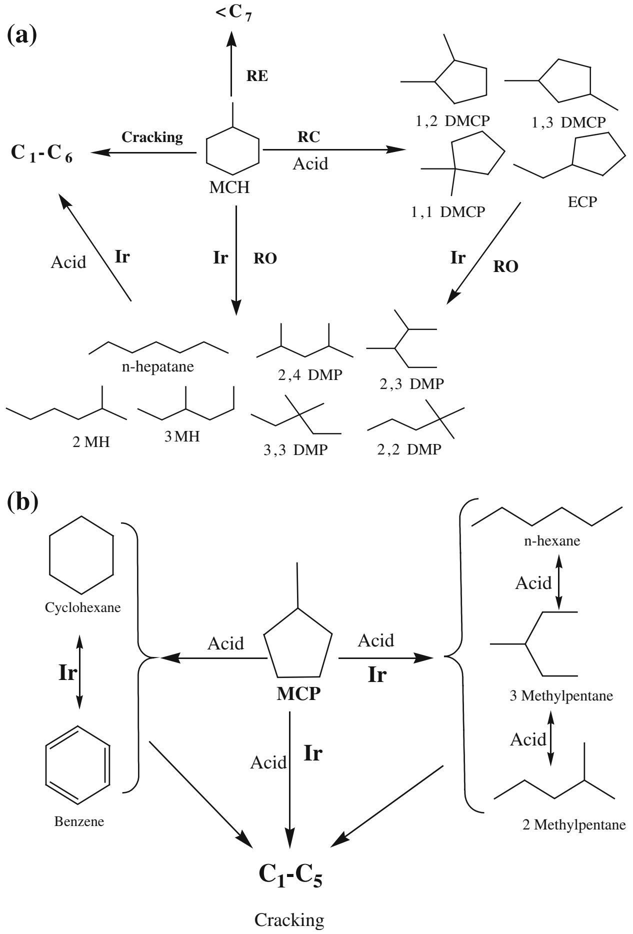

Fig. 4 Possible product forms during hydrocoverstion of **a** MCH [3, 6] and **b** MCP [2, 23]

Figure 5 shows the RO results of (a) MCH and (b) MCP over both 0.9 % Ir/USY and 0.9 % Ir/HZSM-5 catalysts. It

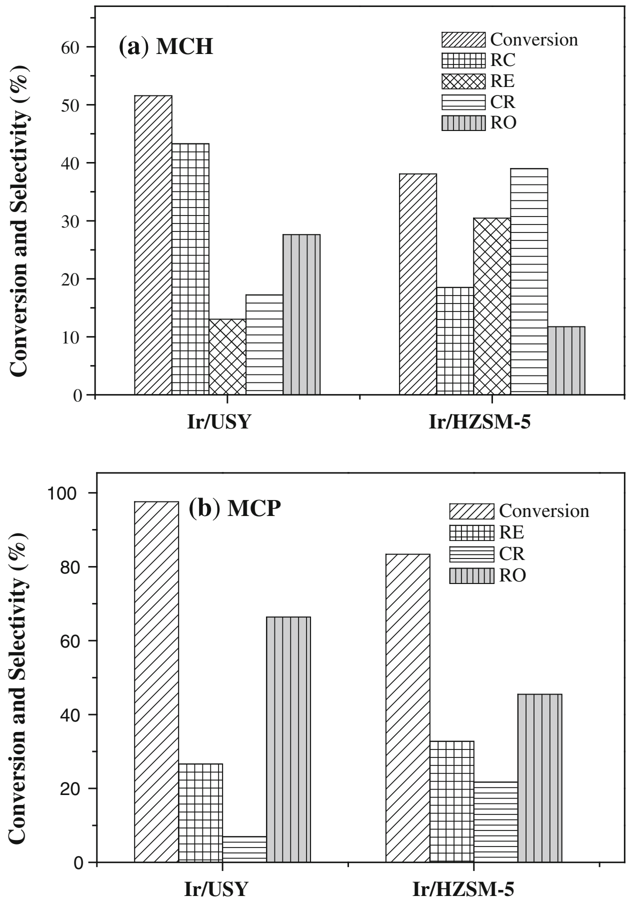

Fig. 5 **a** Conversion and selectivity of MCH. **b** Conversion and selectivity of MCP. Over 0.9 % Ir/USY and 0.9 % Ir/HZSM-5, Reaction condition: $T = 300\ ^{\mathrm{O}}\mathrm{C}$, $P = 30$ bar, WHSV = $1.8\ \mathrm{h}^{-1}$, H_2/feed molar ratio = 40. *RO* ring opening, *RC* ring contraction, *CR* cracking products, *RE* ring enlargement

is clearly seen that the conversion and RO selectivity was higher on 0.9 % Ir/USY as compared to 0.9 % Ir/HZSM-5. In case of 0.9 % Ir/HZSM-5 catalyst, MCP conversion of 83.4 % and RO selectivity of 45.5 % was found. Over 0.9 % Ir/USY catalyst MCP conversion was found to be 97.6 % with RO selectivity of 66.4 %. Similarly, conversion of MCH was 38.1 % observed for 0.9 % Ir/HZSM-5 catalysts and, which can improved to 51.6 % by 0.9 % Ir/USY, and also it improved RO selectivity to 28.6 from 11.8 %.

