

## Evidence of hydrogen spillover contribution to hydrogenation reactions

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### Introduction

Hydrogen spillover refers to the diffusion of surface hydrogen species from metal sites where they are produced by the dissociation of hydrogen molecules to an oxide support that has no activity for dissociative hydrogen adsorption.<sup>1</sup> While the phenomenon of hydrogen spillover has been demonstrated experimentally, there still exist some ambiguities as to whether or not the spillover hydrogen species can produce substantial catalytic effects on the support, and enhance the chemical reactions.<sup>2,3</sup> An impressive positive example of hydrogen spillover was given by Ohgoshi et al.<sup>2</sup> The authors investigated isobutylene hydrogenation over Pt/Ka-zeolite and Pt/Ka-zeolite mixed with NaY zeolite. Pt/Ka-zeolite and NaY both had negligible hydrogenation activity because isobutylene is too large to access the metal sites inside the zeolite pores, and H<sub>2</sub> cannot be activated on NaY zeolite. However, a 93% yield on isobutane was obtained over a hybrid catalyst. Clearly, hydrogen was activated on the Pt/Ka-zeolite, and the resulting hydrogen species spilt over to the NaY zeolite where isobutylene was hydrogenated. Contrary to these findings, in a study of hydrogenation and deuterium exchange of ethylenebenzene by spilt-over hydrogen over a Pt/NaA-zeolite and H-USY system, Miller and Pei observed that spillover hydrogen resulted in only isotopic exchange, but not aromatics saturation.<sup>3</sup>

The present work examines the effect of hydrogen spillover during hydrogenation of 1-hexene and naphthalene over several catalysts such as Pt/Ka-zeolite, Pt/RHO and Pt/CMS (carbon molecular sieve). Our results show for the first time the contribution of hydrogen spillover to these reactions when the catalysts were mixed H-Y zeolite.

### Materials and Methods

1-Hexene, 1-heptane and naphthalene were purchased from Sigma-Aldrich (Oakville, ON). H-Y zeolite (CBV720) was obtained from Zeolyst International (PA, US). The detailed preparation and hydrogenation procedures of Pt/Ka-zeolite, Pt/RHO and Pt/CMS can be found in references 4-6. Briefly, hydrogenation of 1-hexene was conducted in a fixed-bed reactor at atmospheric pressure and 50°C; pure hydrogen flow was used to carry 1-hexene from a saturate to the reactor.<sup>6</sup> Five percent naphthalene in n-heptane was used in the hydrogenation of naphthalene. For Pt/Ka-zeolite, the reaction was carried out in a fixed bed operated at 70 bar and 300°C;<sup>4</sup> for Pt/RHO, the reaction was carried in a autoclave at 70 bar and 300°C.<sup>6</sup> The conversion of 1-hexene was followed by GC-FIMS, 1-hexane was the only hydrogenation product observed.<sup>5</sup> The conversion of naphthalene was determined by HPLC method.<sup>4</sup> Crystal structure of Pt/Ka-zeolite, Pt/RHO and Pt/CMS were confirmed by XRD.<sup>4-6</sup>

### Results and Discussion

Table 1 presents the catalyst mixture compositions tested in this work. In Pt/Ka catalyst system, H-Y and  $\gamma$ -alumina were used as spillover hydrogen acceptors. Total catalyst volume was 3 mL, 3 mL glass beads were also used to dilute the catalyst mixture to achieve better heat distribution. In the case of Pt/CMS, only H-Y was used as spillover hydrogen acceptor. Glass beads were used to give a total catalyst bed volume of 2 mL. In the autoclave

test of Pt/RHO, H-Y was used as a spillover hydrogen acceptor, and no glass beads were used. Hydrogenation conditions and results are presented in Table 2. The results clearly show the positive contribution of the hydrogen spillover on the hydrogenation reactions. Hydrogenation of naphthalene increased from 1 % to 15 % when Pt/Ka was diluted with H-Y zeolite and  $\gamma$ -alumina. It increased from 21% to 91% when Pt/RHO was mixed with H-Y zeolite. A similar trend was also observed when Pt/CMS and Pt/CMS were diluted with H-Y zeolite. Since the reaction systems are different for Pt/Ka and Pt/RHO, it is difficult to determine if the higher enhancement in Pt/RHO over Pt/Ka was due to the higher proportion of H-Y zeolite in the diluents. In addition, the dispersion and the location of Pt particles can also affect the hydrogen spillover. AT NCUT, research is underway to investigate these factors.

**Table 1. Compositions of the catalyst mixtures**

	Pt (wt%)	Catalyst mixture (g)	Formulation (wt%)
Pt/Ka	0.69	0.51	100
Pt/Ka+ H-Y + Alumina		1.31	20:60:20
Pt/CMS	4.6	0.2	100
Pt/CMS-H-Y		0.4	50:50
Pt/RHO	0.37	0.5	100
Pt/RHO + H-Y		1	50:50

**Table 2. Hydrogenation conditions and conversions**

	T	Pressure	LHSV	line-out time	Conversion%	
	(°C)	(bar)	(h <sup>-1</sup> )	(hr)	1-hexene	Naphthalene
Pt/Ka	300	70	1	24	-	1
Pt/Ka+ H-Y + Alumina	300	70	1	24	-	15
Pt/CMS	50	1	-	4	44	-
Pt/CMS-H-Y	50	1	-	4	100	-
Pt/RHO	300	70	-	-	-	21
Pt/RHO + H-Y	300	70	-	-	-	91

### Significance

This work demonstrates the existence of hydrogen spillover and its contribution in the hydrogenation reaction. The positive effects of hydrogen can find application in many industrial applications such as hydroprocessing, isomerisation and reforming. It can also be used for membrane manufacture to increase the permeability and permselectivity of hydrogen.

### References

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