



Short Communication

The effect of Mg and K addition to a Mo₂C/HY catalyst for the hydrogenation and ring opening of naphthalene

Xuebin Liu, Shahrzad Jooya Ardakani, Kevin J. Smith *

Department of Chemical and Biological Engineering, The University of British Columbia, 2360 East Mall, Vancouver, BC, Canada V6T 1Z3

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ABSTRACT

The effect of Mg (0.5–2 wt.%) or K (1 wt.%) added to a 20 wt.% Mo₂C/HY catalyst for the hydrogenation and ring opening of naphthalene, is reported. Mg addition increased Mo₂C dispersion without affecting catalyst acidity, whereas K increased Mo₂C dispersion but decreased acidity by 30%. Both Mg-Mo₂C/HY and K-Mo₂C/HY increased naphthalene and coke-precursor hydrogenation whereas ring-opening selectivity was reduced compared to the Mo₂C/HY. Metal dispersion and catalyst acidity are key parameters that determine bifunctional catalyst performance. Although Mg and K addition improved Mo₂C dispersion they did not provide the optimum acidity needed for increased ring-opening selectivity.

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1. Introduction

Production of synthetic crude oil (SCO) from the Canadian oilsands is expected to double in the next 10 years. SCO is a light sweet crude with some significant quality challenges, largely related to high aromaticity. The heavy gas oil (HGO) bottom cut from SCO (about 38 vol.%) contains as much as 90% cycloparaffins plus aromatics, which cause processing problems, particularly in fluid catalytic cracking (FCC) units. Hydrogenation and ring opening (RO) of the cycloparaffins and aromatics is one approach to address the quality issues and refining challenges associated with SCO [1].

Metal catalysts dispersed on acidic supports are preferred for selective ring-opening and a number of Group VIII metals have been reported to have good activity and selectivity for RO, including Rh, Ru, Ir, Pt, Pd/Pt and Pt/Ir [2–7]. However, these metals are costly and have relatively low resistance to sulphur poisoning. In previous work, molybdenum carbide supported on zeolites of medium acidity were identified as potential alternatives to conventional supported Group VIII metal catalysts for RO [8]. Subsequent studies showed that increased Mo₂C loading decreased the catalyst acidity, as measured by temperature-programmed desorption of *n*-propylamine, and increased the Mo₂C dispersion, as measured by XRD and XPS [9]. With naphthalene as reactant, an increased Mo₂C loading increased conversion up to a

20 wt.% Mo₂C loading, whereas the selectivity to hydrogenation and RO products remained relatively constant. The results from this study also demonstrated that the catalysts underwent significant deactivation during reaction with naphthalene. Carbon deposition (coke formation) over the acidic HY support was identified as the main cause of the fast deactivation with naphthalene as reactant [9]. Reduced acidity of the HY support, as a consequence of increased Mo₂C loading decreased the catalyst deactivation. These results were described in terms of a bimolecular reaction mechanism on acid sites that led to coke formation competing with a monomolecular reaction mechanism on metal and acid sites that yield hydrogenation and RO products [9–11].

Metal dispersion and catalyst acidity are key parameters that determine bifunctional catalyst performance. In the present work, the effect of Mg and K added to a bifunctional Mo₂C/HY catalyst is reported. The impact on Mo₂C dispersion and acidity is discussed in terms of the RO selectivity and stability of the catalysts measured during naphthalene hydrogenation and ring-opening.

2. Experimental

2.1. Catalyst preparation

Catalysts with 20 wt.% Mo₂C supported on HY zeolite and doped with 0.5–2 wt.% Mg or 1 wt.% K, were prepared by co-impregnation of the zeolite (Zeolyst™ CBV720, SiO₂/Al₂O₃ = 30) using a quantified aqueous solution of ammonium heptamolybdate tetrahydrate (MoO₃ 81.0–83.0%, Sigma) mixed with magnesium nitrate hexahydrate (99%,

* Corresponding author.