The main possible reason for the enhancement of activity by 0.9 % Ir/USY was considered due to presences of higher strong acidic strength, which is three times higher than that of 0.9 % Ir/HZSM-5 catalyst. The total acidic strength (acid sites population) seems to be the main responsible factor for the increase of MCH and MCP conversion [23]. For MCH conversion two pathways have been considered, direct path for RO and an indirect path illustrated by two consecutive reactions (RC reaction followed by indirect RO). The relative importance of each pathway is a function of the acidity [3]. The acidity of 0.9 % Ir/HZSM-5 catalyst is not sufficient to initiate RC and RO. But, 0.9 % Ir/USY catalyst have sufficient acidity to contract the ring of MCH before its opening. From the Fig. 5a, it is clearly seen that on 0.9 % Ir/HZSM-5 catalyst, RE, CR product selectivities are 39 and 30 % respectively and RO, RC products are 11 and 18 % respectively. These results are contrast with 0.9 % Ir/USY catalyst results, RC and RO product selectivity is quite high, it gave 43 % of RC and 27 % of RO and RE selectivity of 17 % and CR selectivity of 13 % only been found. 0.9 % Ir/HZSM-5 catalysts with low acidity, leading to a decline in hydrogenolysis ability. In contrast, with high acid strength in 0.9 % Ir/USY should cause no loss of hydrogenolysis ability in the metal, resulting in relatively high selectivity toward RO product in both MCH and MCP. Conversion and selectivity of MCH and MCP up to 10 h of reaction time (TOS) using both catalysts were shown in Fig. 6. The first data point, evaluated after 2 h of catalytic operation, directly reveals the differences in catalytic behavior between 0.9 % Ir/USY and 0.9 % Ir/HZSM-5. The maximum conversion of MCH (52 %) is obtained on 0.9 % Ir/USY (Fig. 6a) whereas the lowest conversion value in between 38–40 % has been observed over 0.9 % Ir/HZSM-5 (Fig. 6c). The decrease in conversion with time on stream has been observed in the first few hours, and then it reached to steady state. RO and RC products selectivity over 0.9 % Ir/USY increase with time and slight decrease in RE and CR products selectivity were observed. But in case of 0.9 % Ir/HZSM-5 catalyst, RC and RO products selectivity initially decrease to some extent (6 h), and then found to be quite steady. There were no significant changes observed for RO of MCP. The conversion of MCP was found to be quite steady with time on both catalysts. RO product selectivity of MCP on 0.9 % Ir/USY found to be decreased and RE selectivity gets increased with time, but CR selectivity was constant at every stage. On 0.9 % Ir/HZSM-5, RO selectivity of MCP initially decreased down, but it maintain steady state after 6 h, on the other hand RE and CR selectivity increased slowly with increase in time.

The change in conversion and product selectivity as a function of time has been clearly observed in Fig. 6. The higher strength of acid sites speed up more isomerization, resulting higher RC and RO selectivity in all cases over 0.9 % Ir/USY catalyst. The primary products RC undergo RO reactions, further they react to form cracking products hence the selectivity of cracking product increases as reaction time increases. The selectivity and distribution of products deriving from RC and RO reactions are strongly affected by the acidity of zeolites [23]. Buchanan et al. [27] studied the relative rates of cracking and resultant product distributions for cracking of C_5–C_8 olefins over ZSM-5 catalyst were quantified and rationalized in terms of