E-mail address: kjs@interchange.ubc.ca (K.J. Smith).

Sigma) or potassium nitrate (99.97%, BDH Chemicals). After aging at 70 °C for 2 h, the impregnated support was dried at 120 °C for 12 h and calcined at 500 °C for 4 h. Carburization of the calcined catalyst precursor was done in a quartz U-tube reactor (i.d. = 7 mm) by temperature programmed reaction in a 100 ml (STP)/min of 20%CH₄/80%H₂ (UHP) and a ramp rate of 5 °C/min up to 700 °C. The catalyst was held at 700 °C for 4 h and then the gas was switched to H₂ (UHP) to remove excess carbon by holding at 700 °C for a further 2 h before cooling to room temperature. Finally, the catalysts were passivated at room temperature in a 1% O₂ in He stream (150 ml (STP)/min) before exposure to air. The resulting MgO-Mo₂C/HY and K₂O-Mo₂C/HY catalysts were subsequently characterized and tested as described below.

2.2. Catalyst characterization and testing

X-ray diffraction (XRD) was performed on the passivated catalysts using a Siemens D500 diffractometer with a Cu K α X-ray source and crystallite size (d_c) estimates were made using the Scherrer equation, as described previously [8,9]. The BET surface area and pore volume of the passivated catalysts were determined from N₂ adsorption–desorption isotherms measured at –196 °C using a Micromeritics ASAP 2020 analyzer. Catalysts were degassed at 250 °C for 24 h under vacuum (5 μ m Hg) before being analyzed. Thermogravimetric analysis (TGA) of the catalysts before and after reaction with naphthalene was done in a flow of dry air (16 ml (STP)/min) and a ramp rate of 5 °C/min to the final temperature of 850 °C using a TGA-50 thermogravimetric analyzer (Shimadzu, Japan). The weight gain and loss were quantified according to the methods described previously [9] and differential TGA (DTGA) was accomplished using standard TGA software.

Catalyst acidities were determined by *n*-propylamine (*n*PA) pulsed adsorption and TPD using a Micromeritics Autochem II 2920 unit equipped with a thermal conductivity detector (TCD). Approximately 40 mg of catalyst was pretreated in He (30 ml (STP)/min) at 120 °C for 1 h to remove water, followed by a 1 h treatment in H₂ (30 ml (STP)/min) at 400 °C to activate the passivated Mo₂C, and finally a 2 h flush in He (30 ml (STP)/min) at 500 °C to remove adsorbed H₂. While under He flow, the catalyst was cooled to 120 °C and a flow of He (30 ml (STP)/min) saturated at room temperature with *n*-PA (99+%, Aldrich) was injected into the He flow in 0.5 ml pulses. Pulses of *n*-PA were injected repeatedly until the TCD signal showed no further adsorption. Following the pulsed adsorption experiments, the system was purged for 1 h in a He flow (30 ml (STP)/min) to remove residual amine. Subsequently, TPD of *n*-PA from 120 °C to 700 °C was performed at a heating rate of 5 °C/min. The detailed interpretation of the *n*-PA adsorption/desorption data have been described previously [9].

The RO performance of each of the catalysts was determined in a stainless steel fixed-bed reactor (i.d. = 9 mm) at 300 °C and a total pressure of 3.0 MPa with 5% naphthalene in *n*-heptane as the model reactant. The reaction products were analysed by gas chromatography (GC) and gas chromatography/mass spectroscopy (GC/MS) and

grouped as hydrogenation (Hydro), ring opening (RO) and polyaromatics (POLY). RO products were mainly alkylcyclohexanes, alkylbenzenes and alkylindenes and POLY products were aromatics and naphthenes with more than 10 carbon atoms, mainly alkyltetralins. Further details of the activity tests and product analysis procedures have been described previously [8,9].

3. Results and discussion

Following calcination, carburization and passivation, the Mg-Mo₂C/HY and K-Mo₂C/HY catalysts had significantly reduced surface area, total pore volume, micropore area and micropore volume (Table 1) compared to the Mo₂C/HY catalyst. However, the surface area was not strongly dependent upon the amount of Mg added, with all the Mg-Mo₂C/HY catalysts having surface areas in the range 389–462 m²/g, compared to 522 m²/g for the Mo₂C/HY. The relative loss in BET and micropore area with Mg or K addition to the Mo₂C/HY, was almost the same. Fig. 1 shows the micropore size distribution of the 2%Mg-Mo₂C/HY catalyst compared to the HY zeolite. Clearly, there was no significant change in the zeolite micropore size distribution upon addition of Mg, although there was a small reduction in micropore volume (Table 1). The pore size distribution data of Fig. 2 shows the reduced volume associated with the mesopores in the range 30–50 Å for the 2%Mg-Mo₂C/HY compared to the Mo₂C/HY and the HY alone. Together these data suggest that the MgO/K₂O (the metal oxides formed during calcination) are located throughout the zeolite mesopores outside of the zeolite micropores. The size of the Mo₂C crystallites (Table 1) confirm that the Mo₂C was located outside of the zeolite micropores [9] and so the reduction in the micropore volume must be due to pore-mouth blocking by Mo₂C or MgO/K₂O crystals.

The acidity data, shown in Table 1 for the Mo₂C/HY catalysts doped with different quantities of Mg, give an average acidity of 0.93 \pm 0.09 mmol/g, in good agreement with the acidity of the un-doped Mo₂C/HY catalyst (0.97 mmol/g). Hence we conclude that the addition of Mg had no significant effect on the acidity compared to the Mo₂C/HY catalyst, whereas the K decreased the acidity by approximately 30% (0.68 mmol/g). The impact of the Mg- and K-oxides is expected to depend on their dispersion, basicity, and their ability to ion exchange with the HY zeolite. The amount of Mg and K added to the Mo₂C/HY was well below the ion exchange capacity of the HY. Clearly, some K was exchanged with the acid sites of the HY support during preparation, but this did not occur in the case of Mg.

The XRD analysis (Fig. 3) of the catalysts showed that the added Mg or K decreased the Mo₂C crystal size (Table 1 and Fig. 3). The improved Mo₂C dispersion is also reflected in the activity data of Table 2. The naphthalene conversion on the Mg- and K-doped Mo₂C/HY catalysts was marginally higher than on the Mo₂C/HY, whereas the selectivity to hydrogenated products increased significantly and the polyaromatic and RO product selectivity decreased. These results suggest an increased hydrogenation capability of the doped catalysts, that not only affected the product selectivity, but that would also be expected to impact catalyst deactivation by reducing coke formation.

Table 1
Properties of Mg-Mo₂C/HY, K-Mo₂C/HY and Mo₂C/HY catalysts used for naphthalene hydrogenation and ring-opening.

Catalyst	BET area m ² /g	Total pore volume cm ³ /g	Micropore area m ² /g	Micropore volume cm ³ /g	Average pore diam. nm	d_c of Mo ₂ C by XRD nm	Total acidity mmol/g
HY	783	0.49	543	0.25	2.52	–	1.80
20%Mo ₂ C/HY	522	0.36	385	0.18	2.76	22	0.97
0.5%Mg-20%Mo ₂ C/HY	451	0.34	322	0.15	2.99	13	0.85
1.0%Mg-20%Mo ₂ C/HY	389	0.30	272	0.13	3.09	11	0.91
1.5%Mg-20%Mo ₂ C/HY	430	0.30	324	0.15	2.82	13	–
2.0%Mg-20%Mo ₂ C/HY	462	0.30	358	0.17	2.60	10	1.02
1.0%K-20%Mo ₂ C/HY	444	0.32	337	0.16	2.84	14	0.68