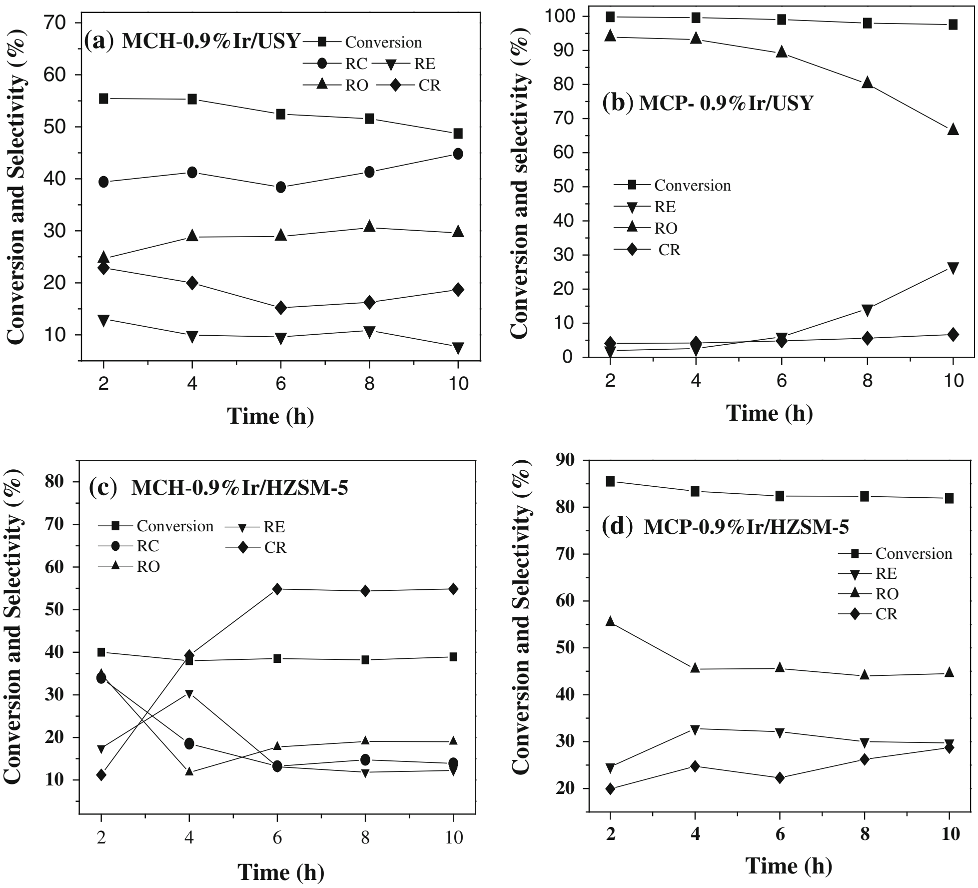

Fig. 6 Conversion and selectivity of **a** MCH and **b** MCP on 0.9 % Ir/USY, conversion and selectivity of **c** MCH and **d** MCP on 0.9 % Ir/HZSM-5 as a function based on time on stream (TOS) were, Conversion (*box*), RC (*circle*), RO (*triangle*), RE (*inverted triangle*) and CR (*diamond*). Reaction condition: T = 300 °C, P = 30 bar, WHSV = 1.8 h^{-1}, H_2/feed molar ratio = 40

carbenium ion mechanisms. They report cracking rates increase more dramatically with carbon number for olefins than for paraffins, as more energetically favorable modes become available for β-scission of the carbenium ion formed by proton donation to the olefin.

Ring opening of MCP resulted in formation of RO, RE and C_1–C_5 hydrocarbons. With increase in reaction time, RO products of MCP converted into cracking and RE. In all the cases cracking and RE product selectivity is much higher over low acidic strength 0.9 % Ir/HZSM-5 catalyst.

4 Conclusions

The activity of 0.9 % Ir loaded on different zeolites (USY, HZSM-5) with same SiO_2/Al_2O_3 has been investigated in the SRO of MCH and MCP at 300 °C in presence of hydrogen. The RO of MCH over both catalysts proceeds via several intermediates, including different isomers mixture (dimethylcyclopentanes and ethylcyclop entane) of MCH.

Both the catalysts have same metal loading and SiO_2/Al_2O_3 ratio and from H_2-TPR analysis it is observed that there is no significant difference of Ir dispersion on both supports. It could clear that the RO mechanism MCH and MCP over Ir catalysts depends strongly on the acidity of support and slightly on the metal dispersion. Influence of different acidic support on conversion and RO selectivity is clearly observed. Acidic strength of 0.9 % Ir/USY zeolite catalyst was found to highly suitable for higher conversion and RO selectivity for MCH and MCP. The conversion and selectivity to RO was higher in case of 0.9 % Ir/USY catalyst than that of 0.9 % Ir/HZSM-5. Variations in conversion and products selectivity of Ir supported on USY and HZSM-5 zeolite during RO of MCH and MCP can be explained in terms of change of support acidity. Thorough study of the influence of zeolite acidity on the catalytic performance of 0.9 % Ir/USY and 0.9 % Ir/HZSM-5 catalysts for the RO of MCH and MCP was carried out.

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