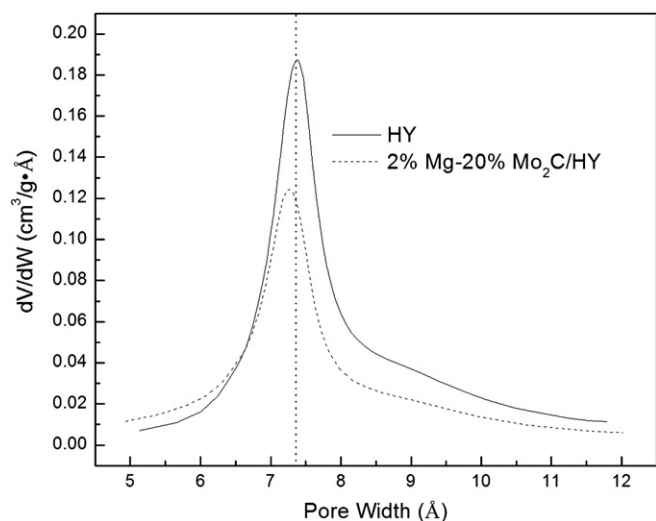


Fig. 1. Micropore size distribution of HY and 2%Mg-20%Mo₂C/HY catalyst.

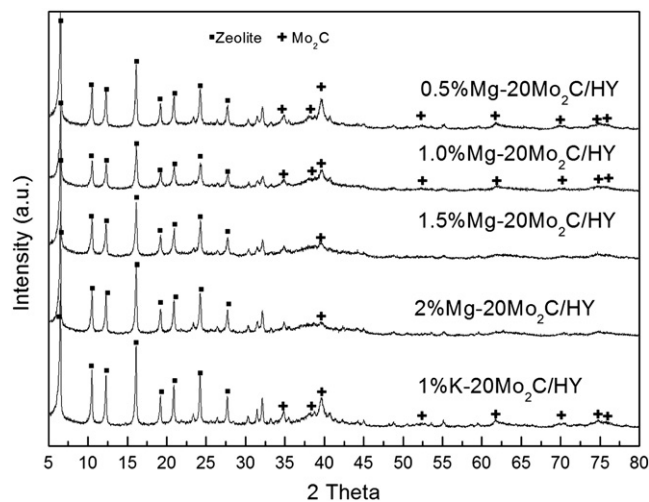


Fig. 3. XRD of Mg-Mo₂C/HY and K-Mo₂C/HY catalysts.

The results of the DTGA analysis of the un-used and used catalysts from the present study are shown in Figs. 4 and 5, respectively. There were two peaks that showed a weight increase during the DTGA of the un-used catalysts (Fig. 4). The peaks appearing at low temperature (<350 °C) are attributed to the oxidization of well dispersed Mo₂C, while those emerging at higher temperature are attributed to the oxidation of a Mo₂C “bulk-phase” species [9]. As shown in Fig. 4, the second peak decreased with increased Mg loading, and this peak nearly disappeared at a Mg loading of 2%, indicating that at this level of Mg loading the Mo₂C was well dispersed onto the HY support, consistent with the XRD results (Fig. 3). A similar analysis of the second weight gain peak of the DTGA spectra shows that the Mo₂C dispersion of the K-doped catalyst was higher than that of the 0.5% Mg-doped catalyst, but not as high as that obtained for the 1% Mg-doped catalyst. These observations are also consistent with the XRD results of Table 1 and Fig. 3. The summary of the TGA analysis, shown in Table 3, demonstrates that the total weight gain of the un-used catalysts decreased from 6.1% to 4.0% as the Mg loading increased from 0.5% to 2%. As noted previously, the weight gain was mainly caused by the oxidation of Mo₂C. This suggests that the amount of oxidizable Mo₂C on the Mo₂C/HY catalysts decreased in the presence of Mg, probably because of a higher Mo₂C

dispersion that results in stronger interaction between the Mo₂C and the HY support, yielding Mo₂C_xO_y species and making the Mo₂C less oxidizable.

Results from TGA/DTGA of the Mg-Mo₂C/HY and K-Mo₂C/HY catalysts after 5 h of reaction with 5% naphthalene in heptane are shown in Fig. 5 and Table 3. Comparison of the spectra in Figs. 4 and 5 shows a larger weight loss below 150 °C for the used catalysts than the un-used catalysts. This means that besides water, some volatile hydrocarbons remained on the catalysts after reaction. The weight loss of the used catalysts at low temperature influenced the analysis of the weight gain at low temperature (because of some peak overlap). Therefore, the weight gain of the used catalysts (due to Mo₂C oxidation) was smaller than that of the corresponding un-used catalysts, as shown in Table 3.

Weight loss peaks between 350 and 550 °C (Fig. 5) are attributed to carbon removal from the used catalysts [9]. However, there is some overlap between these weight loss peaks and the weight gain peak between 350 and 550 °C shown in the DTGA of the un-used catalysts (Fig. 4), and this weight loss was accounted for in the used catalyst weight gain data reported in Table 3. After reaction, the Mg- and K-doped Mo₂C/HY catalysts had a weight loss of 3.9 ± 0.6 wt.%, significantly smaller than the 7 wt.% of the un-doped Mo₂C/HY catalyst and indicative of less coke deposition and catalyst deactivation for the Mg- and K-doped Mo₂C/HY catalysts compared to the Mo₂C/HY. With increasing Mg content from 0.5% to 2%, the amount of coke formed on the catalyst did not change significantly. We speculate that coke accumulation on the HY support was not effectively inhibited by Mg, since addition of the Mg did not impact the catalyst acidity. Furthermore, the lower coke content of the Mg-doped Mo₂C/HY catalysts compared to the Mo₂C/HY must be due to improved Mo₂C

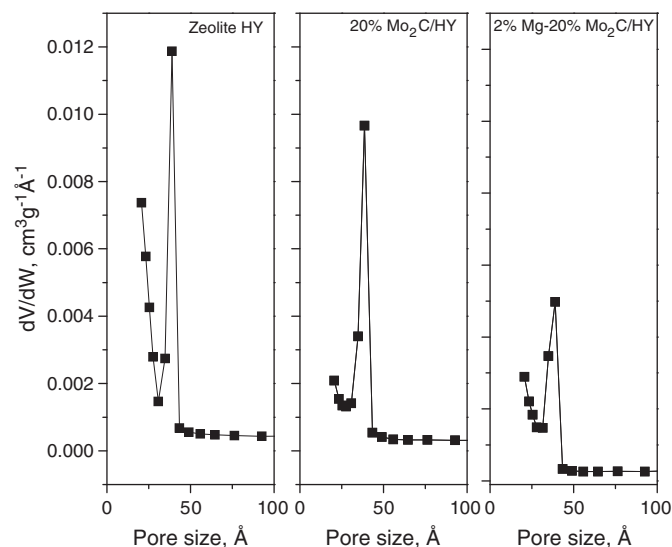


Fig. 2. Mesopore size distribution of HY, 20%Mo₂C/HY and 2%Mg-20%Mo₂C/HY catalysts.

Table 2

Summary of naphthalene conversion and product selectivities measured over Mg-Mo₂C/HY and K-Mo₂C/HY catalysts^a.

Expt.	Mg (K) wt. %	Conv. (%)	Selectivities (%)					Yield (%)	
			Decalin	Tetralin	Hydro	RO	Poly	Hydro	RO
E1	0	91	2.6	61.7	64.3	22.4	13.3	58.5	20.4
E2	0.5	90	2.9	76.4	79.3	13.8	6.9	71.4	12.4
E3	1.0	94	3.4	75.1	78.5	12.3	9.2	73.8	11.6
E4	1.5	93	3.0	76.9	79.9	11.0	9.2	74.3	10.2
E5	2.0	93	3.0	75.2	78.2	14.6	7.3	72.7	13.6
E6	1.0 (K)	94	6.9	84.0	90.9	5.3	3.8	85.4	5.0

^a Reaction conditions: time-on-stream: 1 h; catalyst weight: 500 mg; T: 300 °C; P: 3 MPa; WHSV (referred to the sum of H₂ and naphthalene): 1 h⁻¹; Feed: H₂ and a solution of 5 wt.% Naphthalene in heptane; H₂/naphthalene = 20 mol.

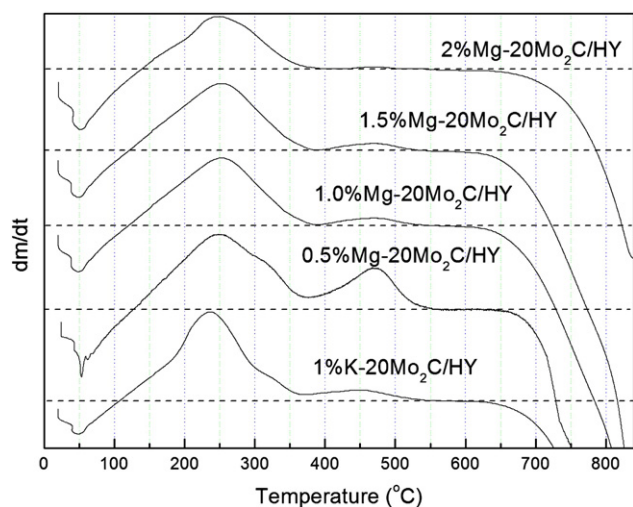


Fig. 4. DTGA of un-used Mg-Mo₂C/HY and K-Mo₂C/HY catalysts.

dispersion (since the acidities were the same), and hence the improved hydrogenation of the Mg-doped catalysts reduced coke formation. In the case of the K-Mo₂C/HY catalyst, however, both decreased acidity and increased Mo₂C dispersion reduced coke formation compared to the Mo₂C/HY catalyst.

In previous work, the reaction of naphthalene over Mo₂C/HY was discussed in terms of two competing reaction mechanisms [9–11]. Accordingly, naphthalene is hydrogenated to tetralin and small amounts of decalin on Mo₂C sites by a mononuclear mechanism. The hydrogenated intermediates migrate to acid sites where further hydrogenation, by spillover hydrogen migrating from Mo₂C sites, and isomerization and rupture of saturated naphthenic rings occurs, leading to the desired ring-opened products. However, when an effective supply of hydrogen to the zeolite acid sites is limited, reactions can follow a bimolecular mechanism. In this scheme, a carbenium ion of alkylbenzene is formed on a Brønsted acid site from one tetralin molecule, which is a consequence of hydride transfer reactions of naphthalene over acidic sites. This carbenium ion molecule then attacks one naphthalene molecule leading to alkyl-naphthalene and multinuclear aromatics that are further transformed into coke by chain reactions.

Results from the present study show that addition of Mg to the Mo₂C/HY increased the Mo₂C dispersion without decreasing the

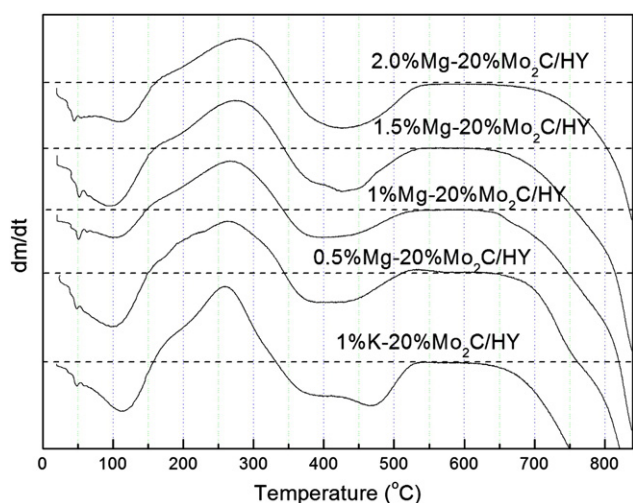


Fig. 5. DTGA of Mg-Mo₂C/HY and K-Mo₂C/HY catalysts after reaction in naphthalene. Reaction conditions give in Table 2.

Table 3
TGA analysis of various catalysts.

Sample	Before reaction		After reaction ^a	
	Weight gain wt.%	Weight loss wt.%	Weight gain ^b wt.%	Weight loss ^c wt.%
20%Mo ₂ C/HY	5.8	0	2.8	7.0
0.5%Mg-20%Mo ₂ C/HY	6.1	0	4.4	4.4
1.0%Mg-20%Mo ₂ C/HY	5.1	0	3.8	2.9
1.5%Mg-20%Mo ₂ C/HY	4.8	0	3.7	4.1
2.0%Mg-20%Mo ₂ C/HY	4.0	0	3.7	4.3
1.0%K-20%Mo ₂ C/HY	5.9	0	4.3	4.0

^a Reaction conditions: time-on-stream: 5 h; catalyst weight: 500 mg; T: 300 °C; P: 3 MPa; WHSV (referred to the sum of H₂ and naphthalene): 1 h⁻¹; Feed: H₂ and a solution of 5 wt.% naphthalene in heptane; H₂/naphthalene = 20 (mole).

^b In some cases, the weight gain corresponded to two peaks in the DTGA spectra.

^c Weight loss refers to the weight loss after consideration of the overlap with the weight gain (between 350 and 550 °C) in TGA of un-used catalysts.

catalyst acidity compared to the Mo₂C/HY. Accordingly, the mononuclear pathway would be enhanced, resulting in increased selectivity to tetralin and reduced selectivity to polymer products, as observed (Table 2). There was also a reduction in coke formation and RO selectivity, even though the acid strength of the Mg-doped Mo₂C/HY was the same as that of the Mo₂C/HY catalyst (Table 1). The increased hydrogenation of naphthalene and tetralin limited the formation of coke precursors that may undergo bimolecular reactions on acid sites that form coke. In the case of K addition to the Mo₂C/HY that resulted in reduced acidity, ring-opening selectivity was reduced compared to the Mo₂C/HY catalyst, even though the Mo₂C dispersion also increased relative to the un-doped catalyst. In the present work, addition of Mg and K resulted in lower coke formation (i.e. lower weight loss after reaction – see Table 3), in the former case because of increased hydrogenation that was a consequence of increased Mo₂C dispersion, in agreement with previous work [9], whereas in the latter case, because of both increased Mo₂C dispersion and reduced acidity. In the case of both Mg and K, however, the reduced coke formation was accompanied by a significant reduction in RO selectivity, especially in the case of the K-doped Mo₂C/HY catalyst that had relatively low acidity. Both Mg and K increased the hydrogenation capability of the Mo₂C/HY catalyst but did not provide the optimum acidity for increased RO selectivity. Together these results point to the difficulty in obtaining high RO selectivity while limiting coke formation.

4. Conclusions

The addition of Mg to Mo₂C/HY catalysts resulted in improved dispersion of the Mo₂C and no significant change in total catalyst acidity. Addition of K also improved Mo₂C dispersion but decreased the total acidity by 30%. Increasing the dispersion of the Mo₂C improved the hydrogenation of naphthalene and reduced coke deposition on the catalyst by limiting the formation of coke precursors that undergo bimolecular coke-formation reactions on acid sites. However, in both cases, ring-opening selectivity was also reduced, especially in the case of the K-Mo₂C/HY catalyst. Although Mg and K provide increased naphthalene and coke-precursor hydrogenation, they do not provide the optimum acidity needed for increased RO selectivity.

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